

Microorganisms for Sustainability 24

Series Editor: Naveen Kumar Arora

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Ram Naresh Bharagava *Editors*

Fate and Transport of Subsurface Pollutants



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Fate and Transport of Subsurface Pollutants

 Springer

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Preface

In many regions around the world, soil–water quality issues are no longer related to just one type of pollution. Thus, a better understanding of the fate and transport of multi-pollutants is required for the restoration of polluted sites and production of safe drinking water. A number of studies have been performed during the past decades to evaluate the effects of a range of geo-bio-hydrological processes on subsurface water flow and transport of various contaminants. This book presents overviews on recent advancements and studies dedicated toward investigating the flow and transport in subsurface pollutants.

The aim of this book is to provide a background for solving the practical problems concerning multi-pollutants contamination and remediation approaches. The book discusses the principles of fate of several contaminants like hydrocarbons, heavy metals, pharmaceuticals and their transport in the subsurface groundwater with the behavior of hydrocarbon pollutants in subsurface and its biomonitoring and bioremediation processes, current status of geogenic and industrial pollutants, aqueous two-phase systems: An alternative process for industrial dye recovery, hazard derived from the metals leaching with phosphogypsum deposits located in areas under stack storage and environmental regulation, use of fly ash, for the hydraulic conductivity and mitigation of the groundwater contaminants, modeling of groundwater and contaminate transport, experimental approaches to extract and investigate the presence of microplastics in soil and groundwater system, trends of monsoonal rainfall using descriptive statistical analysis, rainfall variability index (RVI) followed by frequency and trends analysis, highlights on the plant–microbes–geochemical interactions in a constructed wetland (CW) to understand the biogeochemical and hydrological conditions controlling the performance of CW, the applicability of different adsorbents and microbes in arsenic removal from contaminated water, an insight into biological and chemical technologies for micropollutant removal from wastewater, microbial degradation of nonsteroidal anti-inflammatory drug ibuprofen, VOCs and GHGs intrusion and its impacts on subsurface microbial communities, biological treatment of pharmaceutical and personal care products

(PPCPs) before discharging into environment, mechanistic understanding of heterogeneous photocatalysis for dye degradation in wastewater, development and application of an integrated GIS-MODFLOW model, salt-water intrusion and role of climate change in salinization of coastal aquifers, impact of climatic variabilities on water resources, consequences and recommendations.

Special attention is paid to the role of microbial communities and activities in the remediation of subsurface pollutants. Concepts are illustrated with the aid of graphs, drawings, and photographs. The book describes not only well-established concepts but also the gaps in our understanding of pollutant's behaviors at the field scale, illustrated with examples from the field, laboratory, or modeling studies. It discusses the role and fate of the elements which are identified as major contaminants in surface and subsurface waters and their adverse effects on ecology and human health. The book explores this theme under four sections: (a). Understanding Soil–Water Systems, (b). Fate and Transport of Pollutants, (c). Physicochemical Treatment of Wastewater, and (d). Microbial Techniques Used to Decontaminate the Soil–Water Systems. It offers a spectrum of ideas of new technological inventions to the fundamentals of subsurface water treatment. This book is the result of collaborative efforts between the editors and several contributors with a wide range of experience in research, teaching, and consultancy. The chapters were reviewed by respective experts from international and national institutions. The editors outlined the book, solicited sections from the contributors, and edited the contributions to produce an integrated book.

This book will be useful for a wide range of students, scientists, field engineers, industrial practitioners, and policymakers working in the area of hydrology, groundwater microbiology and biotechnology, and environmental sciences with the fundamental and advance knowledge on environmental management. Thus, in this book, readers will find the updated information as well as the future direction for research in the field of environmental management.

This volume offers detailed information on the behavior of various water pollutants and on the principles and concepts of groundwater flow and transport. It will help readers to understand and execute the planning, supervision, and review of solute transport and groundwater modeling projects. The book also discusses the role and fate of elements that have been identified as major contaminants in surface and subsurface waters and their adverse effects on ecology and human health. The book explores this theme throughout four sections: (a). Understanding Soil–Water Systems, (b). Fate and Transport of Pollutants, (c). Physicochemical Treatment of Wastewater, and (d). Microbial Techniques Used to Decontaminate Soil–Water Systems. Introducing readers to a range of recent advances concerning the fundamentals of subsurface water treatment, it offers a valuable guide for teachers, researchers, policymakers, and undergraduate and graduate students of hydrology,

environmental microbiology, biotechnology, and the environmental sciences. It also provides field engineers and industrial practitioners with essential support in the effective remediation and management of polluted sites.

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profession he has a huge obsession for the wildlife and its conservation and has authored a book, *Splendid Wilds*. He is the President of Society for Conservation of Wildlife and has a dedicated website www.naveenarora.co.in for the cause of wildlife and environment conservation.

About the Editors

Pankaj Kumar Gupta has been a postdoctoral fellow at the Faculty of Environment, University of Waterloo since January 2019. The majority of his works focus on two areas: (1) understanding the occurrence of bio-geo-chemical interactions when pollutants migrate into groundwater systems and (2) developing remediation strategies. He received his Ph.D. from the Department of Hydrology, Indian Institute of Technology Roorkee with a dissertation on “*Fate and Transport of LNAPL Under Varying Subsurface Conditions.*” He has received an AGU Student Travel Grant (2017), JPGU Travel Grant (2018), and EXCEED-SWINDON and DAAD Germany Grant (2018). He serves as an editorial board member for *SN Applied Sciences and Frontiers in Water*. He has published more than 15 research papers, approximately 20 book chapters, and two popular science articles. He has reviewed several research articles for reputed journals including RSC Advances, Groundwater for Sustainable Development, ASCE JEE, ASCE Irrigation and Drainage, Env. Sc, Pollution Research, Ecohydrology, Journal of Contaminant Hydrology, etc. Further, he has led many site restoration and remediation consultancy projects at polluted industrial sites in India.

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Chapter 1

Understanding Hydrocarbon in Subsurface: Biomonitoring and Bioremediation



Pankaj Kumar Gupta, Manik Goel, and Sushi Kumar Himanshu

Abstract The high demand for fuel derived from oil increases the risk of environmental hazard as a consequence of overturning of trains, tractors, and trucks during transport and spotting of fuel on the ground. In vehicle or train cart overturning accidents, a part of the spilled fuel infiltrates and redistributes in the soil according to fuel and its own physical properties. These fuel products contain compounds of BTEX (Benzene, Toluene, Ethylbenzene, and Xylene) that are toxic causing damage to the soil and to human health. The knowledge on transport behavior of fuels in soils has been extensively studied. However, enhanced understanding on the transport behavior of these liquids in specific soils especially in Indian soil-water system is lacking.

Keywords Hydrocarbon · Groundwater · BTEX · Bioremediation · Biomonitoring

1.1 Introduction

Hydrocarbons are widely released into the environment as a result of anthropogenic activities (Mustapha et al. 2018; Gupta and Sharma 2019; Gupta et al. 2019; Gupta 2020a, b; Gupta and Yadav 2020a, b). Emissions from the industries and accidental spillage of petroleum derivatives from tankers, pipelines, and storage tanks are unavoidable circumstances (Salleh et al. 2003). Petroleum hydrocarbons are the most widespread contaminants of soil and groundwater systems (Margesin et al.

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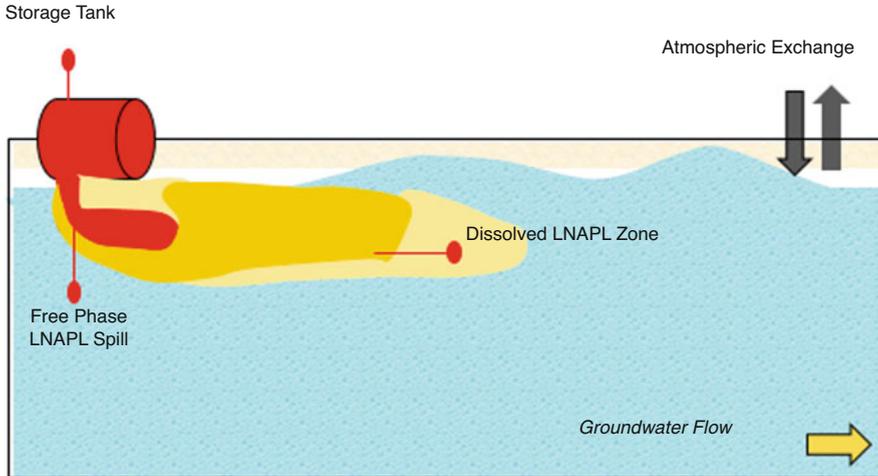


Fig. 1.1 Schematic diagram of hydrocarbon fate and transport in soil-water systems

2000) which are classified as either Light or Dense Non-Aqueous Phase Liquids (LNAPLs and DNAPLs, respectively) depending on their relative density. These NAPLs move downward through the vadose zone when released to the (sub)-surface. The LNAPLs are generally retained nearby to the water table, while DNAPLs penetrate the saturated soils and migrate to deeper locations until they are retained by an impermeable barrier (USEPA 2006). Both types of NAPLs present a potential threat to the receiving zone and nearby environment; however, the regions having complex varying environmental conditions seem more susceptible to LNAPLs threats because of wide coverage and mobilization of small spillages of LNAPLs (Kamath et al. 2004).

The LNAPLs movement in unsaturated porous media is sufficiently complex when only two fluid phases air and water are present; flow becomes even more complicated when a third fluid phase, such as an immiscible organic fluid, is involved. The resulting subsurface flow problem then involves three fluids, air, water, and LNAPL, each having different interfacial tensions with each other, different viscosities, and different capillary interactions with the soil. The LNAPLs movement in the subsurface dominated by advection and hydrodynamics mechanisms (Yadav et al., 2012). Advection and dispersion mechanisms result in translation or spreading of plumes in a porous medium and a large spatial area is covered. Sorption of dissolved constituents on the other hand results in the partition of species between the solid and aqueous phases thereby reducing the mass of contaminant that is in solution; however, sorption is responsible for soil phase soil pollution (MacQuarrie et al. 1990). The biodegradation of organic contaminants by a native subsurface microbial population is the process whereby mass can be removed without physically extracting the contaminant from the aquifer. Figure 1.1, adopted from Rivett et al. (2011), shows the overall mechanisms during the subsurface LNAPLs fate and transports. The environment condition like temperatures, soil

moisture, nutrient supply, water table fluctuation poses distribution of the LNAPLs plumes dynamic in the soil-water system. The water table or water content affected the spatial distribution of LNAPLs within an aquifer (Dobson et al., 2007). The water table rises cause the upward movement of the plume and increase the distributed coverage area of the plume. The water table fluctuation causes the mechanisms of entrapment of LNAPLs in soil pores (Dobson et al., 2007; Lee and Chrysikopoulos 1995). LNAPLs entrapped in the form of isolated blobs or ganglia will increase water interfacial area, which enhanced LNAPLs dissolution (Anderson et al., 1992, Soga et al., 2004). LNAPLs trapped in the porous media become the residual and long lasting pollution sources which very slowly naturally attenuated (Yadav and Hassanizadeh. 2011).

1.2 LNAPLs Fate and Transport Mechanisms

Much of the problem is attributed to facile migration of dense/light non-aqueous phase liquid (D/LNAPL) hydrocarbons to the subsurface or a deeper stratum where LNAPL slowly dissolves into soil-water and its vapor mixing in soil-air. Unsaturated-zone transport and attenuation of LNAPL plumes leached from shallow source zones is conceptualized in Fig. 1.1. Key processes influencing source zone mass transfer and LNAPL transport and attenuation in the unsaturated zone are listed in Fig. 1.1 and are considered in detail in the subsequent sections. Processes include source zone mass transfer due to simultaneous volatilization and dissolution; advection, dispersion, and diffusion in air and water phases influenced by time-variant infiltration, geological heterogeneity, and preferential flows; volatility driven gas-liquid (air-water/LNAPL) phase partitioning resulting in a dynamic interaction of dissolved-phase and vapor-phase plumes; phase partitioning due to sorption to solids phases and the air-water interface; and, biodegradation and chemical reaction. The involvement of such complex processes demands an integrated understanding to allow robust prediction of fate and transport in the unsaturated zone. These processes require collective understanding to enable risks to be assessed, and remediation works appropriately assigned (Rivett et al. 2011). The governing equations based on LNAPLs fate and transport mechanism are summarized in Table 1.1.

In earlier studies, the water table was taken as static for investigating the fate and transfer of LNAPLs near water table with due consideration of the residual LNAPLs (Fried et al. 1979). Water table dynamics can significantly affect the distribution, particularly in the vertical direction and degradation process of LNAPLs (Mercer and Cohen 1990) in addition to the soil moisture and temperature distribution.

A shallow unconfined aquifer is mostly characterized by fluctuating water table. The water table elevation and capillary fringe vary due to the changing water stage in unsaturated zones (Lee et al. 2001). Diurnal stage fluctuations induce a rapid and significant response in the surrounding land mass over shorter distances and damp at further distances (Williams and Oostrom 2000). Seasonal fluctuations may occur when water uptake by vegetation, evaporation, surface recharge, and groundwater withdrawal vary over the course of the year (Zhang et al. 1998; Yadav et al. 2009).

Table 1.1 Overview of governing equations used to simulate LNAPLs fate and transport in subsurface

Mechanisms	Governing equations	Descriptions	
1. Contamination partition (a) Liquid-gas: Henry's law (b) Solid-liquid partition	$C_{\text{gas}} = H \frac{C_{\text{liq}}}{RT}$ $C_{\text{soil}} = K_d C_{\text{Liq}}$ $K_d = K_{oc} f_{oc}$	Where H is expressed in Pa L Mol^{-1} , R is the universal gas constant ($8.31 \text{ J Mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K) K_d is the partitioning coefficient in L kg^{-1} , K_{oc} (L kg^{-1}) is the organic carbon water partitioning coefficient, and f_{oc} is the mass fraction of organic carbon	
2. Advective transport	$F_z = V_z C$ $\frac{\partial C}{\partial t} = -V_z \frac{\partial C}{\partial z}$	Where $V_x = \frac{K}{n} \frac{\partial h}{\partial l}$, V_x =linear velocities (L/T), K is hydraulic conductivity (L/T), n = effective porosity, $\frac{\partial h}{\partial l}$ = hydraulic gradient (L/L), C = concentration of LNAPLs (water, gas), t = time (T)	
3. Dispersive transport	$\frac{\partial C}{\partial t} = n D_z \frac{\partial C}{\partial z} \frac{\partial A}{\partial A}$ $D_L = \alpha_L v_z + D^*$ $D_T = \alpha_T v_z + D^*$	Where dA is the cross-sectional area of REV, D_z = hydrodynamic dispersion coefficient α_L = longitudinal dynamic dispersity α_T = Transverse dynamic dispersity D^* = Diffusion coefficients	
4. Adsorption (LNAPLs to solids mass transfer) (a) Linear isotherm (b) Freundlich isotherm (c) Langmuir isotherm	(a) $S_{\text{eq}} = K_d C_{\text{eq}}$ (b) $S_{\text{eq}} = K C_{\text{eq}}^m$ (c) $S_{\text{eq}} = \frac{K_L S_{\text{max}} C_{\text{eq}}}{1 + K_L C_{\text{eq}}}$	S_{eq} = The adoption concentration, K_d = linear adsorption coefficient. K = Freundlich constant, m = Fitting parameters. S_{max} = The maximum adsorbed concentration mass fraction, K_L = Langmuir adsorption coefficient	
5. Dissolution (LNAPLs to water mass transfer)	$\frac{\partial C}{\partial t} = K_{\text{dissolution}} (C_{\text{max}} - C_w)$ $C_{\text{max}} = SX$	$K_{\text{dissolution}}$ = dissolution rate constant [T^{-1}], C_{max} = Equilibrium concentration, C_w = NAPL concentration in water, S = Solubility limits, X = mole fractions	
6. Natural attenuation/biodegradation $-\frac{\partial C}{\partial t} = \mu_{\text{max}} C \left(\frac{C_0 + X_0 - C}{K_s + C} \right)$		Where μ_{max} is the maximum specific growth rate, C is the contaminant concentration at time t , C_0 is the initial concentration and X_0 corresponding to the contaminate required to produce initial microbial density, K_s is the substrate affinities constant. The two kinetics parameters are μ_{max} and K_s and the other two stoichiometric parameters $Y_{s/x}$ and S_{min}	
Kinetics model	Condition	Equation	Rate constant
Constant or zero order	$X_0 \gg C_0$; $C_0 \gg K_s$	$-\frac{\partial C}{\partial t} = k_0$	$k_0 = \mu_{\text{max}} X_0$
Linear of first order	$X_0 \gg C_0$; $K_s \gg C_0$	$-\frac{\partial C}{\partial t} = k_1 C$	$k_1 = \mu_{\text{max}} X_0 / K_s$
Monod	$X_0 \gg C_0$	$-\frac{\partial C}{\partial t} = k_m \frac{C}{K_s + C}$	$k_m = \mu_{\text{max}} X_0$
Logistic	$K_s \gg C_0$	$-\frac{\partial C}{\partial t} = k_1 C / (C_0 + X_0 - C)$	$k_1 = X_0 / K_s$
Logarithmic	$K_s \gg C_0$	$-\frac{\partial C}{\partial t} = k / (C_0 + X_0 - C)$	$k = \mu_{\text{max}}$

Variations in water table can also occur over longer time if average groundwater withdrawal rates exceed the average water recharge rates or vice versa (Lakshmi et al. 1998). The LNAPLs move downward as the water level falls, leaving behind a residual fraction in the unsaturated zone in the form of isolated ganglia. Conversely, a rise of water table leads to an upward migration of LNAPLs resulting in the entrapment of LNAPLs and air by snap-off or bypassing mechanism in smear zone below the groundwater table (Chatzis et al. 1983; Kechavarzi et al. 2005). On the other hand, the entrapped LNAPLs reduce the free-phase pool and thus mitigate the likelihood of pure LNAPLs migration to down-gradient receptors (Fry et al. 1997). The entrapped air in saturated zone provides additional oxygen to LNAPL-degrading microbes. Also, the pulse of oxygen introduced by lowering the water table exposes the microbes to the air in the soil pore spaces and enhances biodegradation without the injection of oxygen. At the same time, entrapment of LNAPLs increases their water interfacial area resulting in an enhanced dissolution of the hydrocarbons and hence, enlargement of plume size migrating in the direction of water flow (Miller et al. 1990). Nevertheless, the dissolution process of LNAPLs as a result of groundwater flow in saturated zone is by far considered as the main limiting factor of the contaminant removal from the source zone (Abriola et al. 2004; Powers et al. 1991; Kamon et al. 2006). The rise of water level also exposes the upper dryer regions of a polluted site to the moisture necessary to sustain microbial metabolism and growth. Just like domain heterogeneity, the LNAPLs in pure phase is also the realistic condition in pollution problem. Thus, fate and transport of the accumulated LNAPL pool and its associated discontinuous ganglia/blobs in the smear zone are essential considerations in the bioremediation of polluted sites due to additional chemical and hydraulic heterogeneity in space and time introduced by the fluctuating water table.

The overview of laboratory and simulation experimental studies that reported the impacts of water table dynamics and groundwater velocity on LNAPLs fate and transport in subsurface are listed in Table 1.2. The peer-reviewed literature shows the investigations on/using dissolved-phase LNAPLs in fate and transport studies.

A solute transport model (SEAM3D) was employed to simulate advective–dispersive transport over time coupled to LNAPLs dissolution by Mobile et al. (2012). In results, NAPL mass depleted showed limited sensitivity during which over 80% of the most soluble LNAPLs constituent dissolved from the source. Kim and Corapcioglu (2003) investigated the effects of dissolution and volatilization on LNAPL migration and to model subsurface contamination by migrating LNAPL. In these studies, the impact of groundwater velocities and heterogeneity were not incorporated in domain. Table 1.3 lists some laboratory and simulation experiments performed to investigate the pure phase LNAPL dissolution rate under different groundwater velocities during fate and transport in subsurface.

Table 1.2 Summary of laboratory experimental studies on LNAPLs fate and transport reported in the peer-reviewed literature

References	Experimental design/setup	Methodology	Results/comments/gaps
Rühle et al. (2015)	Plexiglas column (14-cm ID, 50 cm long)	– The columns were continuously infiltrated from the top with a constant water flux ($0.19 \pm 0.01 \text{ cm h}^{-1}$) and operated in a downward flow mode using tracer	– The 16 inflow points were distributed evenly, ensuring homogeneous groundwater distribution over the entire diameter of the column
Alfnes et al. (2002)	Column (10-cm ID, 0.5 m long)	–the toluene concentration was applied in the column having Gardermoen delta soil	– A flow rate of 0.8 mL h^{-1} was maintained
Legout and Hamon (2009)	Plexiglas column (0.3 m ID, 1 m long)	– Experiments reproducing one-dimensional vertical flow and tracer transport were performed at two infiltration rates, 12 and 22 mm h^{-1}	– The experimental apparatus with the locations of the six tensiometers (TS)
Henry et al. (2002)	2D sand tank $234 \times 153 \text{ cm}$ (equipped with seven injection ports at the inlet and seven extraction ports)	– TWater was supplied to the microporous tubing from a constant head reservoir. The point source where a flow rate of 210.5 cm/day into the region was applied over a length of 1.9 cm (parallel to the long direction of the flow cell) during contaminant application	– TModelling integrated with HYDRUS 2D
Vishal and Leung (2015)	2D Heterogeneous domain Modelling	– The random walk particle tracking (RWPT) method was applied for 2D heterogeneous domain to evaluate the impact on dispersivity	– The dispersion increases with heterogeneities and travel distance in heterogeneous reservoirs
Luo et al. (2015)	2/3D Heterogeneous domain Modelling	– The MigMOD mode was used to simulate the formation of hydrocarbon migration pathways in heterogeneous carrier beds	– Reservoir heterogeneity is likely the main reason for the irregular distribution of hydrocarbons in the study area and other oilfields
Abdou and Flury (2004)	2D lysimeters based Heterogeneous domain Modelling	– Three different soil structures (isotropic, horizontal, and vertical) were generated, and soil spatially heterogeneous by changing the hydraulic functions at various locations in the flow domain	– Breakthrough curves of a conservative solute showed that solutes are moving faster in the field than in the lysimeters

(continued)

Table 1.2 (continued)

References	Experimental design/ setup	Methodology	Results/comments/gaps
Simmons et al. (2001)	2D heterogeneous domain having the model grid are 9300 m horizontally and 150 m vertically	– Different styles of heterogeneity are considered and range from continuously heterogeneity (sinusoidal and stochastic permeability distributions) to discretely fractured geologic media. Simulation was carried out with SUTRA model	– An ordered heterogeneity, e.g., sets of vertical fractures allows instabilities to propagate at modest combinations of fracture aperture and separation distances
Abreu et al. (2009)	Three-dimensional numerical model simulations	– Homogeneous soil properties and steady-state conditions were simulated which incorporating the natural attenuation from source points	– The vapor intrusion depends upon the source-surface distances and biodegradation was significant for low concentration
Bozkurt et al., (2009)	Three-dimensional numerical model simulations	– A three-dimensional finite element model was used to investigate the importance of factors that could influence vapor intrusion when the site is characterized by nonhomogeneous soils	– In layered geologies, a lower permeability and diffusivity soil layer between the source and building often limit vapor intrusion rates, even if a higher permeability layer near the foundation permits increased soil-gas flow rates into the building
Brusseau (1991)	One-dimensional simulation and laboratory work	– The multi-process non-equilibrium transport (MPNEG) model was coupled to a nonlinear, least squares, optimization program to allow parameter determination by curve fitting of model simulations to experimental data	– Model perfectly simulate advective-diffusive transport affected by mass transfer between immobile water residing in microspores and a flowing gas phase

1.3 Laboratory, Simulation, and Modelling Works

Summary of selected laboratory experiments and simulation studies that have examined fate and transport of LNAPLs plumes under unsaturated-zone conditions are listed in Table 1.4. Powers et al. (1991) investigated the mass transfer and transport mechanisms for the LNAPLs pool and associated residual blobs under constant water table conditions. The study contributed to the understanding of the LNAPLs mass transfer near the water table and thus provided some insight into estimating the time needed for a complete dissolution of LNAPL pools as well as

Table 1.3 Summary of laboratory and simulation experimental studies reported the impact of groundwater velocities on LNAPL dissolution and movements in subsurface

References	Experimental design/setup	Methodology	Results/comments/gaps
Powers et al. (1998)	1D column (8.5-cm diameter \times 6.86) and 2D (10 \times 17.8 cm) experiments having heterogeneous pattern	– Fine sand was packed in the 1/2D cell to surround rectangular coarse sand lens. NAPL was entrapped in the coarse sand by direct injection of a known volume of NAPL through a port installed in the back of the cell and then analyzed from others ports	– Rate-limited dissolution becomes important for low-LNAPL saturations ($S_n < \sim 0.05\text{--}0.15$)
Imhoff and Miller (1996)	2D sand cell	– NAPL pumped in from the lower port at a high flow rate, such that capillary pressures within the cell. The dissolve concentration was analyzed and different dissolution figure were investigated	– The heterogeneous media leads to the heterogeneous dissolution and distribution of LNAPLs in the cell and depends on the flux
Sulaymon and Gzar (2011)	3D saturated sand tank (100 cm \times 40 cm \times 35 cm)	– Dissolution experiments were conducted in the 3D tank having the flow of water from the storage tank.	– The studies concluded that dissolution experiments did not reached the maximum value (1770 mg/L) because the higher dissolution rates can be associated with: (1) higher interstitial velocity, (2) higher LNAPL saturation in the porous media, and (3) increased contact area between LNAPL and water

residual blobs in the unsaturated zone. However, the oversimplified assumptions of steady-state flow and/or static water table conditions rarely exist in the field, particularly in coastal regions. To account for the non-static condition, Sinke et al. (1998) examined the impact of water table dynamics on redox conditions and transport of dissolved toluene and 4-nitrobenzoate in a sand column. Significant differences in contaminant transport and redox conditions were observed after repeated fluctuations of the water table within the column. However, these experiments did not accurately reflect the situation commonly encountered in LNAPL-polluted sites, where the principle groundwater flow direction is nearly horizontal and the low relative permeability influences the amount of water flow through the LNAPL source zone. Furthermore, Williams and Oostrom (2000) performed an

Table 1.4 Summary of simulation experimental studies on LNAPLs fate and transport reported in the peer-reviewed literature

Reference	Model	Model problem (s)	Domain	Applied initial concentration (I.C.)		Applied boundary condition (B.C.)			
				Water flux I.C.	Solute I.C.	Water flux B.C.	Lower B.C.	Upper B.C.	Solute B.C.
Abriola et al. (2004)	MISER	– Volatilization of binary nonaqueous phase liquid mixtures in unsaturated porous media	1D Homo	Pressure head	Measured existing NAPL concentration	Upper B.C.	Zero diffusive/dispersive flux	Third type	Second type
Hamlen and Kachanoski (2004)	Analytical model	– The effect of initial soil water content (θ) and steady and transient water flow boundary conditions (J_w)	1D Homo	Dry and wet uniform condition	Zero concentration profile	Surface flux	(Head pressure equal to zero)	Solute flux	Zero con.
Zeng et al. (2014)	HYDRUS 1D	– Effects of different irrigation amount on solute transport	1D Homo	Irrigated measured flux	Injected know flux	Atmospheric B.C. (incorporating rainfall, evapo data)	Free drainage	Con. Flux	Zero con.
Horel et al. (2015)	HYDRUS 2D	Degradation of hydrocarbon in 2D domain using HYDRUS	2D Homo	Zero flux/zero concentration	No flux	Constant flux	No flux	Third types	No flux

intermediate-scale flow cell experiment with a fluctuating water table to study the effect of entrapped air on dissolved oxygen transfer and transport by taking relative permeability influence into account. Entrapment of air during repeated fluctuations led to significant improvement of dissolved oxygen of the groundwater compared with a system without fluctuations. Later, Ostrom et al. (2006) conducted a 2-D experiment to investigate the migration behavior of two LNAPLs having different viscosity under variable water table conditions.

The results of this experiment showed that more viscous mobile LNAPL, subject to variable water table conditions, does not necessarily float on the water table and may not appear in an observation well. Steffy et al. (1995) utilized hydrophobic and hydrophilic tensiometers for field measurements to study the immiscible displacement of gasoline over a fluctuating shallow water table. Their findings revealed a significant difference in the saturation distribution of the LNAPLs above the water table between a falling and rising potentiometric surface. However, no attention was paid to the dissolution and/or biodegradation of gasoline. But, Lee et al. (2001) found rapid biodegradation in a toluene contaminated aquifer subjected to a water table fluctuation of 2-m amplitude. It is difficult to judge from their study whether the increase in biodegradation and dissolution occurred as a result of water table dynamics, as there was no suitable non-fluctuating reference system. Dobson et al. (2007) studied the effect of water table fluctuation on dissolution and biodegradation of a multicomponent, LNAPL. Results showed that the fluctuation in the water table increased the vertical extent of the source zone by a factor of 6.7. It also led to enhanced biodegradation activity shown by the amount of consumption of electron acceptors. However, there was enhanced dissolution of the LNAPL components due to the water table fluctuation which was even up to 20 times. Summary of different numerical simulator and model used for simulation of LNAPLs in subsurface is listed in Table 1.5.

Lenhard et al. (1995) and Kaluarachchi and Parker (1992) numerically studied the impact of falling water table on the redistribution of the LNAPLs in the unsaturated zone. All model simulators used some type of boundary condition depending on their field of application. Overview of boundary conditions to be used in LNAPLs simulation studies are listed in Table 1.6. Dobson (2007) predicted enhanced dissolution and biodegradation of LNAPL in systems subject to cyclic water table fluctuations. Most recently Robinson et al. (2009) investigated the effect of tidal influence numerically on biodegradation of LNAPLs. The results showed that significant biodegradation of LNAPLs occurred in smearing zone leading to a reduction in total mass transported from aquifer to ocean. Lakshmi et al. (1998) proposed a mathematical formulation for evaluating the water table effect on mass loss from LNAPL pool in the smear zone. Though the presence of discontinuous LNAPL blobs and biodegradation was considered, the model was not validated against the field data. Moreover, the model assumptions on blob characterization (shape and size), constant rate of water table dynamics, and dissolved solute concentration made it somewhat oversimplified.

Table 1.5 Summary of different numerical simulator and model cited for LNAPLs transports in subsurface

Modelling tool	Description	Reference
TOUGH series	Numerical reactive transport model, based on the governing mechanisms of fate and transports	Doughty and Pruess (2004)
HYDRUS 2/3D	A software package for simulating water, solute movement in multi-dimensional variably saturated media	Šimůnek et al. (2008)
CQUESTRA	Semi-analytical model for the reactive transport in subsurface	LeNeveu (2008)
STARS	Multiphase multicomponent numerical model for the reactive transport in subsurface	Law and Bachu (1996)
CRUNCH	Reactive transport simulator (software package) for simulating multicomponent, multi-dimensional reactive transport in porous media	Knauss et al. (2005)
STOMP	Multiple phase flow simulator, it includes capillary trapping, dissolution trapping, and structural trapping	http://stomp.pnnl.gov/
COMSOL	COMSOL multiphysics a multiphase fluid flow model in porous media	M.A. Diaz-Viera et al. (2008)

1.4 Bioremediation and Biomonitoring

Many remediation techniques have been developed for the cleanup of such chemicals. The common physical measures for cleanup of oil spills are physical containment, wiping, booming and skimming, mechanical removal, water flushing, and sediment relocation (Zhu et al. 2004). Use of dispersants as a chemical method is quite common in some countries but not in others due to the disagreement about their effectiveness and long-term environmental toxicity concerns (USEPA 2006). The aforementioned methods often are the first response option, and they rarely achieve complete cleanup of these oil spills (Yadav and Hassanizadeh, 2011). There are secondary techniques like carbon adsorption, electro-remediation, air sparging, filtration, and adsorption by zeolites (Daifullah and Girgis 2003; Yang et al. 2005; Ranck et al. 2005) as well as chemical oxidation, and photo-catalysis (Mascolo et al. 2007). It is seen that the most economically viable and promising option is bioremediation. Bioremediation is a grouping of technologies that use microbiota to either degrade or transform hazardous contaminants to materials such as CO₂, H₂O, inorganic salts, microbial biomass, and other by-products that maybe less hazardous than the parent material. It can be divided into several broad categories. The in situ processes treat soils and groundwater in place while ex situ processes involve the removal of the contaminated media to a treatment area. Ex situ techniques include land farming, turned windrows, bio-venting, and recovery and treatment system. In situ techniques include bio-stimulation, chemical oxidation, vapor extraction,

Table 1.6 Overview of boundary conditions used to simulate LNAPLs fate and transport in subsurface

Boundary conditions types	Formulation	Descriptions
Initial conditions	$\theta(z, t) = \theta_i(z, 0)$ $h(z, t) = h_i(z, 0)$ $C(z, t) = C_i(z, 0)$	Initial conditions characterizing the initial state of the system can be specified either in terms of water content, pressure head, and zero concentration gradients
<i>System-independent boundary conditions</i>		
Type-1/Dirichlet/pressure head boundary condition	$h(z, t) = h_o(z, t)$	When the pressure head at the boundary is known, one can use when simulating ponded infiltration, to specify the water table
Types-2/Neumann/flux boundary condition	$-K(h) \left(\frac{\partial h}{\partial z} + 1 \right) = J_o(z, t)$	This boundary condition is often referred when flux is known, and used to recharge well, etc.
Gradient types boundary condition	$\frac{\partial h}{\partial z} + 1 = J_o(z, t)$	Commonly used to specify a unit vertical hydraulic gradient simulating free drainage from bottom of a soil profile
<i>System-dependent boundary conditions</i>		
Atmospheric boundary conditions	$\left K(h) \left(\frac{\partial h}{\partial z} + 1 \right) \right \leq E,$ $h_A \leq h \leq h_s$	The h_A is determined from the equilibrium condition between soil water and atmospheric water vapor, whereas h_s is usually set to zero
Seepage face	$J_o(z, t) = 0$ for $h(z, t) < 0$ $h(z, t) = 0$ for $h(z, t) \geq 0$	This boundary conditions states that there is no flux across the boundary as long as the boundary is unsaturated and that the pressure head changes to zero once saturated. This boundary condition used at the bottom of certain types (finite) lysimeters, 2/3D sand tanks, along tile drains or at seepage faces.
Deep drainage	$Q(n) = \text{With. } \partial h$ $(n) * A * \exp(B $ $h - \text{GWLOL})$ Where GWLOL = Reference position of the groundwater table	The flux depends upon the portion of the groundwater table
Free drainage/zero pressure head gradient	$h(z, t) = 0$	A free drainage boundary condition is its use as a bottom outflow boundary condition for situations where the water table is situated far below the domain of interest
Variable flux	$J(z, t) = J_n, n = 1, 2, 3, \dots, n$	Variable pumping or fluid injection, and variable sprinkler irrigation, provide examples of a variable flux boundary condition

(continued)

Table 1.6 (continued)

Boundary conditions types	Formulation	Descriptions
Variable pressure head	$h(z, t) = h_n$ $n = 1, 2, 3, \dots, n$	A variable groundwater level is an example of a variable pressure head boundary condition
No flux	$J(z, t) = 0$	No flux boundary conditions are specified for impermeable boundaries where the flux is zero perpendicular to the boundary. Impermeable layers or walls of structures, which form the boundary of the flow domain, are examples of no-flow boundary conditions
Constant flux	$J(z, t) = J_i$	The value of a constant flux boundary condition at a particular node, n , is given by the initial value of the recharge/discharge flux, $Q(n)$. Constant pumping and constant flux sprinkler irrigation are examples of constant flux boundary conditions
<i>Solute boundary conditions</i>		
No flux	$C(z, t) = 0$	No flux boundary conditions are specified for impermeable boundaries where the flux is zero perpendicular to the boundary. Impermeable layers or walls of structures, which form the boundary of the flow domain, are examples of no-flow boundary conditions
Types-1 (Dirichlet or concentration type)	$C(z, t) = C_o(z, t)$	A first-type boundary condition is used when the concentration along the boundary is specified. <i>Note that this type of boundary condition is generally not mass conservative</i>
Types-2 (Cauchy, mixed, or solute flux)	$-K(h) \left(\frac{\partial C}{\partial z} + 1 \right) = J_o(z, t)$	A third-type boundary condition is used when the solute flux along a boundary is specified. <i>This type of boundary condition is mass conservative</i>
Volatile type	–	The usual third-type boundary condition by including an additional term to account for gaseous diffusion through a stagnant boundary layer of thickness d on the soil surface

groundwater flushing, construction of hydraulic barriers, etc. Another way to divide the bioremediation field is based on additives to the environmental media.

Many studies have shown success with enhanced bioremediation. When working conditions at the site are engineered, i.e. designed to accelerate the bioremediation of contaminants, the process is referred to as engineered or enhanced bioremediation

(Scow and Hicks 2005). It facilitates biodegradation by manipulating the microbial environment by supplying chemical amendments such as air, organic substrates or electron donors, nutrients, and other compounds that affect metabolic reactions. It includes bio-stimulation and bio-augmentation. Bio-stimulation is accomplished by the addition of nutrients and electron acceptors to the contaminated wetland system. Bio-augmentation is needed for specific contaminants that are not degraded by the indigenous organisms. Bio-augmentation is a technique for improving the capacity of a contaminated matrix by addition of specialized microbial cultures which are grown separately under well-defined conditions. Bio-augmentation is almost mostly performed in conjunction with bio-stimulation.

The engineered bioremediation emerges to accelerate the bioremediation using modification to the environmental condition and native microflora. This advance bioremediation influences the microbial activities and their neighboring environmental condition for accelerating the practice of biodegradation and categorized as bio-stimulation and bio-augmentation. The bio-stimulation is enhanced by the adding of nutrients, electron acceptors, oxygen, and other relevant compounds to the polluted sites which enhanced the (co)-metabolic actions of the microflora. Bio-augmentation is a microorganism seeding practice for cultivating the volume of a petrochemical degrader by adding of potential microbial cultures which are grown independently in well-defined conditions. Furthermore, the plants also accelerate the petrochemical removal by promoting the microbial re-establishment in polluted soils and water due to constantly delivering oxygen by root zone aeration and nutrients for microbial development by fixation and exudation. Similarly, the constructed wetlands techniques are a concurrent treatment to polluted soil-water resources. The nature, depth, and degree of pollution, type of situation, location, are among the selection measures that are reflected when selecting any bioremediation strategies (Azubuike et al. 2016). Furthermore, performance measures like the amount of nutrient, etc. that control the success of bioremediation are also given major attention prior to bioremediation project. In this manuscript, the art-pertaining to bioremediation of petrochemical polluted soil-water resources is presented with special emphasis on the engineered bioremediation strategies. There are two principal biological approaches to treat the contamination in situ: traditional/ engineered bioremediation systems that rely on microbial metabolism for site cleanup and phytoremediation, which relies on vegetation. Phytoremediation is a biological treatment process that utilizes natural processes harbored in (or stimulated by) plants to enhance degradation and removal of petrochemical in contaminated soil or groundwater. Broadly, phytoremediation can be cost-effective for (1) large sites with shallow residual levels of contamination by petroleum pollutants, where contamination does not pose an imminent danger and only “polishing treatment” is required; and (2) where vegetation is used as a final cap and closure of the site (Basu et al. 2015).

Plant assisted bioremediation refers to the use of selective plant species for the targeted pollutant to mitigate the toxic effects and removal of pollutant mass from (sub)-surface. This technique used the plant-geochemical interaction to modify the polluted site and also supply (micro)-nutrient, oxygen, etc. into the subsurface for

better performance of petrochemical degrader on targeted pollutants (Susarla et al. 2002). Petrochemical is mostly removed by degradation, rhizoremediation, stabilization, and volatilization, with mineralization being possible when some plants such as *Canna generalis* are used (Basu et al. 2015). The plant–geochemical interaction enhances the (1) physical and chemical properties of sites, (2) nutrient supply by releasing root exudates (Shimp et al. 1993), (3) the aeration by transfer the oxygen, (4) intercepting and retarding the movements of chemicals, (5) the plant enzymatic transformation, (6) resistant to the vertical and lateral migration of pollutants. Similarly, the plant-microbe’s interaction accelerate (1) mineralization in rhizosphere (2) numbers of degraders and shorter the lag phase. Some key factors to consider when choosing a plant include root system, which may be fibrous or tap subject to the depth of contaminant, toxicity of pollutant to plant, plant survival and its adaptability to prevailing environmental conditions, plant growth rate, resistant to diseases and pests. The deep root systems of plant improve the aeration in subsurface, which maintains the oxygen level in the deep vadose zone. The root exudates, dead root hair, and fine root serves as an important source of the carbon for microbial growths (Shimp et al. 1993). Also, the root exudates also accelerate the enzyme synthesis of microbial metabolisms (Dzantor 2007). Overall, the plant plays a crucial role in the removal of petrochemical mass, but many issues related to plant application to petrochemical polluted sites are required to investigate before implementation of such techniques. Further, the impacts of static and dynamic environmental variables on the pollutants removal, combination of other bioremediation techniques to plant assisted bioremediation, and multi-scale investigation are needed.

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Chapter 2

Groundwater Pollution by Geogenic and Industrial Pollutants



Manik Goel

Abstract The groundwater accounts for around 98% of the total freshwater available on the earth. Groundwater pollution is an emerging threat to our beloved planet. The chapter explains the two major sources of pollution, each from natural (geogenic) and anthropogenic (industrial) activities, which are responsible for degrading the quality of groundwater. It includes the physio-chemical characteristics of pollutants, governing factors to their fate and transport, their adverse effects on human health and earth as a whole, and possible strategies for their remediation. The latest studies conducted to understand the nature and treatment techniques of these pollutants are also discussed in the chapter. The chapter concludes with the countermeasures required to tackle the problem of groundwater pollution.

Keywords Groundwater pollution · Fluoride · Arsenic · Uranium · Geogenic · Industrial contamination · Nitrate

2.1 Introduction

The water found beneath the earth surface saturating the pores and fractures of subsurface materials is termed as groundwater. The upper layer of the saturated geological material is termed as water table (Fig. 2.1). Depth to the water table may vary from zero feet to a thousand feet below the ground level (bgl), depending on the prevailing geologic, meteorological, and topographical factors.

The groundwater stores in the cracks and voids of soil, sand, and rock in the same way water fills the sponge. It moves through the aquifer material typically at a rate of 7–60 cm per day. Groundwater moves through the vadose zone (containing numerous geological filters) to reach the water table and is generally free from any

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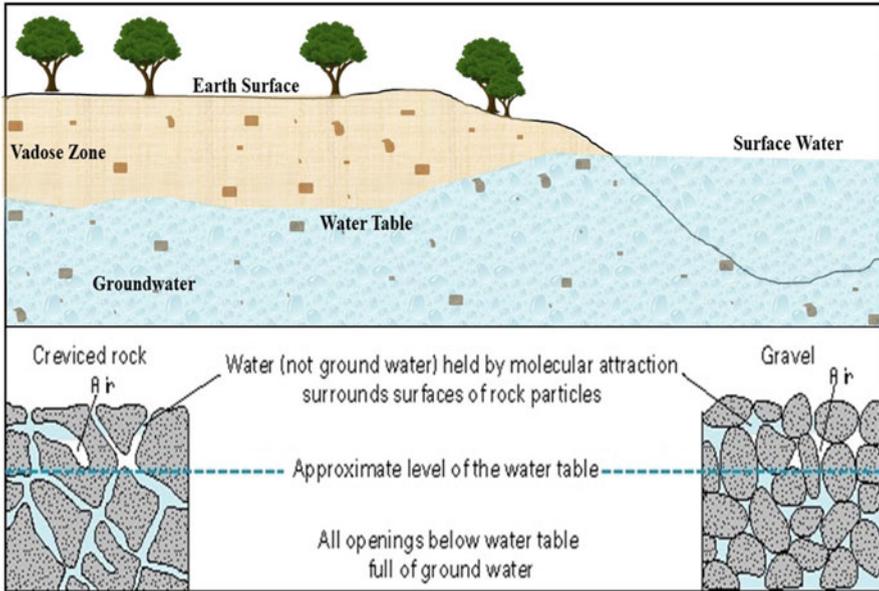


Fig. 2.1 The vadose zone (unsaturated zone), groundwater level, and pores in the subsurface

contaminant or impurity. It can be found all over the earth and hence is a very reliable source of fresh water for multiple uses as domestic, agricultural, and industrial water demand. It is the world's most extracted resource with withdrawal rates in the range of about $982 \text{ km}^3/\text{year}$ (Margat and Van-der 2013).

Groundwater fulfilled about 60% of the agriculture and half of the world domestic water requirement (Smith and Cross 2016). Although groundwater is less vulnerable to the pollution compared with the surface water resources but if contaminated, treatment of the same would be much challenging and costlier. There are numerous groundwater pollutants, but can be broadly categorized in two types:

1. Anthropogenic: caused by human activities like sewage, industries, mining, among others.
2. Geogenic: caused primarily by geological activities.

The scope of this chapter is limited to introduction, cause, effects, and possible remedial measures for geogenic and industrial pollution in groundwater.

2.2 Geogenic Pollution

Geogenic pollution denotes the state when certain naturally occurring elements in the groundwater rise to an objectionable level that can cause potential harm to mankind. It can emanate due to the geochemical decomposition of underlying aquifer material—contaminant the subsurface matrix as a result of dissolution during

geological interaction or may be due to other environmental factors like successive climatic changes, redox condition in an aquifer, change in groundwater flow regime. Anthropogenic activities like mining can also trigger the subsurface changes causing the geogenic pollution in groundwater. Table 2.1 lists some of the prime studies showing the status of geogenic pollutants in groundwater throughout the world. Major geogenic pollutants in groundwater that had proven to be a potential threat are listed below.

2.2.1 Fluoride (F^-)

It is the lightest member of halogens family and is found in varying concentration in rocks: granites (810 $\mu\text{g/g}$); basalt (360 $\mu\text{g/g}$); limestone (220 $\mu\text{g/g}$); shale (800 $\mu\text{g/g}$); sandstone (180 $\mu\text{g/g}$); oceanic sediments (730 $\mu\text{g/g}$), and soils (285 $\mu\text{g/g}$). Besides rocks, it is commonly found in plant, soil, and rock minerals like biotite, muscovite, mica, etc. Its existence in groundwater is predominantly geogenic due to weathering and dissolution of fluoride bearing minerals, hauled by calcite precipitation. Factors like pH, temperature, residence time, porosity, soil structure, depth, groundwater age, and ion exchange capacity of aquifer materials govern the extent of fluoride contamination in groundwater.

Human body needs small concentration of fluoride for prevention of dental caries. But intake of water with concentration more than a specific limit (1.5 mg/l) causes fluorosis, may be dental, skeletal, or non-skeletal fluorosis. Persistent intake of such fluoride contaminated water ultimately leads to severe joints related pain including knee-, pelvic-, and shoulder-joints, and may also restrict movements of cervical and lumbar spine, fluorosis is irreversible and the person once affected cannot be cured.

Treatment methods adopted for the treatment of groundwater contaminated with fluoride are broadly ex-situ techniques. These methods are based on adsorption and ion exchange (by active alumina, red mud, bone char, etc.), coagulation–precipitation (like Nalgonda technique), and membrane techniques (reverse osmosis, nano-filtration, etc.). Sustainable future solutions involve arranging alternate source of potable water, finding fluoride free aquifers by sampling at vulnerable sites, installation of de-fluoridation plants, and supply from appropriate surface water source, wherever available.

2.2.2 Arsenic (As)

Arsenic can be found abundantly in earth's crust and in small amount in soil, rock, air, and water. The typical concentration of arsenic in the interior crust is 1–2 mg/kg, 1.5–3.0 mg/kg in igneous rocks, and 1.7–400 mg/kg in sedimentary rocks. Various forms of arsenic, both organic and inorganic (more toxic), can be introduced to groundwater by geogenic, anthropogenic, or biogenic activities. It keeps circulating

Table 2.1 Some latest studies conducted to understanding the effect of geogenic pollutants in groundwater

S. no.	Reference	Study area	Target geogenic contaminants	Key findings	Possible remediation measures
1	Lapworth et al. (2017)	Bist-Doab region, India	Selenium and uranium	The contamination is due to dissolved minerals and iron oxide present on aquifer grains, the existing toxic and alkaline conditions, and carbonate complexation. The study concluded that the deeper aquifers are vulnerable to vertical breakthrough of mobile contaminants from shallow ones	Controlled groundwater extraction, adsorption-ion exchange process, and adopting redox technologies
2	Egbinola and Amanambu (2014)	Ibadan, South-West Nigeria	Arsenic and fluoride	The As concentration is above the WHO guidelines for drinking water in 98% and 100% of the dry and wet season samples, while 13% and 100% of the dry and wet season samples are having more fluoride. Questionnaire analyses concluded that 85% of respondents have never checked their wells, 55% have no knowledge of geogenic contamination	Dilution of affected areas, detailed geophysical investigation, isotopic and hydrochemical modeling studies
3	Harkness et al. (2017)	Southeast Wisconsin, United States	Molybdenum	The isotope signatures studies in correlation with mean groundwater residence times support a geogenic source of Mo to the groundwater, rather than CCR-induced contamination. The	Use of permeable reactive barriers (PRBs) and nanomaterials can be effective for the treatment

(continued)

Table 2.1 (continued)

S. no.	Reference	Study area	Target geogenic contaminants	Key findings	Possible remediation measures
				study exhibits the effectiveness of a multi-isotope approach to distinguish between anthropogenic and geogenic source of contaminant	
4	Selck et al. (2018)	Goshen Valley, UT, USA	Arsenic	The study finds out two distinct triggers that can lead to the release of As in groundwater: (1) development of high pH (>8.5) environment in semi-arid environments and (2) introduction of reducing situations at a neutral pH, which causes the reductive dissolution of As that is co-precipitated with Mn and Fe oxides. It may be from Paleozoic carbonate rocks or quaternary fill deposits found in the area	An integrated approach must be implemented for efficient, equitable, and sustainable groundwater management
5	Naeem et al. (2019)	Gaza coastal aquifer, Palestine	Salinity	Factor analysis (FA) comprised of three factors, viz. F1 as salinization, F2 as mixing of sewage invasion and water hardness, and F3 as carbonate dissolution, proved that high salinization in groundwater was the result of three main factors loadings accounts for 83.86% of the total variance. Areas dominantly	Techniques like micro-filtration and solar humidification can be implemented along with reactive barriers to control sea water intrusion

(continued)

Table 2.1 (continued)

S. no.	Reference	Study area	Target geogenic contaminants	Key findings	Possible remediation measures
				affected by the different hydro-geochemical processes are clarified by factors' scores. Ionic deltas and ionic ratios reveal the dominance of reverse ion exchange process	

all over the environmental compartments in a complex cycle. Due to alteration in gastrointestinal absorption, humans are more sensitive to arsenic contamination than animals and plants.

Arsenic contaminated groundwater has serious health impacts on human's in the form of respiratory distress (bronchitis or rhinitis, laryngitis, myocardial depolarization, etc.) and gastrointestinal effects (thirst, nausea, burning lips, painful swallowing, and abdominal colic). Overdue interaction with arsenic causes arsenic poisoning that leads to anemia and leucopenia. Ingestion of inorganic arsenic can cause neural failure, hallucinating, hypopigmentation spots generation, lungs or even skin cancer. Arsenic contamination in the unconsolidated aquifers of the world especially along alluvial and deltaic plains in southern and eastern parts of Asia is a chief concern for groundwater hydrologists.

The arsenic concentration in groundwater is intricately linked to the subsurface geometry, soil matrix, and groundwater flow regime. Planning of sustainable arsenic remediation techniques involves understanding of various physicochemical processes in subsurface, aquifer framework geometry, lithological information and flow regime of the study area. Treatment methods include options ranging from ex-situ treatment, searching alternative aquifers, dilution by artificial recharge. The arsenic free deep aquifers can be located beneath the affected shallow aquifers identified through detailed geophysical investigation, isotopic and hydro-chemical modeling studies.

2.2.3 *Salinity*

Salinity level is a suitable macro parameter defining the groundwater quality. It refers to the amount of salt (particles or ions) dissolved in water. The salinity is highly variable both in terms of quality (anhydrite, carbonates, halides, fluoride-salts, gypsum, and sulfate salts) and concentration levels throughout the world. It is generally expressed as either total dissolved solid (TDS) in milligram per liter of water or electrical conductivity (EC) in micro Siemen per centimeter. Geogenic phenomenon responsible for the salinity of groundwater includes deposition under

marine environment, sea water fluctuations (often accelerated by climate change), sea water intrusion, and various meteorological (like evaporation) and hydrological cycle (like carbon cycle).

High salinity levels in groundwater damage the plant growth, lower the crop yield, degrade aesthetic importance of groundwater, destroy aquatic life, and damage industrial equipment. These dissolved salts generally do not attenuate naturally and remain in groundwater for long time period of decadal scale. Intake of groundwater having higher concentration of salts like sodium can cause heart disease and high blood pressure.

Salinity reduction techniques in groundwater require a huge amount of financial as well as technical resources. The method of salinity reduction includes distillation methods (like vapor compression, solar humidification, multi-stage flash), membrane technologies (like reverse osmosis, micro-filtration, electro dialysis reversal), and providing freezing or hybrid facilities.

2.2.4 Uranium (Ur)

Uranium has an average concentration of only 0.0003% in the Earth's crust with three primary ore minerals, namely uraninite, pitchblende, and davidite. Naturally occurring igneous and sedimentary rocks contain uranium from 0.5 to 4.7 µg/g. It is gaining fast notoriety in the field of groundwater geogenic contaminants. Along with the radiotoxicity of uranium, its aqueous form has chemical toxicity also due to formation of complex compounds, hydrolytic processes, and redox properties. Uranium in groundwater is predominately geogenic but anthropogenic activities like groundwater table decline and nitrate pollution may further enhance uranium mobilization.

Uranium contamination in groundwater may lead to chronic kidney disease and cancer in humans. Its concentration in groundwater cannot exceed much due to inclination towards complex formations. Uranium generally found to accumulate in the soil and plant fruits irrigated by the uranium contaminated water. It may generate mutagenicity and reproductive toxicity on long exposure. World Health Organization (WHO) set up a provisional, owing to outstanding uncertainties regarding the toxicology and epidemiology of uranium, threshold limit of 30 µg/l for drinking water.

Treatment of uranium contaminated groundwater can be done in broadly two ways: (1) Ex-situ techniques (adsorption and ion exchange, reverse osmosis, reactive sorption, and precipitation) and (2) In-situ methods (phosphate precipitation, flushing, and redox technologies).

2.2.5 Radon (Rn)

It is a gas generally produced during decaying of uranium ore radium-226. It can be found in phosphate rock, uranium ores, black shales, metamorphic and igneous

rocks such as schist and granite. It may accumulate in small caves and fractures, but concentration of radon varies significantly with different seasons and environmental conditions. Radon has a solubility co-efficient of 0.254 at 20 °C in groundwater. Radon concentration in groundwater depends upon mineralogy of rocks, grain size, uranium content, permeability, fracture geometry in the host rock, and its tectonic history. The concentration of radon found to be inversely varying with the pH value of groundwater.

Consumption of radon contaminated groundwater can cause lung cancer, emphysema, respiratory lesions, and pulmonary fibrosis, chronic interstitial pneumonia, and silicosis. It can also generate genotoxic effects—higher incidence of chromosomal aberrations in humans.

The principal methods to remediate radon contaminated groundwater is stripping, aeration, and adsorption. Aeration technique of radon remediation from groundwater can ultimately proves to be a large source of air-borne radon.

2.2.6 Chromium (Cr)

It is the transition element found in groundwater either due to weathering and erosion of chromium-containing rocks or volcanic eruptions. Oxidation state of chromium varies from -2 to $+6$ and the distribution oxidation ratio governs by complex biochemical factors like pH, redox and nutrient levels that govern bacterial activity in the subsurface.

Chromium (III) compounds and metal are not included in potential geogenic contaminants, while chromium (VI) can be a serious threat to humans due to its toxicity and carcinogenic properties. Because of the selective transport mechanism of Cr, quantity of Cr (III) entering the cell is limited. Chromium (III) in the cell can lead to DNA damage as verified by several vitro studies. Acute oral toxicity for chromium ranges between 1.5 and 3.3 mg/kg. Once in contact with the blood stream, it can damage the kidneys, liver, and blood cells through oxidation reactions.

Remedial measures for chromium contamination include methods to reduce either its toxicity or concentration in groundwater. Chemical, microbial, and phyto-remediation techniques are used to reduce the toxicity of Cr by altering the oxidation state. Ex-situ measures for reducing the chromium concentration incorporates ion exchange methods, granular activated carbon, adsorbents, and membrane filtration techniques. In-situ methods involve soil flushing and electro kinetics.

2.2.7 Selenium (Se)

It is a non-toxic metalloid discovered by Swedish chemist Jons Jacob Berzelius in 1817. It is an important geogenic contaminant due to its ability to produce compounds like hydrogen selenide, aluminum sesquioxides, and cadmium selenide that

are extremely toxic to humans. Mobility of selenium and its complexes in groundwater governs by the temperature, moisture, concentration, climate, microbial activity, and organic matter content of the geological formations.

Major concern with the selenium is its ability to accumulate in the food chain as different compound. Exposure to selenium contaminated water in humans is responsible for loss of keratin protein, progressive deterioration of health, nausea, headache, and staining of teeth and nails with brittleness and longitudinal streaks. Techniques used for selenium remediation include ion exchange, activated alumina (AA), reverse osmosis (RO), and distillation.

2.3 Industrial Pollution

Apart from the geogenic processes occurring in the subsurface, industrial effluents are major source of groundwater pollution. Effluents from the factories whether in the form of chemical waste, solid waste, or in other toxic and hazardous form when reach the groundwater, exacerbated and aggravated the groundwater pollution. Industries are primarily related to the point source groundwater pollution due to mismanagement of their waste discharged either directly or indirectly to the groundwater. Fate and transport of these discharged effluents determine the extent and severity of groundwater contamination caused. They are usually more toxic than geogenic contaminant and have a long lasting effect on groundwater. There are numerous incidents of groundwater pollution by industries found all over the world listed in Table 2.2. Industrial pollutants include a wide variety ranging from heavy metals to complex biochemical compounds.

2.3.1 Lead (Pb)

It is a soft, malleable but denser metal having relatively low melting point. It is sparingly soluble in water and has the ability to combine with chloride, hydroxyl, and organics to form complexes. Tendency to form complexes increases the lead mobility in the subsurface. This increased mobility elevates its concentration in the groundwater. Lead contamination of groundwater due to industrial activities has been reported in many parts of the world.

It is a non-putrescible contaminant that is hard to remediate completely. It can inhibit the action of bodily enzymes resulting in potential threat to human and animal race. It may also affect the vegetation and aquatic life nearby the contaminated site. The existence and transport of lead depends on process like adsorption, dissociation, absorption along with various complex chemical and biological reactions.

Table 2.2 Recent studies emphasizing the presence of industrial pollutants in groundwater

S. no.	Reference	Study area	Contaminants and there source	Highlights
1	Miglietta et al. (2017)	Salento (Southern Italy)	Mercury (Hg), vanadium (V) from the industries located nearby (Cutrofiano and Galatina)	Climatic characteristics and human activities involving the extensive use of water resources influence the level of groundwater contamination, leading to reduced water availability and to progressive deterioration of its quality
2	Wu and Sun (2016)	Guanzhong Plain, mid-West China	Nitrate from a fertilizer industry name Shanhua	The study concluded that the over 60% of groundwater samples are not fit for drinking, and total hardness, nitrate, nitrite, TDS, and fluoride are the main contaminants degrading its quality for drinking purpose. Spatial variability of pollutants indicates the groundwater pollution by some anthropogenic point source
3	Li et al. (2016)	The Hutuo River plain, China	Iron, manganese, and other organic contaminants like CCl ₄ industrial sewage discharge, landfills, and mining	The study revealed that 21.5% of the groundwater samples collected are exceeding the Class III water standard, and these are concentrated in areas receiving industrial sewage discharge, mining water, or susceptible to landfill leakage
4	Kumar et al. (2016)	Coimbatore, Tamil Nadu, India	Mercury and arsenic from Kurichi Industrial Cluster	The study used atomic absorption spectrophotometry (AAS) using Perkin Elmer AA 200 model to evaluate the levels of Hg, As, and Cd based on Indian Standards-3025

2.3.2 Mercury (Hg)

It is a transition or post-transition metal found in liquid state at room temperature. It is injurious, even lethal, to most of the living organisms. Its contact via contaminated groundwater can cause damage to respiratory, neural, and renal systems. The fate and transport of mercury is governed by various physio-chemical process like oxidation–reduction, precipitation–dissolution, aqueous complexation, and adsorption–desorption reactions at soil–air–groundwater interface.

2.3.3 Organics Pollutants

They are the most common and deadliest pollutants released into the groundwater majorly from petrochemical and automobiles industries. While some of them can degrade, most of the organic pollutants are either non-biodegradable or will take years to attenuate naturally. Groundwater primarily polluted by volatile organic compounds (VOCs) like aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylene) and chlorinated solvents (tetrachloroethylene (PCE), trichloroethylene (TCE), and vinyl chloride (VC)). Extent of contamination by such pollutants is governed by geological controls (i.e., intrinsic vulnerability), the degree of concealment of aquifer, the hydraulic properties of the overlying soil and underneath aquifer system. The Karstic aquifers are predominantly at risk from diffuse and point sources of these pollutant due to constrained natural attenuation in the vadose zone during recharge.

2.4 Countermeasures

Groundwater pollution is a serious concern and must be addressed adequately for sustainable developments. Most of the regulatory and governing agencies become active only after the area is being affected by groundwater pollution. Some of the precautions that must be adopted for the perseverance of groundwater resources are shown in Fig. 2.2.

Fig. 2.2 Precautionary measures must be adopted to obtain safe and sustainable groundwater



It must be collective efforts of all including politicians, industrialists, and other common peoples to protect the precious natural resource. Table 2.3 lists some case studies that depict the methods used for checking the status of groundwater pollution throughout the world. Steps listed in Fig. 2.2 can be further explained as:

1. *Sampling and monitoring*: The groundwater samples should be collected periodically for detection of any possible pollutants. The sampling locations should be spatially and temporally well distributed so that they can represent the quality of whole aquifer system.
2. *Awareness toward environment*: Awareness activities and programs should be planned to encourage environmental concern in people. The committee forming the laws and legislation for environmental components must comprise local residents of the concerned area.

Table 2.3 Case studies conducting to detect the groundwater pollution status worldwide

S. no.	Reference	Study area	Technique used	Key findings
1	Zhua et al. (2018)	Guangxi Province, China	CCME WQI and PLEIK (P: Protective cover; L: Land use; E: Epikarst development; I: Infiltration conditions; K: Karst development) method is used for hazard influence	A 36.35% and 49.73% of the groundwater samples in Guangxi and Luzhai, respectively, are contained hazardous levels of pollution. The study finds Karst area to be more vulnerable
2	Kumar et al. (2016)	Uttar Pradesh, India	The study performed the spatio-chemical assessment and multivariate statistics analysis of groundwater samples	The area is found to be polluted severely by both geogenic and industrial pollutant. The hazard quotient (HQ) value exceeded the safe limit of 1 which for As, B, Al, Cr, Mn, Cd, Pb, and U at few locations while hazard index (HI) > 5 was observed in about 30% of the samples which indicated potential health risk from these tubewells for the local population if the groundwater is consumed
3	Shrestha et al. (2016)	Katmandu, Nepal	GIS based DRASTIC and GRAM models are used for groundwater vulnerability assessment to nitrate pollution	More than half of the valley is vulnerable to the groundwater pollution and 87% of the subsurface basin are at moderate residual risk to nitrate pollution
4	Akinbile and YusoFf (2011)	Akure, Nigeria	Three dimensional, i.e., physical, chemical, and bacteriological analyses of groundwater samples	The groundwater in area I severely polluted by heavy metals and pathogens. Physical water quality parameters are in recommended limits for most of the samples

3. *Integrated waste management approaches*: Sewage mismanagement, industrial effluents, and leachates from solid waste are primarily responsible for groundwater pollution. An integrated waste management approach can lead the world toward the goal of sustainable development.
4. *Effective legislations*: The world needs more effective and strict laws governing the groundwater use and safeguarding it from pollutants. These laws can be drafted and implemented on a national or even local scale but will be more effective if they have international binding.

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Chapter 3

Aqueous Two-Phase Systems: An Alternative Process for Industrial Dye Recovery



Luan Victor T. D. Alencar, Lais M. S. Passos, Renato Nery Soriano, Ram Naresh Bharagava, Luiz Fernando Romanholo Ferreira, and Ranyere Lucena de Souza

Abstract The release of large volume of dyes through industrial aqueous effluents has become a growing concern, as effluents containing dyes are harmful to the environment and to living things. In this scenario, different methods (physical, chemical and biological) were developed for dye removal from wastewater. However, environmental and economic constraints can hamper industries' access to these technologies. Therefore, this chapter explores the use of aqueous two-phase systems (ATPS), considered an economically viable, efficient and environmentally low-impact technology for the recovery of dyes. Inherent aspects, such as classification of dyes, composition and behaviour of phases and influence on the recovery of dyes in ATPS, are examined.

Keywords Textile effluent · Toxicity · Dye recovery · Aqueous two-phase systems (ATPS) · Low-impact technology

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3.1 Introduction

Dyes are some of the most significant aquatic pollutants discharged by industry. It is estimated that more than 7×10^5 tonnes of wastewater containing dyes are generated by various industries worldwide each year (Hasan and Jhung 2015; Rajoriya et al. 2017; Zamora-Garcia et al. 2018). The effects of the inadequate disposal of these effluents can have significant impacts on the environment by altering the physical, chemical and biological properties of the aquatic environment (Dellamatrice et al. 2016; Hossain et al. 2018; Roy et al. 2018). One of the main sources of dye-contaminated wastewater is the textile industry, which involves the consumption of various types of dyes (Hussain and Wahab 2018; Rahman et al. 2018; Rovira and Domingo 2018). In view of increasingly stringent laws and regulations, associated industries are obliged to find effective treatments for dye-borne industrial effluents before releasing them into the environment (Hessel et al. 2007; Liu et al. 2014; Vajnhandl and Valh 2014).

Several treatment techniques (physical, chemical and biological) are proposed to remove residual water dyes (Patra et al. 2018; Rahman et al. 2018). However, most treatment methods have limitations, among which generation of hazardous waste, slow degradation rates and high costs stand out (Alvarenga et al. 2015; Nidheesh and Gandhimathi 2013; Katheresan et al. 2018; Sinha et al. 2018). Accordingly, efficient alternative methods that are cleaner, safer and economically viable are required for the removal of dyes from industrial effluents before releasing them into bodies of water (Alvarenga et al. 2015; Chauhan et al. 2015; Chen and Chen 2009).

Aqueous two-phase systems (ATPS) are an efficient method for extracting compounds in various technological processes. In recent decades, these systems have been introduced as a promising alternative for the removal of dyes from aqueous matrices, as they are environmentally safe, recyclable, economical viable; they also involve short processing times and are scalable for application in industrial processes (Alencar et al. 2020; Alvarenga et al. 2015; Borges et al. 2016; Passos et al. 2016; Zhang et al. 2018).

This chapter addresses information related to the characteristics of dyes and their toxicological effect on the environment. It covers conventional techniques for dye removal and introduces ATPS as an alternative separation process. Important aspects, such as system composition and interaction mechanisms, are also explored for the purpose of showing the potential uses of ATPS in the recovery of industrial dyes.

3.2 Dyes

Dyes are organic compounds that give colour to materials. They are used in various industries, such as textiles, cosmetics, food, paper and plastic (Suteu et al. 2013). Currently, it is estimated that there are more than 100,000 different commercially

available dyes (Abdi et al. 2017; Mojsov et al. 2016; Zamora-Garcia et al. 2018). In the past, dyes were usually produced on a small scale from available natural resources, such as insects or plants (Kant 2012). However, natural dyes have limited variety and produce muted tones that fade when exposed to sunlight and washing (Solís et al. 2012). Because of this, synthetic dyes currently account for the largest share of applications in industries: more than 90% of industrially used dyes are synthetic (Nagendrappa 2010).

Synthetic dyes were discovered as a result of the search for new colourfast tones. In 1856, William Henry Perkins developed the first synthetic dyes, providing different shades for the textile industry, and their large-scale production began due to increased demand for dyes (Gupta and Suhas 2009; Kant 2012). Synthetic dye molecules are complex and stable structures due to the presence of auxochromes (water-soluble bonding compounds) and chromophores (sets of atoms in a molecule responsible for its colour), so that the colour of the dyed material is fixed more stably (Katheresan et al. 2018). For this reason, they are composed of complex organic substances that can resist degradation upon contact with water, detergents or other washing agents (Al-Alwani et al. 2018).

3.2.1 Classification of Dyes

There are many types of dyes; these may be classified according to chemical structure (Table 3.1) or by their usage (Table 3.2) (Hunger 2007; Mojsov et al. 2016). Acid, basic, direct and reactive dyes are examples of soluble dyes, and azo, disperse, sulphur and vat dyes are examples of insoluble dyes (Rauf and Salman 2012). In addition, dyes are usually classified based on their particle charge upon dissolution in aqueous application mediums, such as cationic (all basic dyes), anionic (direct, acid and reactive dyes) and non-ionic (dispersed dyes) (Yagub et al. 2014).

Table 3.1 Classification of dyes according to the chemical structure

Class of dyes	Chromospheres	Class of dyes	Chromospheres
Azo		Nitroso	
Anthraquinone		Nitro	
Indigoid		Triarylmethane	

Table 3.2 Classification of dyes

Class of dyes	Substrate	Method of application	Chemical types
Acid	Wool, nylon, silk, inks, leather and paper	Generally from neutral to acidic bath	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitrous
Basic	Inks, paper, polyacrylonitrile, treated nylon, and polyester	Generally from neutral to acidic bath	Hemicyanine, azo, cyanine, diazahemicyanine, azine diphenylmethane, xanthene, triaryl methane, acridine, anthraquinone and oxazine
Direct	Nylon, rayon, paper, leather and cotton	Applied from neutral or a slightly alkaline bath containing additional electrolytes	Phthalocyanine, azo, oxazine and stilbene
Disperse	Polyamide, acrylic polyester, acetate, and plastics	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye may be padded on cloth and thermo fixed	Benzodifuranone, azo, anthraquinone, nitro and styryl
Reactive	Wool, cotton, silk and nylon	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH	Anthraquinone, formazan, phthalocyanine, azo, oxazine and basic
Sulphur	Rayon and cotton	Aromatic substrate vatted with sodium sulphide and reoxidised to insoluble sulphur-containing products on fibre	Indeterminate structures
Vat	Wool and cotton	Water-insoluble dyes solubilised by dropping in sodium hydrogen sulphite, then exhausted on reoxidised and fibre	Indigoids and anthraquinone

Adapted from Adegoke and Solomon (2015), Hunger (2007), and Gupta and Suhas (2009)

3.2.2 Toxicity of Dyes

Effluents generated during industrial processing generally contain a high dye load. These wastes are discharged into bodies of water, changing the colourless, clean water to coloured and contaminated water (Katheresan et al. 2018). The presence of dyes can cause the formation of a visible layer on the surface of the water, interfering with the penetration of sunlight and, consequently, the process of photosynthesis; this, in turn, can trigger damage to the aquatic communities present in the ecosystem (Chacko and Subramaniam 2011; Gupta and Suhas 2009; Patra et al. 2018). In addition, dyes may be toxic to aquatic organisms because they contain metals and aromatic compounds (Holkar et al. 2016; Yagub et al. 2014).

Table 3.3 International standard for discharge of dye effluent into the environment

Parameters	Standard/allowed
BOD	Below 30 mg/L
COD	Below 50 mg/L
Colour	Below 1 ppm
pH	Between 6 and 9
Suspended solids	Below 20 mg/L
Temperature	Below 42 °C
Toxic pollutants	Not allowed to be released

Adapted from Mojsov et al. (2016)

Effluents containing incorrectly discarded dyes may also affect human health: when in contact with the eyes, burns or even permanent injury may occur (Amran et al. 2011; Katheresan et al. 2018). Likewise, when dyes are inhaled, shortness of breath or difficulty in breathing can occur, and when they are ingested, dyes may cause extreme sweating, methemoglobinemia, mouth burns, nausea or vomiting (Rafatullah et al. 2010). Dyes are also conventional carcinogens, and long-term effects to one's body or unborn child are unavoidable (Holkar et al. 2016; Katheresan et al. 2018; Patra et al. 2018). Even the natural dyes are high impact, due to certain mordants that have to be used with them. Mordants, such as chromium, are substances used to fix colour onto the fabric. They may be very toxic and may have a strong impact on the wastewater quality (Bhatt and Rani 2013; Kant 2012).

Textile wastewater is rich with pollutants, such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), suspended solids, colours, hazardous chemicals, a wide range of pH values and dissolved salts (Solís et al. 2012). The international permissible standard for dye effluent pollutant discharge is shown in Table 3.3, in which the levels of the released effluent parameters must be below the permitted amount to discharge into the environment. Toxic pollutants are not allowed to be released into the environment due to the dreadful consequences of doing so (Mojsov et al. 2016).

3.2.3 Methods of Dye Removal

It is estimated that more than 7×10^5 tonnes of wastewater with dyes are generated worldwide each year (Hasan and Jhung 2015; Zamora-Garcia et al. 2018). Figure 3.1 illustrates the major industries responsible for the disposal of dye effluents into the environment. Among the main industrial sectors, the textile industry stands out for contributing more than half of the existing dye effluent worldwide (Katheresan et al. 2018).

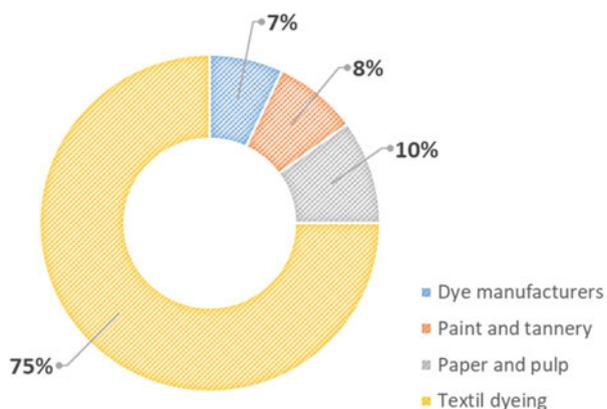


Fig. 3.1 Percentage of industries responsible for the presence of dye effluent in the environment

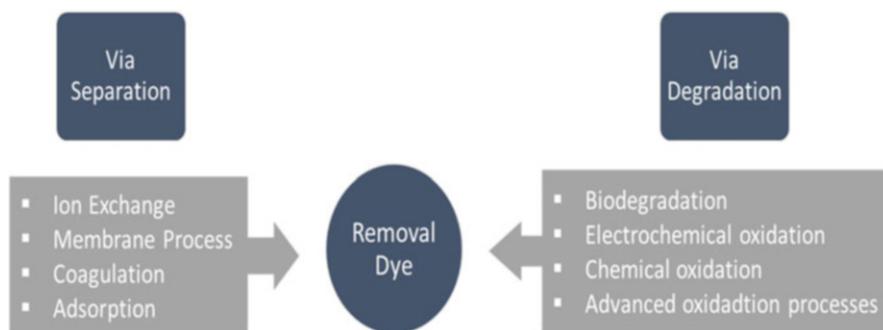


Fig. 3.2 Schematic representation of some methods of dye removal from water via separation or degradation

Due to their toxic effects, the industrial use of these dyes generates an enormous environmental concern (Yagub et al. 2014). Therefore, considering increasingly strict legislations and regulations worldwide, the associated industries must find the means to treat industrial dye-laden effluents before they are discharged into the environment (Hessel et al. 2007; Liu et al. 2014; Vajnhandl and Valh 2014). Consequently, various treatment techniques have been developed to remove synthetic dyes from aqueous solutions. These include coagulation (Gadekar and Ahammed 2016), biodegradation (Mona et al. 2011), electrochemical techniques (Módenes et al. 2012), adsorption (Zhou et al. 2014), ion exchange (Wawrzkievicz and Hubicki 2015), membrane filtration (Kebria et al. 2015), chemical oxidation (Cotillas et al. 2018) and advanced oxidation processes (Manenti et al. 2015).

Based on the principal mechanism behind the removal of dyes, these methods can be divided into two broad classes: separative (physical) and degradative (chemical and biological) (Nidheesh et al. 2018). The schematic diagram of the various

Table 3.4 Efficiency of various dye removal methods

Method	Dye	Maximum efficiency (%)	Reference
Adsorption	Malachite green	99.8	Garga et al. (2003)
Coagulation	Acid red 119	96.5	Moghaddam et al. (2010)
Membrane process	Direct yellow	98.3	Mustafa and Nakib (2013)
Ion exchange	Acid Orange 7	87.0	Wawrzekiewicz (2012)
Biodegradation	Remazol Black B	85.2	Aksu (2005)
Chemical oxidation	Reactive blue 19	90.0	Khan et al. (2015)
Advanced oxidation processes	Direct Blue 86	8.0	Hassaan et al. (2017)
Electrochemical destruction	Remazol Brilliant Blue	70.4	Mukimin et al. (2012)

methods used for the dye removal and examples of the efficiency of these methods are shown in Fig. 3.2 and Table 3.4, respectively.

Although they present a good efficiency ratio in dye removal, these methodologies may present some disadvantages that can make their large-scale application unfeasible. Among these, it is possible to highlight the significant costs associated with treatments involving adsorption (Holkar et al. 2016), electrochemical (Nidheesh and Gandhimathi 2013) and advanced oxidation processes (Comminellis et al. 2008). Large amounts of concentrated sludge are also generated by methods involving coagulation (Wang et al. 2011) and membrane filtration (Robinson et al. 2001). Besides that, the exchange ion method is not effective for some dyes, such as disperse dyes (Amran et al. 2011; Crini 2006), and the methods of biodegradation method require a large area and long treatment time. Beyond this, dyes are not easily biodegraded (Brillas and Martínez-Huitle 2015; Rauf and Salman 2012).

Conversely, efficient alternative methods that are cleaner, safer and economically viable seem to be the key to preventing the inappropriate disposal of dyes (Alvarenga et al. 2015; Chauhan et al. 2015; Chen and Chen 2009). In this context, the use of aqueous two-phase systems may be an alternative with good prospects of real-world application (Borges et al. 2016; Ferreira et al. 2014; Ventura et al. 2013).

3.3 Aqueous Two-Phase Systems (ATPS)

Aqueous two-phase systems (ATPS) are liquid–liquid extraction systems consisting of the combination of two different compounds in an aqueous medium, which, above certain concentrations, forms two liquid phases coexisting in equilibrium, each phase being enriched with one of the compounds (Baghlani and Sadeghi 2018; Neves et al.

2016; Pereira et al. 2015; Rodrigues et al. 2009; Sanglard et al. 2018). The basis for the solutes partitioning in these systems is a direct result of their selective distribution between the two phases, governed by the affinity of the target molecule for a given phase (Cienfuegos et al. 2017; Ferreira et al. 2014; Mourão et al. 2014).

The use of these systems has been satisfactorily studied for more than 40 years for use in the separation and purification of biological molecules, such as nucleic acids (Gomes et al. 2009), proteins (Sheikhian et al. 2013; Zeng et al. 2013), enzymes (Souza et al. 2015; Ventura et al. 2011), alkaloids (Flieger and Zelazko 2015; Reis et al. 2014), antibiotics (Chen et al. 2014; Li et al. 2009), antibodies (Rosa et al. 2013; Taha et al. 2015), oestrogens (Dinis et al. 2015) and compounds of non-organic origin, such as metallic ions (Akama and Sali 2002; Sousa et al. 2016).

The ATPS separation efficiency depends on the properties of the the compounds to be separated as well as on the properties of compounds that form the ATPS. For this purpose, the constituents should be carefully selected considering the ability to form two immiscible aqueous phases, promoted by the addition of water-soluble compounds. These systems are usually formed by polymer/polymer, polymer/salt or salt/salt combinations (Mourão et al. 2014; Nascimento et al. 2018; Shukla et al. 2018). Additionally, molecules like ionic liquids (IL) (Alvarenga et al. 2015; Freire et al. 2012a, b), deep eutectic solvents (DES) (Farias et al. 2017; Xu et al. 2014) and organic compounds, such as alcohols (Li et al. 2015) and acetone (Lu et al. 2013), have been recently applied as phase formers targeting efficient ATPS.

The ATPS compositions are represented by phase diagrams that express the concentration of the components of the system. In systems with three components (ternary systems), the phases are represented by triangular phase diagrams, or ternary diagrams, where the composition is indicated by a point in an equilateral triangle as shown in Fig. 3.3 (Freire et al. 2012a, b).

For ATPS, where the water concentration is very high (40–80%, w/w), the Cartesian axis can be used to represent the compositions of the compounds (Fig. 3.4a), which excludes water composition (Zaslavsky 1995). In these diagrams it can be observed the chemical composition of the two phases that are in thermodynamic equilibrium, expressed in different units corresponding to the molar or mass fractions. Normally, units of concentration in mol (mol kg^{-1}) are used to avoid potential discrepancies caused by the different molecular weights of the solutes involved in the formation of ATPS. However, for extraction or purification purposes, most data in the literature correspond to the mass fraction unit (% w/w). The authors generally compared efficiency or extraction yields as a function of the blend compositions (in mass terms) between the ATPS (Freire et al. 2012a, b; Shukla et al. 2018). In these systems, the total composition of the mixture of components is represented by the mixing point (M) (Fig. 3.4b). The mixture separates into two phases, which contain the fractions of the forming constituents.

The compositions of these two phases are represented by the points of the top phase (T) and the bottom phase (B). The union of these points forms tie-lines, where the tie-line length is a numerical indicator of the composition difference between the two phases that is generally used to correlate trends in the partitioning of solutes between both phases. From the union of the extreme points of each tie-line, it forms

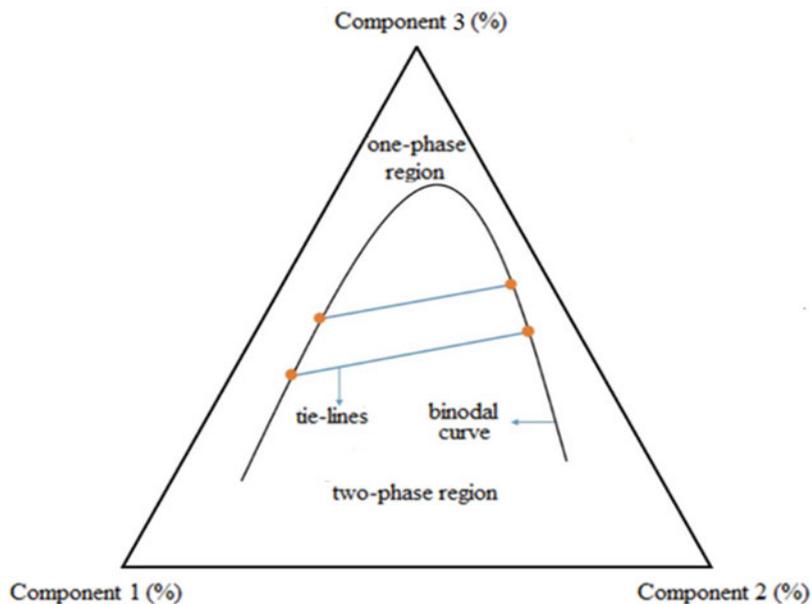


Fig. 3.3 Phase diagram in triangular coordinates. —: binodal curve; —: tie-line. Inside the binodal curve, the system is biphasic; outside it, the system is monophasic

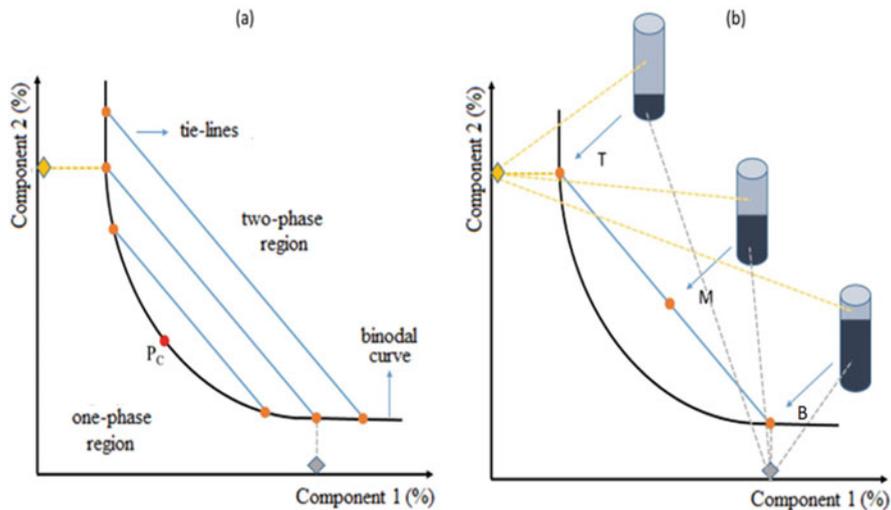


Fig. 3.4 Phase diagram for an ATPS. (a): —, binodal curve; —, tie-line; ●, critical point— P_C . Above the binodal curve, the system is biphasic; below it, the system is monophasic; (b): Three systems (blue tubes) belonging to the same tie-line. The compositions of the top and bottom phases are shown

the binodal curve, which separates two regions in the diagram. Above the binodal curve is the biphasic region, and below is the monophasic region. Finally, there is the critical point at which the volume and composition of coexisting phases are equal (Freire et al. 2012a, b; Glyk et al. 2014; Zaslavsky 1995).

Therefore, ATPS applications may offer an alternative to conventional liquid–liquid extraction due to their properties, such as low interfacial tension and fast mass transfer rate, which allow high yields. Also, ATPS offers environmentally friendly features, as they have high water content, besides presenting ease of scaling up, short process time and lower costs (Barrueto et al. 2015; Lucena et al. 2017; Ventura et al. 2013; Zhang et al. 2015).

3.3.1 Applications of ATPS for Dye Extraction

Due to their favourable properties, ATPS have been considered effective processing methods that can be satisfactorily used for the recovery of different dyes from aqueous mediums (Table 3.5). However, efficient applications of ATPS for these purposes depend, in addition to the properties of the compounds to be extracted, upon the constituents forming the ATPS. In this sense, knowing and evaluating the effects provided by the phase-forming constituents is extremely important when the objective is to control the partition of an analyte of interest between the two phases of the system (Alencar et al. 2020; Junqueira et al. 2018; Mageste et al. 2012; Passos et al. 2016; Zhang et al. 2018).

3.3.1.1 Effect of Polymers

The distribution of a solute in ATPS can be significantly affected by the molar mass of the polymeric constituent (Alvarenga et al. 2015; Borges et al. 2016; Mageste et al. 2009, 2012). Most polymers used in ATPS for dye partitioning involve the use of polyethylene glycol (PEG), polypropylene glycol (PPG) and polyethylene oxide (PEO) due to their easy availability and their non-toxic nature (Guan et al. 1992).

Mageste et al. (2009) investigated the influence of PEO molar mass on the partitioning of carmine dye in systems formed with different PEO (1500, 4000 and 6000 gmol^{-1}) + lithium sulphate + water. The increase in the polymer's molecular weight decreased the partition coefficient, thus reducing the distribution of the dye molecules in the top phase (polymer rich). This feature is common in the partitioning of biomolecules using polymer/salt systems. Biomolecules, when partitioned into the system, have a defined size (molar mass and hydrodynamic diameter) and geometry (three-dimensional conformation), and these are subjected to the steric effects imposed by the system components. These effects, because of their entropic nature, are typically related to the volume available for the solute to migrate to one of

Table 3.5 Extraction efficiency (EE) of ATPS for removal of dyes

Dye	Type of ATPS	Compound 1	Compound 2	EE (%)	References
Remazol Yellow Gold RNL	Polymer—salt	PEG 1500	Li ₂ SO ₄	100	Alvarenga et al. (2015)
Amaranth	DES—salt	[PPG 400]: [TBAB]	Na ₂ CO ₃	98	Zhang et al. (2018)
Sunset Yellow FCF	DES—salt	[PPG 400]: [TBAB]	Na ₂ SO ₄	95	Zhang et al. (2018)
Sudan III	Salt—IL	C ₆ H ₅ K ₃ O ₇	[P ₄₄₄₄]Cl	100	Ferreira et al. (2014)
Anthraquinone	Surfactant—surfactant	SPFO	C ₁₂ NE	100	Tong et al. (1999)
Methyl Red	Surfactant—surfactant	SDS	C ₁₂ NE	100	Akama et al. (1999)
Methyl Violet	Surfactant—surfactant	SDS	C ₁₂ NE	90	Akama et al. (1999)
Remazol Brilliant Blue R	Organic solvent—salt	(CH ₃) ₂ CHOH	(NH ₄) ₂ SO ₄	97,2	Sanglard et al. (2018)
Malachite Green	Polymer—salt	PEO 1500	Na ₂ C ₄ H ₄ O ₆	99,9	Borges et al. (2016)
Methylene Blue	Polymer—salt	PEO 400	Na ₂ SO ₄	99,74	Borges et al. (2016)
Reactive Red 195	Polymer—salt	PEO 400	Na ₂ SO ₄	99,76	Borges et al. (2016)
Chloranilic Acid	Salt—IL	C ₆ H ₅ K ₃ O ₇	[P ₄₄₄₄]Br	100	Ferreira et al. (2014)
Indigo Blue	Salt—IL	C ₆ H ₅ K ₃ O ₇	[P ₄₄₄₄]Cl	100	Ferreira et al. (2014)
Natural Red Colorants	Salt—IL	Citrate Buffer	[N ₄₄₄₄]Br	98	Ventura et al. (2013)
Pigment Blue (PB29)	DES—polymer	[C ₂ H ₄ O ₃]:[N ₁₁₁ (2OH)]Cl	PPG 400	100	Passos et al. (2016)

the phases and can be controlled by the molecular mass of the polymer (Andrews et al. 2005; Forciniti et al. 1991).

However, the nature of the electrolyte (especially the cation) used may mediate the carmine—macromolecule interaction, as observed with systems formed by PEO (1500, 4000 and 6000 gmol⁻¹) + sodium sulphate + water. The carmine partition is mainly based on enthalpic intermolecular interactions, whereby the increase in the molar mass of the polymer does not significantly affect the partition values (Mageste et al. 2009). Similar results were also found in the partitioning of the dyes norbixin, malachite green and Remazol Yellow Gold RNL, in ATPS based on PEO and PEG (Mageste et al. 2012; Borges et al. 2016; Alvarenga et al. 2015). Conversely, the partition of the dyes chloranilic acid and rhodamine 6G was significantly affected by changing the molecular weight of the PEG from 1500 (gmol⁻¹) to 8000 (gmol⁻¹), in a system formed by PEG + K₂HPO₄/KH₂PO₄ (pH 7) + water (Souza et al. 2014).

Therefore, it is important to consider that there is no clear rule for dye partitioning between the phases of a system formed with polymers and salts, as the molecular nature of the polymer, salt and dye should be considered for efficient separation between the phases of the system.

3.3.1.2 Effect of Salts

The composition of the salts in ATPS is of great relevance for the successful separation of the molecules. Usually, buffer solutions are used to maintain the pH at the desired value, as the pH changes the partitioning behaviour. However, where partitioning of certain compounds is desirable, other salts may be added without the need to use a specific linker (Rito-Palomares 2004). Systems with different salts can present significant changes in the partition coefficients for the same solute. This means that ions have different affinities for the two phases, reflected by their hydration energy, $\Delta_{\text{hyd}}G^*$ (Franco et al. 1990). The phosphate salts (PO_4^{3-} , $\Delta_{\text{hyd}}G^* = -2765$) have higher affinity for the bottom phase in ATPS composed of polymer + salt, while the lithium salts (Li^+ , $\Delta_{\text{hyd}}G^* = -475$) have greater affinity for the top phase. This condition the use of salts in ATPS as excellent salting-out agents. Therefore, the appropriate selection of salts will have great influence in the difference of electric potential between the phases of the system (Albertsson and Tjerneld 1990).

Alvarenga et al. (2015) investigated the effect of different cations (lithium, magnesium and ammonium) conjugated in the anion sulphate for partitioning of the Remazol Yellow Gold RNL (YR) dye in a system composed of PEG 1500 + salt + water. ATPS formed by lithium salt are more efficient in the transfer of YR to a polymer-rich phase. When compared to other cations, a higher concentration of Li^+ is necessary to energetically saturate the polymer chain. Thus, the macromolecule structure of the polymer is more positively charged in the ATPS when composed of lithium sulphate, and this enables a stronger electrostatic interaction between the polymer-cation and YR in the lithium sulphate system. This same effect was also demonstrated for the carmine dye partition in systems formed by PEO 1500 + lithium sulphate + water (Mageste et al. 2009).

The partition of the chloranilic acid, indigo blue and Sudan dyes in ATPS formed by IL (phosphonium- and imidazolium-based) + inorganic (aluminium sulphate) or organic salt (potassium citrate) + water was evaluated (Ferreira et al. 2014). Both aluminium sulphate and potassium citrate, when combined with ILs, obtained 100% extraction efficiency for all three dyes. Thus, it was concluded that both salts are strong salting-out agents and are able to further induce the partitioning of the dyes to the IL-rich phase. Depending on the purpose and specific application, either an inorganic salt used in water-treatment processes or a biodegradable and less toxic organic salt can be chosen.

Borges et al. (2016) explored the effect on the partitioning of Malachite Green (MG) dye in systems formed by PEO 1500 + lithium sulphate or sodium sulphate or

sodium tartrate + water. In comparative tests of the three salts, the effects of the anion and cation could be evaluated separately. For the same anion (using sodium sulphate and lithium sulphate), the systems containing the Na^+ cation provided greater extraction efficiency ($\text{EE} = 99.4\%$) for the MG dye, compared to the systems containing Li^+ . For the same cation (using sodium sulphate and sodium tartrate), it was found that tartrate provided greater removal efficiency ($\text{EE} = 99.9\%$) of MG. Optimization of the electrolytes used for removal of the dyes, therefore, showed that the best extraction efficiencies were obtained using sodium tartrate for MG dye.

3.3.1.3 Ionic Liquids-Based ATPS

Ionic liquids (IL) have attracted extensive attention in many areas of chemistry, biotechnology and environmental engineering, mainly due to their unique combination of physicochemical properties, such as negligible volatility, non-flammability, high thermal and chemical stability and large liquid temperature range (Gusain et al. 2018; Królikowski 2018; Marsousi et al. 2018; Severiano-Carrillo et al. 2018). Since 2003, alternative ATPS constituted by IL have been proposed (Gutowski et al. 2003). Among the main advantages of the use of IL in ATPS has been that ATPS based on these compounds have a wide polarity range and the possibility of manipulating their physicochemical properties using a proper combination or manipulation of the cation, anion and alkyl chains of the ILs (Freire et al. 2012a, b; Lucena et al. 2017; Naushad et al. 2012).

Alvarenga et al. (2015) explored the effect of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{B}_{\text{mim}}]\text{BF}_4$) on the partitioning of the Remazol Yellow Gold RNL (YR) dye in a system formed by $[\text{B}_{\text{mim}}]\text{BF}_4$ + salt + water, which tested two different salts: magnesium sulphate and ammonium sulphate. It has been observed in $[\text{B}_{\text{mim}}]\text{BF}_4$ + ammonium sulphate + water ATPS that the top phase is rich in IL and the bottom phase is rich in salt. The partitioning coefficient behaviour in this system was attributed to an entropic contribution resulting in an increase in the dye partition coefficient with increasing tie-line length (TLL). However, in $[\text{B}_{\text{mim}}]\text{BF}_4$ + magnesium sulphate + water, the partitioning coefficient values decrease with increasing TLL. This surprising partitioning behaviour can be rationalized by considering that this system exhibits phase inversion.

Therefore, the IL-enriched phase, which is the less dense top phase, becomes the bottom phase. At smaller TLL values, partitioning of YR was enthalpically driven and for this reason, this dye tends to migrate preferentially to the bottom phase due to interactions with the IL. Interestingly, when the TLL increases, the density of the salt-rich phase is higher than that of IL-rich phase due to the significant water content of the bottom phase. Thus, the entropic contribution predominates with regard to the enthalpic contribution, resulting in a decrease in the partitioning coefficient values of YR.

Ventura et al. (2013) evaluated three different ionic liquids in the partitioning of three natural dyes produced by a submerged culture of *Penicillium purpurogenum* DPUA 1275 from the fermentation broth in ATPS composed of IL + citrate buffer + water. The ILs investigated were tetraethyl ammonium bromide ($[N_{2222}][Br]$), tetrabutyl ammonium bromide ($[N_{4444}][Br]$), and 1-butyl-3-methylimidazolium chloride ($[C_{4mim}][Cl]$). The results suggested that the three colorants have a preferential migration towards the top IL-rich phase, which was reflected by the large partition coefficients (4.3–41.7). The results showed that the migration of the colorants can be significantly increased by some structural features of ILs. It was observed that the quaternary ammonium-based ILs (an acyclic and non-aromatic cation) have a larger capacity to extract the colorants from the fermentation broth than the imidazolium-based ILs (a cyclic and aromatic cation). Moreover, the increase of the alkyl chain length of the IL enhanced the extraction of the colorant.

Dimitrijević et al. (2016) evaluated the influence of four 1-alkyl-3-ethylimidazolium bromide ionic liquids on the partitioning of Congo red and rhodamine B dyes in a system formed by IL + tripotassium phosphate + water. The ILs studied were 1,3-diethylimidazolium bromide ($[eem][Br]$), 1-butyl-3-ethylimidazolium bromide ($[beim][Br]$), 1-hexyl-3-ethylimidazolium bromide ($[heim][Br]$) and 1-octyl-3-ethylimidazolium bromide ($[oeim][Br]$). The studied dyes were extracted from IL-rich phase in all investigated ATPS with partitioning coefficient values in the range from 19 to 537. The partition coefficients of the targeted dyes increased with increasing the alkyl chain length in the position N-1 of the imidazolium ion, reaching the maximum in the case of $[heim][Br]$. The effects of the increasing the alkyl chain in the position N-1 are that the free IL volume increases, the IL surface tension and hydrogen bond strength between the anion and cation decreases and the energy of cavity formation which accommodate a solute molecules decreases. It was found that electrostatic interactions play the most important role in the dye partitioning in the investigated ATPS based on 1-alkyl-3-ethylimidazolium bromide ionic liquids.

Souza et al. (2014) used imidazolium-based ILs as adjuvant in the formation of ATPS, constituted by potassium salts + water + PEG, to explore the differences induced by the presence of the IL as adjuvant the partition behaviour of two dyes, chloranilic acid and rhodamine 6G. The ILs studied were 1-ethyl-3-methylimidazolium chloride ($[C_2mim][Cl]$), 1-butyl-3-methylimidazolium chloride ($[C_4mim][Cl]$), 1-hexyl-3-methylimidazoliumchloride ($[C_6mim][Cl]$) and 3-octylimidazolium chloride ($[C_8mim][Cl]$). The results showed that both dyes have more affinity for the more hydrophobic, PEG-rich phase, suggesting the hydrophobic interactions as the controlling forces of the dye partition. However, based on the partitioning coefficient values, it seems that more than just the hydrophobic interactions control the partition, which is modulated by the presence of the ILs. Meanwhile, despite the clear affinity of both dyes for the PEG-rich phase, when the ILs are not present, the partition coefficients of both dyes are higher. This can be easily explained by the increased hydrophobic nature of the PEG-rich phase. Thus, the huge impact that a small quantity of IL has on the dyes partition was noticeable.

Ferreira et al. (2014) analysed the influence of IL phosphonium- and imidazolium-based, on the partitioning of dyes: chloranilic acid, indigo blue and Sudan dye, in ATPS formed by IL + salt (inorganic or organic salt) + water. In the studied ATPS, the top phase has corresponded to the IL-rich aqueous phase while the bottom phase was mainly composed of salt and water. It was observed that, in general, the more hydrophobic phosphonium-based ILs lead to higher partition coefficients when compared with the imidazolium-based counterparts. These features also mirror the low affinity of the organic and more hydrophobic dyes for water and their preferential partitioning to organic-rich phases. Thus, among the studied ILs, the phosphonium-based ILs are generally more efficient in the extraction/removal of textile dyes from aqueous media.

Therefore, IL-based aqueous biphasic extraction is an efficient and suitable method for partitioning of dyes into IL phases. The IL-based ATPS extraction systems provide an efficient extraction of dyes that are easier and cheaper than usual methods (Sheikhian et al. 2014). The results of the papers discussed have showed the enormous potential of IL for the removal of dyes from industrial effluents.

3.4 Conclusions

The presence of effluent dyes in environmental bodies of water is a major cause of water pollution. To avoid this phenomenon, efficient dye removal techniques must be used to treat dye effluents before they are released into the environment. This chapter showed the ability of ATPS as a promising alternative for the removal of dyes from aqueous matrices, showing the efficiency of this method and respective phenomena that govern the partitioning of dyes in ATPS. In this way, the potential for application of this technology is inherent to the results of removal efficiency, adjustment for interaction according to the proper selection of the constituents. Associated with this, the known advantages of ATPS are ease of scaling up, short processing time, economic viability, environmentally safe composition and recyclability.

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Chapter 4

Dynamic of Heavy Metals and Environmental Impact of Waste Phosphogypsum



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Abstract The production of phosphoric acid from natural phosphate rock by the wet process gives rise to an industrial by-product called phosphogypsum. About 5 tons of phosphogypsum are generated per ton of phosphoric acid production, and worldwide phosphogypsum generation is estimated to be around 100–280 Mt per year. This co-product is mostly disposed of without any treatment, usually by dumping in large stockpiles. These are generally located in coastal areas close to phosphoric acid plants, where they occupy large land areas and cause serious environmental damage. Phosphogypsum is mainly composed of gypsum but also contains heavy metals and other trace elements. All of this adds up to a negative environmental impact and many restrictions on phosphogypsum applications. Up to 15% of world phosphogypsum production is used to make building materials, as soil amendment, and as a set controller in the manufacture of Portland cement; uses that have been banned in most countries.

In other context of sustainable development, the phosphate chemical industry develops different ways of phosphogypsum valorization, which makes its storage in stack inevitable for the potential exploitation of this by-product. Although, this storage can cause an environmental impact largely represented by the transfer of trace elements (TEs) to groundwater by leaching phenomenon. It is, therefore, important to evaluate the impact linked to the storage in order to limit this transfer. The evaluation is usually performed through leaching tests in columns or batch reactor. In this work, leaching tests were performed in columns by infiltration–percolation on two filter mediums: phosphogypsum and simulated sandy soil. The aim of this study is to evaluate the behavior of heavy metals present in phosphogypsum; indeed less research has been published regarding the leaching

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behavior of phosphogypsum and mobility of these elements by infiltration–percolation. It is within this context that the present study has been undertaken aiming both at the characterization of phosphogypsum and the determination of its heavy and major leaching behavior. Relevant attention was given to the leaching behavior of the sample which was subjected to three leaching tests at the height of 15, 30, and 45 cm. Broadly, mobility of trace metals in phosphogypsum was classified into two degrees: elements with moderate mobility were As, Ba, Cd, Cr, and Ni then those with low mobility were Cu, Pb, Se, and Zn. The increase and decrease of TEs quantity in the leachate during the variation of the height parameter show that the phosphogypsum is acting as a filter, which can both retain and release TEs during leaching by infiltration–percolation.

This paper offers a database on the distribution of heavy metals in phosphogypsum and their leaching as a first step towards modulating its behavior. Physical, chemical, and leachable characteristics are determined in order to draw up an accomplished synopsis of studied phosphogypsum.

Keywords Phosphogypsum · Sandy soil · Columns · Leaching behavior · Heavy metals · Groundwater contamination

4.1 Introduction

The phosphate fertilizer industry is basic to maintain the levels of farming production worldwide. The main raw material used in the industrial process is the phosphoric acid, which is usually produced by two different approaches: by pyrometallurgy, applying thermal reduction of phosphate rock in an electric furnace to produce elemental phosphorus, or by a more common and cheaper hydrometallurgical method, from the chemical reaction of phosphate rock with sulfuric acid (Lottermoser 2010). This latter process, known as “wet digestion,” accounts for around 90% of the worldwide phosphoric production (USGS 2017) though also generates an unwanted by-product; a solid waste known as phosphogypsum.

Phosphogypsum is mainly composed of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) although may also contain other minor solid phases (e.g., alkali fluorosilicates, fluorides, quartz, and feldspars), traces of unreacted phosphate rock, and organic matter. In addition, phosphogypsum also contains remains of process waters, which are used in the industrial process, trapped in the interstices of mineral particles. The term phosphogypsum is, therefore, a collective term for a waste mixture comprising major solid and minor liquid waste components (Lottermoser 2010). The amount of phosphogypsum produced during phosphoric acid production exceeds the mass of the final product, i.e., 4.5–5.5 tonnes of phosphogypsum are generated per tonne of phosphorus pentoxide produced (El-Didamony et al. 2012). The total amount of phosphogypsum produced up to 2006 is estimated to have been about 6 billion tonnes, of which 2.2 billion tonnes (37%) were produced in United States (IAEA 2013).

World resources of phosphate rocks are more than 300 billion tonnes, including the largest sedimentary deposits found in northern Africa, China, the Middle East, and United States, and significant igneous deposits found in Brazil, Canada, Finland, Russia, and South Africa (USGS 2017). Although China is currently the main phosphate rock producer worldwide. World phosphate rock production capacity is expected to increase by 2% per year, with Africa and the Middle East as the leading areas of planned growth (USGS 2017). Associated with such level of production, a proportional increase in the generation of unwanted by-products is, therefore, expected. Assuming that approximately 95% of phosphate rock production is allocated to phosphoric acid production (USGS 2017) and around 5 tonnes of phosphogypsum are produced per ton of phosphate rock, then around 1.1 and 1.2 billion tonnes of phosphogypsum could have been generated worldwide during 2015 and 2016.

Several disposal options have been considered to deal with this problem; the discharge of phosphogypsum directly into the sea, the filling of mined-out open pits, and the stacking in large heaps in the vicinity of the factory, being the latter the most common practice applied (Lottermoser 2010). The storage process begins with the filtering and washing of phosphogypsum at the processing plant to remove any trace of soluble phosphate. Then, the phosphogypsum is converted into a slurry with the process water, freshwater, or seawater in origin, and pumped to the top of the stack. Finally, the water is indirectly removed, after seeping through the stack and collected by perimeter channels to avoid the release of contaminants to the environment, and subsequently treated (Lottermoser 2010). However, the stacking is not completely watertight and the treatment of these polluted waters is not always carried out (Pérez-López et al. 2015; Pérez-López et al. 2016). These waters are highly acidic (pH 1–3) and contain high concentrations of fluoride, sulfate, phosphate, ammonia, radionuclide, and metal(loid)s. Indeed, the wastes generated by the fertilizer industry are of environmental concern due to the high pollutant content (Bolívar et al. 2002; Tayibi et al. 2009; Pérez-López et al. 2015; El Zrelli et al. 2015). Thus, the huge amount of phosphogypsum produced causes a serious disposal quandary and expensive managing costs.

Indefinite stacking is now imposing a negative externality on the phosphate industry because it constitutes disproportionately costs. For this reason, the adoption of more safe and sustainable solutions to the management of these wastes is required in order to reach the objective of developing cleaner production of fertilizer products worldwide.

4.2 Characterization of Phosphogypsum

Phosphogypsum is primarily $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, but also contains impurities of environmental concern such as residual acids, fluoride, heavy metals, and naturally occurring radionuclides. Impurity composition within phosphogypsum can vary greatly depending on the source of phosphate rock used in phosphoric acid production. The

chemical composition of phosphogypsum from different sources is listed in Table 4.1 (Tayibi et al. 2009). According to this data the main components of the phosphogypsum are CaO, sulfates (expressed as SO_3), SiO_2 , Al_2O_3 , Fe_2O_3 , P_2O_5 , and F^- .

Table 4.2 shows the trace metal contents (arsenic, silver, barium, cadmium, chromium, lead, mercury, and selenium) in (mg/kg) in some phosphogypsum sources. These elements are on the Environmental Protection Agency (EPA 1998) list of potentially toxic elements. One can see that the phosphogypsum generally has a high total content of Ag, Au, Cd, Se, Sr, some light rare earth elements. Phosphogypsum from Central Florida has higher As content than Alberta phosphogypsum (Idaho), but a lower concentration of Cd and Zn. Meanwhile, Tunisian phosphogypsum has been reported to contain very high Zn levels (Rutherford et al. 1994; Choura 2007). With regard to radioactivity, as mentioned above phosphogypsum contains relatively high levels of U-series radionuclides naturally present in the phosphate rock. Depending on the quality of the rock source, phosphogypsum can contain as much as 60 times the levels normally found prior to processing (Table 4.1).

4.3 Environmental Impacts

Phosphogypsum management is one of the most serious problems currently faced by the phosphate industry. Only 15% of worldwide production is recycled, while 85% is stored in the vicinity of factories in coastal regions. The storage of phosphogypsum without any prior treatment requires large land areas and can cause serious environmental contamination of soils, water, and the atmosphere. Negative atmospheric impacts can be caused by the erosion of phosphogypsum piles and the release of highly polluting substances, due to the presence of hazardous dust containing heavy metals, sulfates, fluorosilicates, hydrogen fluorides (Szlauer et al. 1990) and phosphorus, cadmium, and ^{226}Ra (Marovic and Sencar 1995). Atmospheric agents can transport the contamination to neighboring areas.

4.3.1 Atmospheric Contamination

Air pollution results from the fly-off of toxic dust during dry periods. Furthermore several studies have discussed the impact of phosphogypsum radionuclides. Bolivar et al. (2000) concluded that 90% of Po and Ra originally present in phosphate rock remain in phosphogypsum, whereas the remaining U percentage is well below 20%. Thus the potential problem of phosphogypsum piles is the emanation of ^{222}Rn from the alpha-decay of ^{226}Ra , a radionuclide classified by the USEPA (National Emission Standards for Hazardous Air Pollutants, Subpart R) as a Group A human carcinogen, whose common presence in phosphogypsum led to the regulation of

Table 4.1 Content of major elements in different phosphogypsum sources

Component	References	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	P ₂ O ₅	F ⁻
USA	Taha and Seals (1992)	25–31	3–18	0.1–0.3	0.2	–	55–58	–	0.5–4.0	–
Russia	Valkov et al. (2014)	50.5	2	0.9	0.5	0.1	–	0.6	39.1	2.9
China	Weiguo et al. (2007)	30.79	1.88	2.10	–	0.8	42.56	–	–	–
Morocco	Sebbahi et al. (1997)	30.5	9.5	2.8	0.9	0.3	42.9	–	0.5	0.15
Tunisia	Rouis and Bensalah (1990), Choura (2007)	31–32	–	0.1	0.1	0.4	46	0.3	1.2	1.2
Turkey	Degirmenci et al. (2007)	32.04	3.44	0.88	0.32	–	44.67	0.13	0.50	0.79
Egypt	Taher (2007)	32.13	8.78	0.29	0.35	0.09	37.60	–	1.82	0.80
India	Manjit and Mridul (2005)	31.09	0.29	0.54	–	1.31	43.21	0.29	0.47	0.86

Table 4.2 Content of some TEs (ppm) in different phosphogypsum sources

Element	Morroco (Renteria- Villalobos et al. 2010)	Florida (Rutherford et al. 1994)	Idaho (Rutherford et al. 1994)	South Africa (Rutherford et al. 1994)	Tunisia (Rutherford et al. 1994)
Cr	3.70	–	<10–70	–	20
As	3.58	40	<1–2	–	–
U	3.48	–	6–13	–	–
Ni	2.49	2	3–15	13	15
V	2.10	19	10–40	–	–
Se	1.97	–	4–64	–	–
Cd	1.34	7	9–28	–	–
Pb	1.20	–	3–7	–	5
Zn	0.92	9	18–112	6	315

phosphogypsum disposal under the National Emission Standards for Hazardous Air Pollutants (NESHAP) and the National Emission Standards for Radon Emission from Phosphogypsum Stacks (Federal Register 1999). The EPA ruling restricts phosphogypsum exceeding 370 Bq/kg of ^{226}Ra from being used on agricultural soil. The maximum regulatory limit of ^{222}Rn exhalation (the flux density of ^{222}Rn gas entering the atmosphere from the surface of a ^{226}Ra -bearing material) established by the EPA (1998) is 0.74 Bq/m²/s. According to Mas et al. (2006), phosphogypsum stacks located on salt marshes in Huelva (Spain) contain about 100 Mt. of phosphogypsum (area of approx. 1200 ha, with an average height of 5 m) and are generally not completely watertight or even covered with any inert material, leading to a local gamma radiation level between 5 and 38 times the normal rate (0.74 Bq/m²/s). Measurements by CRIIRAD (Commission for Independent Research and Information about RADiation) (Chayeyron, 2007) of the equivalent dose to one square meter of soil showed a result of 2–7 times the normal rate. In other words, 9 min human exposure per day is equivalent to an accumulated dose of more than 10 mSv/year. This value is well above the recommended worldwide exposure limit of 2.4 mSv/year (UNSCEAR Report 2000) and may thus pose a health threat to workers on the site or people living nearby (EURATOM Council Directive 1996). Lysandrou et al. (2007) measured the ^{222}Rn emanation rate of phosphogypsum samples dumped in a coastal area of Cyprus, placing them in a sealed plastic container and monitoring radon activity growth as a function of time for about 80 h. The ^{222}Rn emanation rate ranged from 0.35 to 1.1 Bq/h, which is higher than the geological background radon emanation rate in Cyprus. This could cause an increase in radon levels and thereby generate excessive radiation exposure for humans, in extreme cases reaching values of up to 17 mSv/year. In Huelva (Spain), Duenas et al. (2007) made measurements of ^{222}Rn exhalation over 24 h from active phosphogypsum stacks and from restored and unrestored inactive phosphogypsum stacks, correlating the results with various factors. The ^{222}Rn exhalation of active phosphogypsum stacks (0.523 Bq/m²/s) was two times higher

than that of unrestored inactive stacks, while the ^{222}Rn exhalation of restored phosphogypsum stacks was eight times lower than that of active stacks. It should be noted that all the recorded values were lower than the aforementioned EPA limit value (EPA 1998, Code of Federal Regulations) and that the authors found a correlation between the exhalation value and the ^{226}Ra activity concentration and soil porosity and density.

4.3.2 Water and Soil Contaminations

Another matter of concern is the leachability of hazardous elements from phosphogypsum and thus the contamination of groundwater underlying phosphogypsum stacks (May and Sweeney 1982, 1983; Carter and Scheiner 1992; Berish 1990). Since phosphogypsum waste is generally transported and disposed as an aqueous slurry, phosphogypsum piles can be affected by tidal variations and dissolution/leaching of the elements naturally present in the phosphogypsum can occur. Dissolved elements may be deposited in nearby soils or transferred to waters and finally to living beings (Reijnders 2007). The international limit prescribed by the European Atomic Commission (EURATOM) is 500 Bq/kg (Sunil 2002; EURATOM Council Directive 1996). ^{226}Ra leachability from phosphogypsum stockpiles has been evaluated by several researchers.

Haridasan et al. (2002) conducted leaching studies on phosphogypsum samples from Kochi, India, using distilled water (pH = 6.0) and rainwater (pH = 5.0–5.8) as leachants in different contact time and solid/liquid ratio conditions. The laboratory results indicated that rainwater leached less ^{226}Ra (0.09–0.28 Bq/L) than distilled water (0.08–0.38 Bq/L). When phosphogypsum was exposed to natural weather conditions (rain) the maximum ^{226}Ra activity in the leachate was 0.53 Bq/L, while the minimum was 0.07 Bq/L. Most ^{226}Ra values determined in the leachates exceeded the limit value of 0.1 Bq/L prescribed by the Bureau of Indian Drinking Water Standards.

Burnett and Elzerman (2001) evaluated the migration of radionuclides from Florida phosphogypsum stacks. Sampling was carried out through monitor wells in the surface aquifer close to phosphogypsum stacks and in older phosphogypsum piles. It was deduced that the stack solutions were characterized by a very low pH of 2.43, a high ionic strength, and a high total dissolved solids content (18.700 $\mu\text{g}/\text{kg}$), while the aquifer water around the stacks had a lower average total dissolved solids content (around 3300 $\mu\text{g}/\text{kg}$) and a pH value of 6.33 comparable to the normal groundwater value in the area. From a radiochemical point of view the stack solutions were more enriched in ^{238}U (10–17 Bq/L), ^{222}Rn (300–1200 Bq/L), and ^{210}Pb (7–70 Bq/L) than the aquifer water. With regard to ^{226}Ra , the specific activity in the stack fluid was low (0.1–0.2 Bq/L) but slightly higher than normal groundwater values. Furthermore, most of the stack solutions displayed lower ^{226}Ra activity than the majority of the measurements made around the phosphogypsum stacks, which in no case exceeded the USEPA ^{226}Ra in drinking water standard value

(0.2 Bq/L) (USEPA 2000, Report EPA-815-2-00-003). On the other hand, modeling of the environmental radio-chemistry of U, Pb, and Ra showed that within the stacks these radionuclides were mainly in the form of complexes with sulfate and phosphate, which are relatively mobile uncharged or negatively charged solution species. However, as the pH below the stack increased, the precipitation of multi-component solid phases prevented the large-scale migration of these radionuclides to the underlying aquifer. The results of studies carried out by Bolívar et al. (2000) on the aquatic environment of the estuary formed by the rivers Tinto and Odiel (Huelva, Spain) indicated the presence of severe contamination by U-series radionuclides contained in phosphogypsum stacks located close to the estuary's tidal prism. The total mobile content of Cu and Ni from the phosphate rock and the U and Ni content from phosphogypsum waste end up in the bioavailable fraction. Furthermore, due to the exposure of phosphogypsum to weathering conditions, the effluents resulting from leaching of this waste may also present a high concentration of these metals. Taking into account the total mass of phosphogypsum (100 Mt), the water-soluble metals released into the estuary were estimated to be: Ba (6509 t), Zn (6726 t), Ni (232 t), Cu (1158 t), Cd (667 t), and Sr (54,219 t). This means serious contamination which can be extended a long way around the coast by tide and wave action.

4.4 Health Issue

Due to its high content in some elements such as Ca, P, and S, phosphogypsum has been traditionally considered as an amendment in order to improve the physico-chemical properties of soils. This valorization route is not recent; Alcorido and Rechcigl (1993) reviewed the potential use of this by-product in agriculture. Since then, much research has been devoted to the agricultural uses of phosphogypsum, mainly to improve soil structure and crop yield (e.g., Tang et al. 2006), reduce soil erosion (e.g., Zhang et al. 1998), treat acidic or metal-rich soils (e.g., Takahashi et al. 2006; Rodríguez-Jordá et al. 2010), or increase available soil concentrations of S and P (Delgado et al. 2002). In order to assure a safe long-term application in agriculture, the characterization of phosphogypsum impurities as well as their mobility and bioavailability is of critical relevance. Some authors have addressed this issue by applying different extractants to phosphogypsum in order to simulate the migration of pollutants from phosphogypsum-amended soils to agricultural products. Saueia et al. (2013) studied the leaching of element traces from Brazilian phosphogypsum using EDTA solutions, and compared the results with those obtained using different phosphate fertilizers. These authors concluded that the use of phosphogypsum is safe for agriculture given that all metals remained below the limits values, with values even lower than those obtained by applying phosphate fertilizers. The bioavailability of element traces from phosphogypsum has been addressed by other researchers using aqua regia digestion and sequential extractions (e.g., Santos et al. 2006; Al-Hwaiti et al. 2010). These studies concluded that the toxic metals in phosphogypsum are not likely to be leached, and, thus,

phosphogypsum could be considered to be used as an amendment to agricultural soils. However, the real transfer of metals to soils and the effects on the living organisms should be properly addressed. Nisti et al. (2015) reported a low release of metals (i.e., As, Cd, Ni, Cr, Se, Pb, and Hg) from Brazilian phosphogypsum amended soils in doses 10 times higher than those needed to achieve 50% of the soil base saturation (around 15 g phosphogypsum/kg soil). On the other hand, Abril et al. (2008) and Enamorado et al. (2014) studied the trace-elements uptake by plant in soils amended with different doses of phosphogypsum in SW Spain. After three decades of phosphogypsum amendments in agricultural soils, these authors reported Cd levels in shoots and tomato fruits below, but close to, the limit values for food safety. In fact, these authors estimated that accumulated phosphogypsum amendments greater than 16 g phosphogypsum/kg soil would be enough to exceed such a limit. Similar conclusions were obtained from Al-Hwaiti (2015), who reported contamination in soils and vegetables (i.e., tomatoes and green peppers) in amended soils with Jordanian phosphogypsum. Thus, these authors obtained contradictory conclusions to those reported by Nisti et al. (2015) applying similar phosphogypsum doses to soils, which could be attributed to the higher metal content in phosphogypsum used by Enamorado et al. (2014) and Al-Hwaiti (2015). This high variability in trace element content of phosphogypsum worldwide has been recently reported by Macías et al. (2017) and evidences that the assessment of the metal/loid content of this by-product, and their release capacity before its use as soil amendment is of critical in agriculture to avoid the transference of these elements to the chain food. In addition, any change in the soil properties may have a significant impact on its habitat. In this sense, the impact of phosphogypsum soil amendments on bacterial biota, plants, and invertebrates has not been evaluated until recently. Hence, Hentati et al. (2015) provided evidences of remarkable ecotoxicological effects on invertebrates, attributed mainly to Ca, due to metabolism disruption with consequences in the reproduction and even in the survival. Metals, Ca, and P provided to soils by phosphogypsum may be easily mobilized to the aqueous solutions, affecting the aquatic life, in particular invertebrates like cladocerans, which have a critical role on the equilibrium of aquatic food chains.

4.5 Regulatory Aspect

The concept “regulation” is offered for debate against such a background in the hope it may enable a new coherent and consistent policy for both phosphate and phosphogypsum management. The collective goal is to achieve a new, sustainable equilibrium for the future, balancing public health and safety requirements with the need to maintain a viable and affordable global production capacity for these life-critical resources, managed by a profitable phosphate industry. In some institutions, phosphogypsum is considered as a hazardous, radioactive waste (USA, National Emissions Standard for Hazardous Air Pollutants (NEHSAP n.d.)). In others it is not regulated at all. Morocco, which has draft legislation in place but has not yet

passed it into law (August 2008). In others it is used, but as a licensed product. (Spain, 12,378 Real Decreto 824/2005, de 8 Julio, sobre productos fertilizantes, 19 July 2005, BOE 171, p. 25592). In many countries small stacks have simply got lost, or have been engulfed as cities, once remote, have expanded around them. Such is the case in Athens, Greece, for example, which follows the relevant European Commission Directives. (Commission Regulation (EC) No 2557/2001 of 28 December 2001 amending Annex V of Council Regulation (EEC) No 259/93 on the supervision and control of shipments of waste within, into, and out of the European Community). Historically, production has been predominantly in Europe and North America where regulation has relied on laws and standards carried across from other sectors; and models rather than evidence have been used as the basis of risk assessment. The result, when seen from an international perspective, has been an inconsistent, even conflicted picture, heavily biased towards regulatory practices of the developed world. Globalization of trade in food and energy products, and consumer demands for traceability of all foods now require that a more coherent and consistent approach be found, one that would also satisfy similar requirements recently articulated by the International Commission on Radiological Protection (ICRP 2008). The amount of phosphogypsum produced in the wet digestion are such that stacking is essential. The question at issue, therefore, is not whether or not to stack, but whether or not to regard a stack as a final destination (dump, tomb) or as holding a resource pending future use (Hilton 2006). Sometimes the reason for mandatory stacking is in part definitional, as in the United States where phosphogypsum is characterized by the US Environmental Protection Agency as a waste of no commercial value. Phosphogypsum must be reclassified as a resource. A waste is something “for which no foreseen or foreseeable use” can be found; obviously phosphogypsum does not conform to such a definition. But the problem is compounded by the law of unintended consequences which has meant that there is an urgent need for a safe and cost-effective method to manage the huge quantities of phosphogypsum produced stacking has shown signs of becoming an expensive solution. Indefinite stacking is now imposing a negative externality on the phosphate industry because the cost of stacking now runs into \$billions. For example, in the United States the cost of remediating the unlined Piney Point Stack in Florida is estimated to date to have been of the order of 300 million US dollars which allowed Florida legislature to require a 150 millions dollars (Florida statute 403.4154 n.d.). The state of Florida has some 20 phosphogypsum stacks, at least half of which are of the old style.

In the light of the experience in Florida, the use of stacking is being reconsidered in other parts of the world. Based on their own analysis of stacking in Minas Gerais state Brazil, a major center of both production and use of phosphogypsum, the regional environmental protection agency has recently challenged the principles of indefinite stacking on both design and environmental safety grounds. In the Netherlands, the policy reversal has gone even further, based on the externality cost that was imposed by an unworkably strict regulatory regime (Van der Steen 2008). Mandatory reuse of process residues/by-products is now included in the terms of the production licence itself. It is unclear over what time frame such an approach

could be applied to phosphogypsum, but once the principle is established the opportunity is offered to the industry to respond in a positive way and use its phosphogypsum. Under the umbrella of corporate social responsibility, or what is nicely termed a “good corporate citizenship,” some visionary industry leaders are willing to take such a positive approach, not least because it also deals with a problem of potentially indefinite liability for a legacy stack.

4.6 Methodology

Evaluation of the leaching behavior of contaminated soil is very important for an accurate assessment of the risk of contaminated soils transferring pollutants into seepage water, groundwater, or surface water. Several leaching methods have been developed and implemented into environmental regulations in many countries. These include batch tests (US EPA Method 1316 2013), column tests [(ISO/TS 21268-3 2007; US EPA Method 1314 2013)], lysimeter tests (Ahmed et al. 2010; Fritzsche et al. 2016), and sequential leaching tests (Arain et al. 2008; Pueyo et al. 2008). These methods aim to determine the concentrations of chemicals expected in water that has come in contact with contaminated soil or other solid materials such as phosphogypsum for a certain period of time (Grathwohl and Susset 2009). Batch tests have been extensively used worldwide for compliance testing because their low costs, simple design, and low test duration (usually 24 h) make them convenient for routine testing. However, the disadvantage is that the information produced from the batch test is limited as it only provides a single result at one liquid-to-solid (L/S) ratio, which does not reflect real world conditions. Moreover, with certain type of solids, batch tests require additional effort for centrifugation, minimizing carry over, filtration, and separation of suspended solid and water, managing formation of emulsions, etc. This may lead to a higher work load than expected and varying results depending on the experimental conditions before chemical analysis.

Column tests, on the other hand, resemble field conditions more closely and are suitable to assess the long-term release of chemical constituents from phosphogypsum into water bodies. The column test’s advantage over a batch test is that it allows for the observation of high initial concentrations of percolates at low L/S ratios and the time-dependent release of chemicals, which is required for the prediction of leaching behavior under field conditions.

Focusing on the diameter and the dimensions of the column, Hassoune et al. (2017) conducted experiments using two columns. The first column is made of transparent glass and filled with a filter medium 1 consisting of a mass of phosphogypsum. The second column used transparent polypropylene, is filled by a filter medium 2 containing two matrices of soil (anthracite sand, sea sand). To prevent soil material loss and to facilitate uniform distribution of the eluent, we placed a filter paper and glass beads. However, the heights of phosphogypsum was varied in order to determine the optimum height. The operating protocol for leaching percolation tests is characterized by introducing phosphogypsum in layers of 2–3 cm

depth in the first column, each layer is statically compacted (without vibration) with a pestle. The leaching agent solution is injected into the column by means of a peristaltic pump which maintains the flow rate constant, a leachate 1 is generated downstream of the filter medium 1 which is due to the phosphogypsum contact with the solution of the leaching agent (distilled water).

The percolation tests were carried out in a percolation column in which a height of twenty centimeters of sand was set up in layers of 4–6 cm, these layers are gradually soaked with water so that avoid segregation between grains of different sizes. The leachate 1 from the first column infiltrates into the sand and then percolates through the filter media 2 which is finally recovered in a tank in the form of a percolate (leachate 2).

The leaching methodology are divided into two parts: the first is devoted to the study of the influence of four parameters (height of phosphogypsum, successivity of lixiviation, compaction of phosphogypsum) on the toxicity of leachate 1, while the second is dedicated to the study of the retention efficiency of some trace elements by two media-filters, and then compare the values of those transferred to leachate 2 to the limit values.

4.7 Case Study

The management of these large quantities, which have been continuously generated, is one of the most serious problems in many countries. Several studies have been recommended to use phosphogypsum as building materials (Ajam et al. 2009), agricultural fertilizers (Papastefanou et al. 2006), and as an amendment to the soil (Hentati et al. 2015). However, only a few of them were put into practice due to the absence of information about long-term behavior of phosphogypsum, indeed the leaching potential of phosphogypsum has received little attention. Leaching test can be used to predict the mobility of trace elements (TEs) in waste samples in a wide pH range (Kamali et al. 2008; Quina et al. 2011). The aim of this study is to evaluate the TEs quantity dissolved by rainwater using column leaching tests with deionized water as leaching agent. The contents of TEs dissolved in the leachates (Pb, As, Cd, Se, Zn, Cu, Ni, Cu, Cr) of phosphogypsum were determined by inductively coupled plasma mass spectrometer (ICP-MS) (ISO 1185 1996).

4.7.1 *Chemical and Mineralogical Composition*

Heavy metals are not in the same form in the Earth's surface. Their future in the environment will differ. It is, therefore, essential to have access to the distribution of metals between the various constituent solid phases of the soil before even reasoning about their environmental impact. Previous studies show that Pb, Zn, Ni, Cr, and Cu are attached to the amorphous and crystalline phases rather than to the water-soluble

mineral phase. Pb and Zn are more attached to the amorphous phases than Ni, Cr and Cu; Pb has the highest proportions in the amorphous phase, while Cd was detected only in the crystalline phase.

The highest proportion of manganese in the middle phase indicates the presence of manganese ores as amorphous ores. Manganese and Fe are treated as environmental geochemical parameters by the spectral behavior of the minerals in which they occur (Swayze et al. 1995, 1998, 2000). Manganese is known as an important extractor of trace metals because it exists in several oxidation states. Iron oxides are almost ubiquitous in the soil environment and are the most abundant of the current metal oxides. In both cases manganese and iron play a major role in the retention of heavy metals and make them as “sorbents”.

Analysis spectra measured by the spectrophotometer was performed for the qualitative and quantitative interpretation of the mineral. The specific positions of the absorption bands are used as a basis for the interpretation of the measured spectra: around 1000 nm for absorptions of iron; around 1400 and 1550 nm for OH; around 1400 and 1900 nm for water; around 2160–2220 nm for Al-OH; around 2230–2295 nm for Fe-OH; around 2300–2360 nm for Mg-OH; around 2300–2350 nm, 1870 nm, 1990 nm, and 2155 nm for CO₃, and around 2700 nm for strong absorptions of water and carbonate (Ben-Dor et al. 1995, 2002, 2003). In spectroscopy, the absorption bands in the wavelength range, 400–2500 nm, are very important for the identification of ores that have the physico-chemical photon absorbing structure. There are two spectral regions in this range: the electronic region (VNIR) (0.4–1.35 μm) where the absorptions are caused by the transition metals, for example, Fe, Pb, Mn, Ti, Cu, Co, and Cr and the vibrational region (SWIR) (1.35–2.5 μm) where absorptions are caused by OH⁻, H₂O, NH₄⁺, SO₄²⁻, and CO₃²⁻ (Swayze et al. 2000) (Figs. 4.1 and 4.2).

4.7.2 Leaching Behavior

The leaching behavior of phosphogypsum was conducted in neutral to slightly acid condition of rainwater. Previous study was carried out to determine the optimal height of phosphogypsum. Three leaching experiments were investigated using three different heights of phosphogypsum 15, 30, and 45 cm, respectively (Table 4.3).

According to the quantity of TEs transferred to leachate by infiltration–percolation during the leaching test we can say that the first height shows the best results as it is mentioned on the table the contents of Cd ranged from 5.7 ppm in natural phosphogypsum to 1.558 ppm in the leachate. And from 8.6 ppm to 0.539 ppm for Cr, which confirm that these elements were transferred to phosphogypsum leachate. But for the third height, the TEs contents were found to be increased in the phosphogypsum leachate. The increase and the decrease of the TEs quantity in the leachate prove that the phosphogypsum released TEs by dissolution during the first leaching experiment with first height, which means that the by-product is prepared to

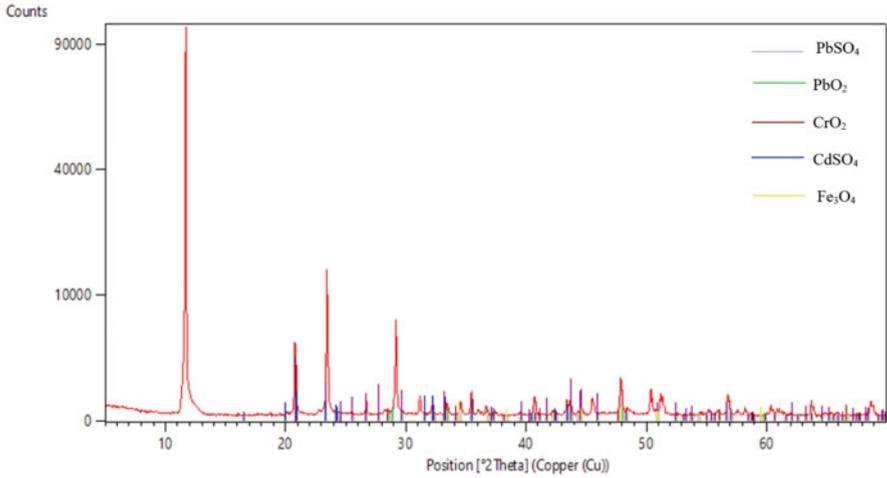


Fig. 4.1 Diffractogram of phosphogypsum

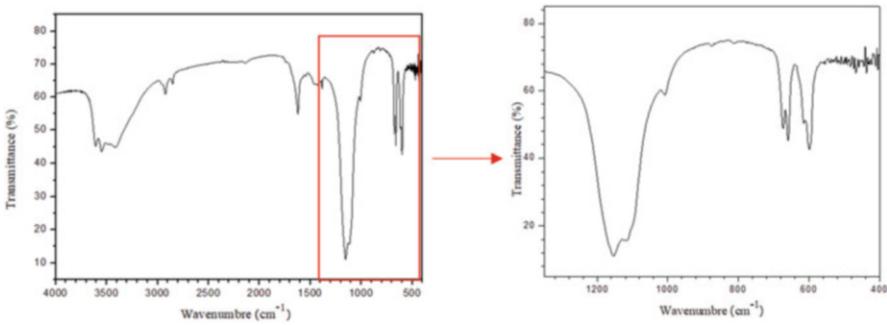


Fig. 4.2 FTIR spectra of phosphogypsum

hold them back in its empty seats during the second leaching experiment with second height.

4.7.3 Infiltration Tests

Dynamic leaching tests is a process whose leaching medium is continuously fed to a column containing the tested waste, simulating the leaching behavior of the waste material in short-, medium-, and long-term release close to real environmental conditions (Tsiridis et al. 2015). Laboratory tests were performed in conditions that closely mimicked the actual situation. In this experience, a deionized water infiltrated through both filter mediums (phosphogypsum and simulated sandy soils)

Table 4.3 The effect of phosphogypsum height on TEs quantity transferred to leachate by infiltration–percolation during leaching test

Elements	Concentration (ppm)			
	Natural PG	Leachate H1	Leachate H2	Leachate H3
As	5.9	0.074	0.018	0.057
Ba	–	0.047	–	0.011
Cd	5.7	1.558	0.397	1.155
Cr	8.6	0.539	0.111	0.408
Pb	<3	0.021	0.011	0.017
Se	–	0.017	0.008	0.007

which gave rise to two different leachates (L1 and L2), respectively. Tables 4.4 and 4.5 describes the input and output of TEs quantity dissolved in both leachates through two sand natures (anthracite and sea sand, respectively). The quantity of pollutants dissolved in both leachates were measured and the values of the output leachate (L2) were compared with maximum contaminant levels.

The results showed high retention of Cd, Cr, Pb, Se, and Cu on the sea sand (% retention >50%) compared to the anthracite sand, but quantity of some TEs (Cd and Cr) in the leachate 2 was extremely high compared to maximum contaminant levels. However, contents of Pb and Se were always under maximum contaminant levels. The element of Ni was highly retained on the anthracite sand (85.600%), but its content in the leachate 2 exceeded significantly maximum contaminant levels. Both of simulated sandy soils retained almost totally the element of Ag due to its very low content in the input leachate (0.005 mg kg⁻¹). The most important factor influencing TEs is soil reaction. If pH value is low, some TEs (Cd, Cr, Pb, Zn, and Ni) have maximum mobility (Barančíková et al. 2004). For example, the potential transfer of Cd to the leachate 2 is due to its high mobility in soil acid conditions and to the absence of organic matter which has strong affinity for Cd. The high retention of Pb, Zn, and Cu on the sea sand is due to their sorption into mineral soil phases (Kassir et al. 2012).

4.8 Conclusion

Much interest has focused on finding uses for this by-product, such as a soil amendment for the remediation of problem soils. There are still unanswered questions about the environmental implications associated with the storage and agricultural use of phosphogypsum. Research has determined that acidity, F⁻, SO₄²⁻, some trace elements, and some radionuclides may be highest in the waste product and have the potential to be mobile in the environment. Both the acidic process water and the phosphogypsum itself are potential sources of contamination. Much concern is related to the possible contamination of groundwater under phosphogypsum stacks, and to radon exhalation which may pose a health risk to people working on or living close to a stack. The largest concern related to the use of phosphogypsum as an

Table 4.4 The retention efficiency of TEs by anthracite sand

	Trace elements (mg/L)									
	As	Cd	Cr	Pb	Se	Ag	Zn	Cu	Ni	
Leachate 1	0.165	1.512	0.700	0.030	0.025	0.015	2.750	0.492	0.131	
Leachate 2	0.106	0.585	0.156	0.005	0.009	–	2.000	0.032	0.110	
Retention (%)	35.757	61.310	77.714	83.333	64.000	100.000	27.300	93.496	16.030	
Maximum contaminant levels (MCLs) for drinking water quality	0.050	0.005	0.050	0.050	0.010	0.010	5.000	1.000	0.050	

Table 4.5 The retention efficiency of TEs by sea sand

	Trace elements (mg/L)									
	As	Cd	Cr	Pb	Se	Ag	Zn	Cu	Ni	
Leachate 1	0.074	1.558	0.539	0.021	0.017	0.005	1.143	0.496	0.125	
Leachate 2	0.062	1.285	0.415	0.019	0.010	–	0.931	0.400	0.018	
Retention (%)	16.216	17.522	23.005	9.524	41.176	100.000	18.548	19.355	85.600	
Maximum contaminant levels (MCLs) for drinking water quality	0.050	0.005	0.050	0.050	0.010	0.010	5.000	1.000	0.050	

amendment to agricultural soils is not plant uptake of radionuclides but the risk of elevated indoor radon levels if the agricultural land is later converted to residential usage. For this reason the USEPA has ruled that no phosphogypsum may be used as a soil amendment if its Ra²²⁶ content exceeds 370 Bq kg⁻¹.

There have been some inconsistent reports regarding the mobility of phosphogypsum constituents. Some laboratory studies have concluded that significant levels of contaminants do not leach from phosphogypsum; however, some field studies have found elevated levels of F⁻, SO₄²⁻, acidity, trace elements, radionuclides, and total dissolved solids in groundwater near phosphogypsum stacks. Clearly, further research is required to improve our understanding of the geochemistry occurring within, and beneath, phosphogypsum stacks. To accomplish this it is necessary to identify the solubility controlling solids of the elements contained within phosphogypsum, especially those for trace elements and radionuclides (Eary et al. 1990). It is also necessary to determine which conditions (e.g., redox, pH, and ionic strength) exist within, and beneath, phosphogypsum stacks in order to predict the dominant chemical species present. It is also important to identify the reactions which occur when contaminants originating from phosphogypsum contact soil materials to determine if attenuation occurs before chemical species contact groundwater.

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Chapter 5

Mitigation of Groundwater Pollution: Heavy Metal Retention Characteristics of Fly Ash Based Liner Materials



Chandra Bhanu Gupt, Anamika Kushwaha, Atma Prakash, Alok Chandra, Lalit Goswami, and Sreedeeep Sekharan

Abstract Leachates generated from the landfills are considered as one of the major source of groundwater contamination and surrounding geoenvironment. An efficient engineered liner for the landfills assists to mitigate the groundwater contaminants by acting as an effective hydro-chemical barrier for the leachate. For geomaterials used in liners, it is important to determine the appropriate range of compaction parameters that would ensure hydraulic conductivity and mitigation of the groundwater contaminants within safe limits. Fly ash based liner materials can be much effective as it not only will solve the problem of proper and safe disposing of fly ash but also will be better liner material in comparison to sand bentonite mixes. The addition of cohesionless fly ash would improve the strength and reduce the shrinkage behavior of bentonite but at the same time might increase the hydraulic conductivity. Hence, it is important to determine the ranges of water content and dry unit weight for different bentonite–fly ash mixes that would satisfy the desired ranges of hydraulic conductivity and strength. The objective for the present chapter is to identify the bentonite–fly ash mix that enables maximum use of fly ash, for the hydraulic conductivity and mitigation of the groundwater contaminants. Various literatures have reported the potential valorization of a bentonite–fly ash mix as a compacted landfill liner compacted at optimum moisture content, satisfying the regulatory requirements of landfill liners. In addition, the groundwater contaminants retention characteristics of fly ash–bentonite mixes were also reported. Hence, the laboratory results discussed in this chapter would be quite handy for deciding the appropriate bentonite–fly ash mix to be evaluated at field scale.

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Keywords Groundwater pollution · Fly ash · Heavy metal · Retention capacity · Landfills

5.1 Introduction

With the rapid industrialization and urbanization, there is an enormous increase in the generation of toxic and hazardous solid wastes, which is among the top unprecedented vital issues confronting globally and is intricately associated with the environment and human health (Hoorneweg and Bhada-Tata 2012; Das et al. 2019; Goswami et al. 2019a, b). In addition, the demand for water is increasing exponentially which is usually fulfilled either by the surface water or sub-surface water (Kumar et al. 2016; Alcamo et al. 2017; Gupt et al. 2020a, b). Therefore, nowadays all over the world facing the problem of depletion of groundwater table and the groundwater pollution (Sathe et al. 2018; Kumar et al. 2019; Goswami et al. 2020). Figure 5.1 represents the distribution of water on the earth, which highlights that only 1% of them is usable water for the living beings. It also shows 99% of usable water comes from the groundwater and only 1% from other sources.

In a report by the World Bank, it is predicted that by 2025, municipal solid waste (MSW) will be around 2.6 million tons for the urban settlements. In India, about 0.3–0.4 million tons of solid waste is generated annually in the rural areas (NIRD and PR 2016). Among all the MSW management, landfilling is the simplest, adaptable, and economical method for disposing of the solid waste in both developed and developing nations (Barrett and Lawlor 1995). The solid wastes dumped to landfill sites lead to contaminate either groundwater underflow or infiltration from precipitation. This phenomenon leads to the leachate formation via the possessing of various organic and inorganic pollutants that further percolates to the bottom of the landfill and finally leading to contaminate the geoenvironment (Mor et al. 2006).

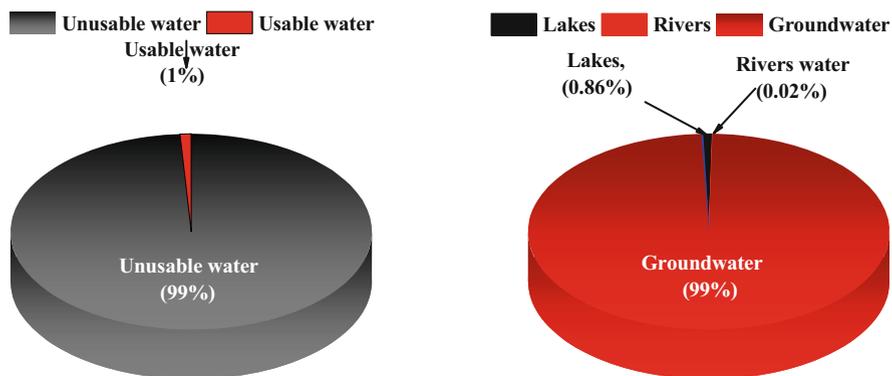


Fig. 5.1 Distribution (usable and unusable) of water on Earth and distribution of usable water (data adopted from <http://ga.water.usgs.gov/edu/earthwherewater.html>)

Improper or un-engineered landfills are among the major threats to groundwater (USEPA 1984; Han et al. 2016). The scale of this threat depends on (1) concentration and toxicity of contaminants in leachate, (2) type and permeability of geologic strata, (3) depth of water table, and (4) the direction of groundwater flow (Al-Khadi 2006). Over the past few decades, landfills are considered to be among the main cause of groundwater pollution (Santos et al. 2006; Jhamnani and Singh 2009; Longe and Balogun 2010; Nagarajan et al. 2012; Han et al. 2016). Thus, for the mitigation of the groundwater pollution caused by the improper landfilling, there is an urgent requirement of engineered landfills.

One of the main components of the landfills is the liner, which acts as a hydro-chemical barrier for leachate generated due to the interaction of waste/contaminants with water (Younus and Sreedeeep 2012; Deka and Sreedeeep 2017; Yadav et al. 2017). It is a layer of compacted soil possessing low permeability, which acts as a hydraulic barrier and prevents the leachate from contaminating the groundwater. Bentonite is the most commonly used material for the construction of liner for landfills due to its self-sealing property and high contaminant retention capacity (Kayabali 1997; Kaya and Durukan 2004; Gupt and Sreedeeep 2014; Gupt et al. 2020a). In the current scenario, sand mixed with bentonite acts as suitable liner material for constructing the landfills (Daniel 1984; Chalermyanont and Arrykul 2005; Eid et al. 2008; Mohamedzein et al. 2016; Srikanth and Mishra 2016; Mukherjee and Mishra 2017, 2019). Furthermore, for the fulfillment of the ever-growing electricity demand, the thermal power has resulted in the generation of large quantities of fly ash and needs the proper and safe disposal. With only a very small utilization of about 38% of fly ash produced in India, compared to the global utilization of 56%, the ash deposits at the thermal power plants are heaping up rapidly (Alam and Akhtar 2011). The problem of its disposal is expected to be at an alarming situation with time due to the limited space (land) available. Henceforth, efforts are now underway for the application/s of fly ash where it can be utilized effectively in bulk quantities, particularly as a suitable liner material in landfill applications. Bowders Jr et al. (1990) reported that the permeability and leachate characteristics of stabilized class-F fly ash revealed that the addition of bentonite decreased the permeability values. Further, the results showed that the leachate from the landfill had a minimal impact on the groundwater resource. This had attributed to the existing soil stratigraphy at the site consisting of clay, which is deduced to have a significant influence on the natural attenuation of leachate into groundwater (Aderemi et al. 2011).

5.2 Groundwater Pollution and its Sources

In most cases, the waste contains hazardous contaminants that cause a serious threat to the quality of the groundwater (Goswami et al. 2019c). Identification and characterization of the hazardous sources are difficult as they are generally hidden from sight and could be spread with changes in the groundwater table. Some of the

groundwater contaminants that could cause serious threat to the environment and human health are iron, manganese, arsenic, chlorides, fluorides that are naturally occurring in soils and rocks and could be easily dissolved in groundwater (Maheshwari 2006; Naik and Sivapullaiah 2012; Bind et al. 2019; Sathe et al. 2020). Also, the septic tanks that are improperly sited, designed, constructed, or maintained cause an outflow of waste and contaminate the groundwater with bacteria, viruses, nitrates, detergents, oils, and chemicals. Improper disposal of hazardous waste such as paints and paint thinners, disinfectants, medicines, photographic chemicals, and swimming pool chemicals, spills from storage tanks of gasoline, diesel fuel, fuel oil, or chemicals oils, leads to the landfill contamination (Naik and Sivapullaiah 2012; Verma et al. 2016; Goswami et al. 2017a; Goswami et al. 2018a, b).

Among the various sources, landfills have been identified as one of the major threats to groundwater resources (US EPA 1984; Fatta et al. 1999). Waste placed in landfills or open dumps containing innumerable organic and inorganic compounds gets decomposed and accumulates at the bottom of the landfill as “leachates.” When these leachates are subjected to either groundwater underflow or infiltration from precipitation, they percolate through the soil leading to groundwater contamination in nearby areas (Saarela 2003; Abu-Rukah and Al-Kofahi 2001). The problem becomes severe when the industrially generated wastes are involved, which are resistant to biological or chemical degradation and are expected to spread contamination for a very long period. In the environment, the heavy metals are generally more persistent than organic contaminants such as pesticides or petroleum by-products (Arul Manikandan et al. 2016; Goswami et al. 2017a, b). They can become mobile in soils depending on soil pH and their speciation (Hashim et al. 2011). Further, the consequences of contaminated groundwater are often serious and can degrade the quality of drinking water. Drinking water containing bacteria and viruses can result in illnesses such as hepatitis, cholera, or giardiasis (Keesari et al. 2019).

5.3 Pollutants and their Toxicity in the Groundwater

The change in consumption patterns in urban societies resulted in an upsurge of heterogeneous consumption patterns, causing an extensive increase in the generation of solid hazardous waste (Buenrostro and Bocco 2003; Jayawardhana et al. 2016). Landfilling is the most common practice for the disposal of waste since it is the most cost-effective option. During landfilling, the generation of various gases and leachate causes serious problem to the environment and living biota (Modin 2012).

Landfills consist of diverse types of pollutants such as heavy metals, organic compounds (pesticides, herbicides, xenobiotic compounds, hydrocarbons, chemical compounds present in pharmaceutical and personal care products), volatile organic compounds, dissolved solids, and organic carbon (Christensen et al. 2001; Kjeldsen et al. 2002; Goswami et al. 2017c). These pollutants end up in the form of leachate

and penetrate through the soil thereby contaminating the groundwater. In developing countries, the generation of contaminated water embracing a wide array of pollutants is commonly due to the landfills (Mahmud et al. 2012). The generation of leachate is due to the existing liquid in the waste and from water present outside including rainwater. Various factors govern the concentration and quantity of leachate, which includes (1) the characteristics and quantity of waste discharged, (2) climatic conditions, (3) disposal area, (4) operational techniques functional at the landfill, (5) hydrogeology of the area, and (6) age of the waste heap (Armstrong and Rowe 1999; Jayawardhana et al. 2016). Table 5.1 summarizes various sources, permissible limit, and toxicity by various heavy metals present in groundwater.

5.4 Mitigation of Groundwater Pollution: Role of Landfill Liner

One of the main sources of groundwater contamination is leachate that is generated from the wastes due to improper planning of waste management and is a serious concern for the mitigation of groundwater pollution. In past decades, landfills are utilized for the safe disposal of wastes generated from various sources all over the world. It mainly consists of two components viz. liner and cover. Generally, the wastes generated from the domestic houses, agricultures, and industries are dumped in an open system without any provision of a suitable liner, especially in the developing country. The liner acts as a barrier for leachate generated from the wastes and it retards the migration of leachate, and its toxic constituents, into underlying aquifers or nearby rivers, causing contamination of the water bodies (Han et al. 2016). Earlier, compacted clay liners (CCLs) were used in landfills having low permeability. Cawley and Jones (1999) suggested that CCLs are the viable solution for landfill leachate containment. Clay liner retards the rate of contaminant migration by its low permeability and high contaminant retention capacity. Bentonite, which is rich in montmorillonite clay mineral, is most widely used clay for the construction of liners (Sivapullaiah and Baig 2011). However, due to its high swelling and shrinkage characteristics with the variation of water content results in the cracking of liners (Ameta et al. 2007). Hence, the qualitative and quantitative characteristics of leachates are very important in the design and management of landfills.

There are various experimental and analytical studies that throw light on the utilization and application of fly ash and bentonite mixture as liner material and adsorption studies on soil with various admixtures (Bellir et al. 2005; Mohammed and Naik 2010; Shankara et al. 2014; Deka and Sreedeeep 2017).

Table 5.1 Sources, permissible limit, and toxicity of various heavy metals present in groundwater

Heavy metals	Sources	Permissible limit in drinking water	Toxicity	References
Arsenic	Enters environment from natural processes, industrial activities, pesticides, and industrial waste, smelting of copper, lead, and zinc ore	0.01 mg L ⁻¹ (WHO 2011)	Causes acute and chronic toxicity, cancer of bladder, liver, lung, kidney, skin; decreases blood hemoglobin; skin diseases (change in color and hard patches on soles and palms), affects blood vessels of feet and legs	Waller (1982); WHO (2011); Shankar and Shanker (2014); Kushwaha et al. (2015)
Cadmium	Found in low concentrations in rocks, coal, and petroleum and enters the groundwater and surface water when dissolved by acidic waters. May enter the environment from industrial discharge, mining waste, metal plating, water pipes, batteries, paints and pigments, plastic stabilizers, and landfill leachate	0.003 mg L ⁻¹ (WHO 2011)	Causes high blood pressure due to the replacement of zinc in the body, liver and renal tubular damage, and anemia, destroys testicular tissue and red blood cells, disorders in calcium metabolism, hypercalciuria, and kidney stone formation. High concentration of cd can lead to lung and prostate cancer	Waller (1982); WHO (2011); Burke et al. (2016); Goswami et al. (2017b); Idrees et al. (2018)
Chromium	Enters environment from old mining operations runoff and leaching into groundwater, fossil-fuel combustion, cement-plant emissions, mineral leaching, and waste incineration. Used in metal plating and as a cooling-tower water additive	0.05 mg L ⁻¹ (WHO 2011)	As compared to Cr (III), Cr (VI) is more toxic. Cr (VI) damages respiratory tract leading to perforation in septum, bronchitis, pulmonary dysfunction, and pneumonia. Increased level of Cr (VI) exposure damages kidney, liver, immune system and gastrointestinal, causes internal hemorrhaging, dermatitis, and skin ulcer	Saha et al. (2011); WHO (2011); Mishra and Bharagava (2016); Arul Manikandan et al. (2016)

(continued)

Table 5.1 (continued)

Heavy metals	Sources	Permissible limit in drinking water	Toxicity	References
Copper	Sources of copper in environment includes water pipes, fittings and valves, fungicides, industrial and domestic waste, mineral supplements, mining, and mineral leaching	2 mg L ⁻¹ (WHO 2011)	Causes abdominal pain, diarrhea, inky urine, headache, difficulty in breathing, intestinal distress, jaundice, hair loss, arthritis, asthma, autism, liver and kidney damage, anemia, male infertility, insomnia, circulatory collapse, coma precede death	WHO (2011); Ashish et al. (2013); Gaetke et al. (2014); Bind et al. (2018)
Lead	Enters environment from industry, mining, plumbing, gasoline, coal, and as a water additive	0.05 mg L ⁻¹ (WHO 2011)	Affects red blood cell chemistry; delays normal physical and mental development in babies and young children. Causes slight deficits in attention span, hearing, and learning in children. Cause slight increase in blood pressure in some adults. Probable carcinogen	WHO (2011); Kushwaha et al. (2017a, b); Kushwaha et al. (2018); Kushwaha et al. (2020); Singh et al. (2019)
Mercury	Occurs as an inorganic salt and as organic mercury compounds. Enters the environment from industrial waste, mining, pesticides, coal, electrical equipment (batteries, lamps, switches), smelting, and fossil-fuel combustion	0.006 mg L ⁻¹ (WHO 2011)	Oral consumption leads to abdominal cramps and bloody diarrhea, gastrointestinal necrosis, and renal failure. Long exposure leads to memory loss and nervous system disorders	Adeniji (2004); WHO (2011); De et al. (2014)
Nickel	Occurs naturally in soils, groundwater, and surface water. Mostly used in production of stainless	0.07 mg L ⁻¹ (WHO 2011)	Damages the heart and liver of laboratory animals exposed to large	Waller (1982); Cempel and Nikel (2006); WHO (2011)

(continued)

Table 5.1 (continued)

Heavy metals	Sources	Permissible limit in drinking water	Toxicity	References
	steel and other alloy. Nickel metal and its alloys are widely used in the chemical, food processing, and metallurgical and electroplating industries		amounts over their lifetime	
Silver	Enters environment from ore mining and processing, product fabrication, and disposal. Often used in photography, electric and electronic equipment, sterling and electroplating, alloy, and solder	0.1 mg L ⁻¹ (WHO 2011)	Causes a discoloration of the skin, hair eyes, mucous membranes, and organs in humans and animals with chronic exposure	Waller (1982); WHO (2011); Fewtrell (2014)
Thallium	Enters environment from soils; used in electronics, pharmaceuticals manufacturing, glass, and alloys	2 µg L ⁻¹ (USEPA 2015)	Causes intestinal and stomach ulcers, alopecia, insomnia, internal bleeding, myocardial injury, damages liver, kidneys, intestine, brain and in consequence, death	Xiao et al. (2004); USEPA (2015), Karbowska (2016)

5.4.1 Compacted Clay Liners (CCLs)

The engineered liners should meet two requirements (1) to ensure practical impermeability to prevent leachates from infiltrating to the groundwater and (2) to possess retention properties preventing contaminant migration by convection and diffusion (Drescher 1997). As the liner is one of the most important components of the landfills, it retards the movement of harmful chemical through retention or by reducing the movement. Movement of any chemical present in the leachate is controlled by the hydraulic conductivity of the liner (Daniel 1993). For the construction of liner of the landfills, compacted clay is used, satisfying the hydraulic conductivity criteria ($\leq 10^{-9}$ m/s) as per EPA guidelines (EPA 1995). Plasticity of the clay varies from place to place, i.e., either low or high depending on the availability of the geomaterials. Yilmaz et al. (2008) reported that hydraulic conductivity of the clays varies with varying concentration of inorganic salts. With an

increase in salt concentration, the hydraulic conductivity of low plastic clay decreases while increases for the high plastic soil. The geotechnical properties of the clay liner are usually governed by the chemistry of leachate (Arasan 2010). Liquid limit and swelling decreases with an increase in chemical concentration for high plastic clays whereas increases for low plastic clays. It has been reported that shear strength of the clay liner increases with the addition of chemicals (Arasan 2010), whereas shear strength of the clay materials decreased when prepared with leachate (Fang and Evans 1988). Usually, the landfills liner is designed for over an average period of 100 years. Therefore, long-term assessment of the compacted clay liners is an essential task. It was noted that there is no degradation in the hydraulic conductivity for long-term permeation of the leachate at the laboratory scale (Francisca and Glatstein 2010). It was observed that silty clays of low plastic for the barrier application have more resistance towards containment than the use of high swelling clays (Arasan 2010).

Akgün et al. (2017) assessed the potential of Ankara clay as a compacted clay liner for landfill sites and reported that the hydraulic conductivity of the samples was below the acceptable limit, thus, making it suitable for the compacted clay liner. It was also justified based on the mineralogical and geotechnical test performed for the suitability of compacted clay liner of Ankara clay. Hydraulic performance of CCLs depends on many factors; therefore, it is essential to focus the hydraulic conductivity of CCLs at different exposure conditions (Aldaef and Rayhani 2014). Table 5.2 summarizes the hydraulic performance of CCLs at different exposure conditions. A typical cross section of the compacted clay liner is shown in Fig. 5.2.

5.4.2 Composite Clay Liner

Composite clay liner, also called as composite barrier system, is usually used in modern landfill systems to isolate the waste from the environment and, therefore, to provide a sustainable environmental solution to the groundwater contamination. It consists of a geo-synthetic clay liner (GCL) or compacted clay liner overlain by a plastic geo-membrane (high-density polyethylene, HDPE) to minimize the movement of contaminants into the surrounding environment from the landfill (Southen and Rowe 2005; Dickinson and Brachman 2008; Azad et al. 2012). A typical cross section of composite clay liners of modern landfill is presented (Fig. 5.3). GCLs consist of bentonite clay or other materials having very low hydraulic conductivity, which is sandwiched between geo-textiles and/or geo-membrane and is used as hydro-chemical barriers in the landfill. GCLs hydraulic conductivity values depend on the mass of bentonite embedded between the geo-textile and/or geo-membrane per square meter (Mandal 2018). The variation in hydraulic conductivity of GCLs with the variation of mass of bentonite clays embedded per square meter is presented (Table 5.3). The various types of GCLs are manufactured as per the requirement, suitability of the site, and geographic region of the landfills. Figure 5.4 represents various types of GCLs as per bentonite embedded between geo-textile and/or geo-membrane.

Table 5.2 Hydraulic performance of CCLs at various exposure conditions

S. no.	Materials of CCLs	Exposure conditions	Impact on hydraulic conductivity	References
1	Leda clay (Navan landfill, Ottawa) and Halton clay (Halton landfill, Toronto)	Combined temperature and leachate exposures	Lower hydraulic conductivity was measured for high plasticity soil. Plasticity of the soils increases under combined thermo-chemical effect	Aldaef and Rayhani (2014)
2	Residual soil (Hebei Province, China)	Vegetation on clay liner to control erosion	Vegetation roots minimize the cracking at early stage of wetting drying cycles. Also, the vegetation roots increase saturated hydraulic conductivity by three orders due preferential flow path	Li et al. (2016)
3	Natural clay (Changshankou landfill, Wuhan City) and Na-bentonite, (Beipiao City, Liaoning Province)	Desiccation cracking and leachates	Hydraulic conductivity of CCL is more affected by desiccation cracks and bentonite while simulated leachates have little effect on hydraulic performance	He et al. (2015)
4	Commercially available bentonite clay	Exposed to inorganic and organic chemicals (aluminum hydroxide and acetic acid)	Hydraulic conductivity decreases by 12% in case of aluminum hydroxide and 17% for the acetic acid	Singh and Prasad (2007)
5	Natural soils from brown, oxidized, surface crust of the thick clay deposits (Sarnia, Ontario)	Exposed to hydrocarbon as permeating liquid	Hydraulic conductivity of natural soil increases (from 1×10^{-9} to 5×10^{-9}) when dielectric constant of permeating liquid decreases from 80 to 2	Fernandez and Wigley (1985)
6	Commercially available kaolinite and locally naturally available illite-chlorite contains mix of clay minerals	Hydraulic conductivity was determined using four organic chemicals: Methanol, acetic acid, trichloroethylene, heptane, and water	Heptane and trichloroethylene at their solubility in water have no effect on hydraulic conductivity of either soil	Bowders Jr and Daniel (1987)

GCLs have various advantages over CCLs. For the GCLs construction, no water is needed which can be critical in arid areas (Maubeuge et al. 2012). Since GCL is a manufactured material, therefore, a consistent and uniform material can be prepared with no detailed material characterization at different site is required. In addition,

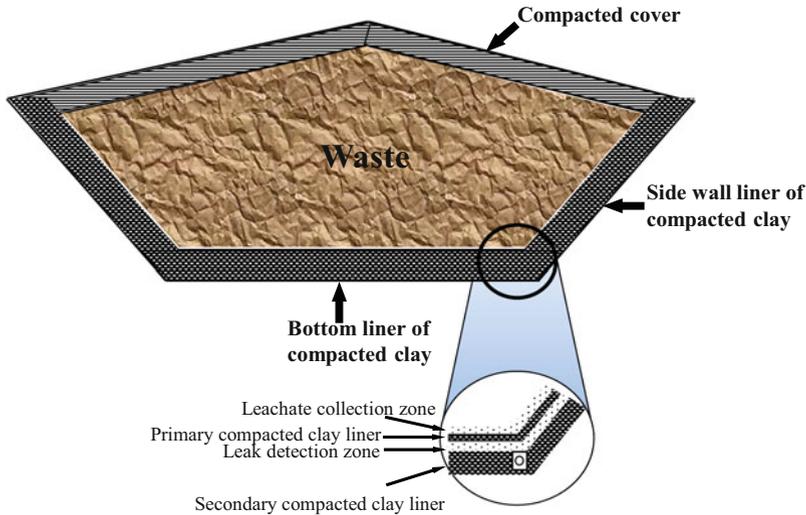


Fig. 5.2 Cross section of landfill with compacted clay liner

quality assurance is simpler for a GCL than for a CCL, which is site specific. In addition, it (GCLs) can serve better, when exposed to freeze/thaw and wet/dry cycles than CCLs (Bouazza 2002; Maubeuge et al. 2012). As there is no requirement of water during the construction of GCLs, therefore, these are not vulnerable to desiccation damage, which results in cracking of liners during construction and may be less susceptible after the construction. These undergo less settlement underlying waste as compared to CCLs due to lighter weight of GCLs (Maubeuge et al. 2012). These can also tolerate significantly more differential settlement than the CCLs.

5.5 Landfills Liner Based on Fly Ash Materials

Fly ash is the finer fraction of unburnt residue generated by coal fired thermal power plants (Ahmaruzzaman 2010). It is mainly composed of glassy hollow spherical particles called cenospheres, which acts as a storage house for the harmful pollutants (Fomenko et al. 2011; Paul 2007). The use of fly ash in a liner application can not only be economically attractive in the regions nearby the thermal power plant but also can save the naturally occurring material (sand). Utilization of fly ash in this manner also has the advantage of reusing an industrial waste by-product without adversely affecting the environment or potential land use (Gupt et al. 2019; Cokca and Yilmaz 2004; Nhan et al. 1996). The pozzolanic and self-cementing properties of fly ash have naturally made it a suitable material for construction use. Landfill liner is typically designed to have hydraulic conductivity $\leq 1 \times 10^{-9}$ m/s. However,

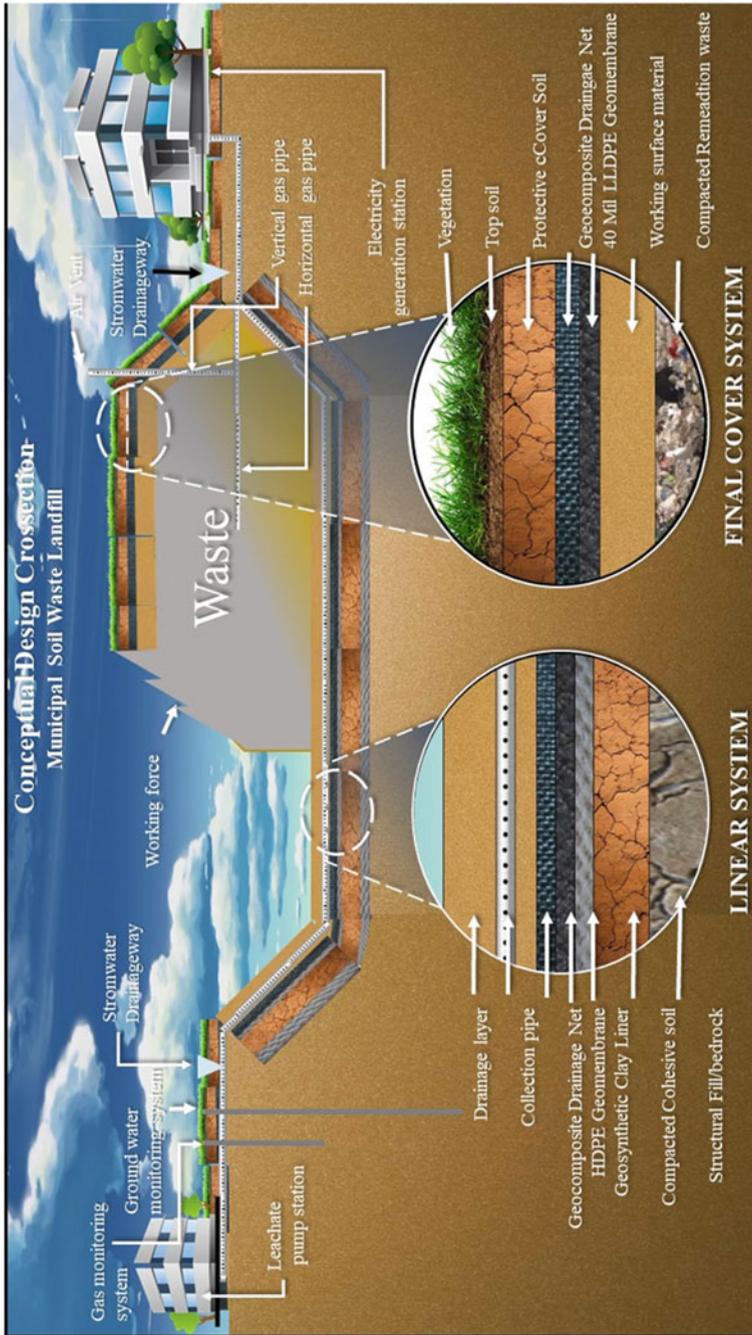
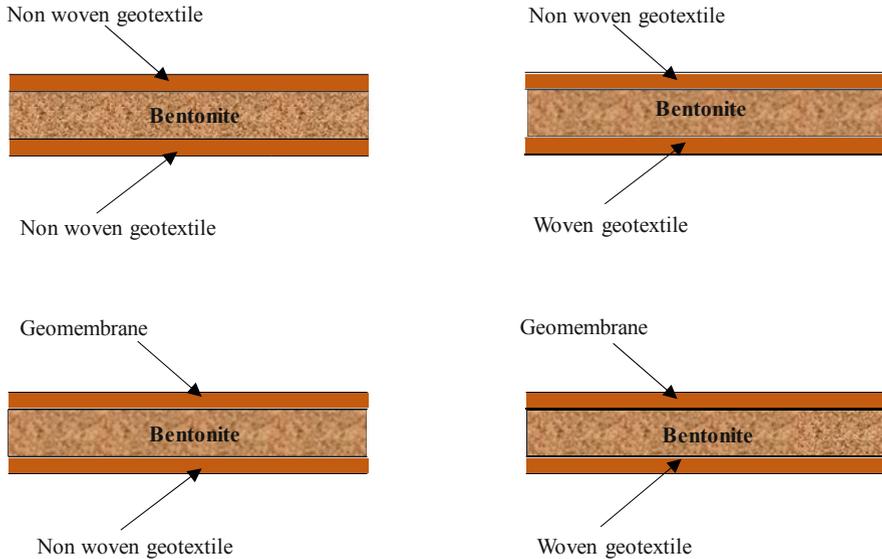


Fig. 5.3 Cross section of modern landfill of MSW with composite clay liner

Table 5.3 Hydraulic conductivity of GCLs with varying amount of two bentonite clays (Mandal 2018)

Mass of bentonite clay per unit area (kg/m ²)	Hydraulic conductivity of for GCL-1 (m/s)	Hydraulic conductivity for GCL-2 (m/s)
3.5	4.5×10^{-8}	6.7×10^{-9}
4.5	7.1×10^{-10}	3.1×10^{-10}
5.0	2.6×10^{-10}	7.4×10^{-11}
5.5	5.5×10^{-11}	4.2×10^{-11}

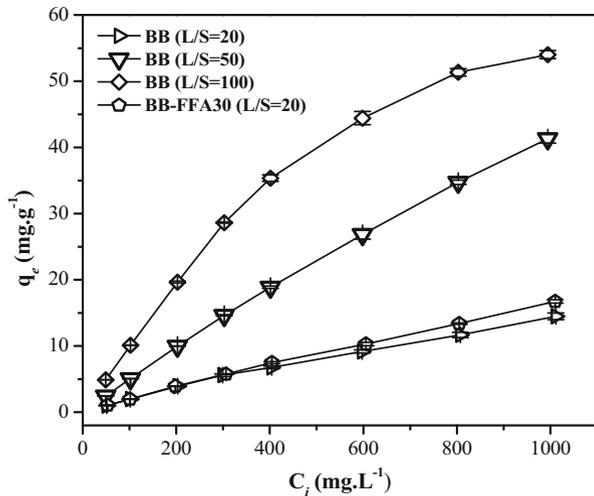
**Fig. 5.4** Geo-synthetic clay liners, bentonite embedded between geo-textile and geo-membrane (modified after Mandal 2018)

fly ash alone does not satisfy the hydraulic conductivity criteria of landfill liner $\leq 1 \times 10^{-9}$ m/s (Younus and Sreedeeep 2012). The self-contaminant retention characteristics of fly ash makes it more appropriate material for the landfills liner (Deka and Sreedeeep 2017). However, no specific guideline is available in the literature for the contaminant retention characteristics of materials used as the liner of landfills. Fly ash based liner saves capital in constructing the landfill by reducing the thickness of liner too. The assessment of contaminant retention characteristics of the geomaterials used in the waste containment facility lying below the wastes is utmost important for effective containment of waste and minimizing groundwater pollution.

5.5.1 Contaminant Retention Characteristics of Barmer Bentonite

Figure 5.5 shows the effect of liquid to solid ratio (L/S) on sorption of lead (Pb^{2+}) on Barmer bentonite (BB) and BB-FFA30 (bentonite 70% and fly ash 30% by wt.) corresponding to varying initial concentration. It can be seen that a drastic increment in the metal ion sorption capacity from 14 mg.g^{-1} to 41 mg.g^{-1} was obtained via increasing L/S from 20 to 50 for BB, thereby clarifying the role of gel consistency (L/S = 20) on sorption phenomena. In comparison to this, a low increment of sorption capacity was reported (41 mg.g^{-1} to 54 mg.g^{-1}) for L/S varying from 50 to 100 (Gupt et al. 2018). Similarly, Du and Hayashi (2006) reported increase in sorbed Pb^{2+} with increase in L/S for the sorption of Cd^{2+} on Ariake clay. Melichová and Hromada (2013) studied the removal of Pb^{2+} and Cu^{2+} by natural bentonite collected from Lieskovec (Slovakia) and reported a decline in adsorption capacity with the increase in adsorbent dosage. In this study, the maximum amount of sorbed Pb^{2+} was observed at L/S of 100 (four times higher than L/S = 20) and lowest at L/S of 20. Figure 5.5 depicts the variation of Pb^{2+} sorption with an initial concentration exhibited a linear trend for L/S 20 and 50 and non-linear trend for L/S 100. It can be inferred that sufficiently large sorption sites are available for Pb^{2+} uptake for L/S 20 and 50, whereas the sorption sites progressively decrease with concentration for L/S = 100 (less number of solids).

Fig. 5.5 Effect of L/S on the sorption of Pb^{2+} on BB and BB-FFA30 (modified after Gupt et al. 2018)



5.5.2 Contaminant Retention Characteristics of Fly Ashes

It is reported that q_e for different fly ashes (FAs) collected from different thermal power plants ((1) Farakka fly ash (FFA) (NTPC Farakka, West Bengal, India), (2) Badarpur fly ash (BFA) (NTPC Badarpur, New Delhi, India), and (3) pond ash (PA) (NTPC Singrauli, Uttar Pradesh, India), remains same, i.e., up to 2.5 mg.g^{-1} for an equilibrium concentration of Pb^{2+} up to 100 mg.L^{-1} of the initial level (Fig. 5.6). With further increase in the initial concentration, free surface site of the FA is progressively saturated and becomes exhausted and is depicted by the inclined portion of the isotherm (Fig. 5.6) (Deka and Sreedeeep 2017). Poly and Sreedeeep (2011) and Younus (2010) reported similar trends, i.e., FFA and BFA isotherms were nearly comparable, indicating the same retention capacity for Pb^{2+} ions. PA exhibited marginally low retention among all the FAs at a high concentration range. The retention characteristics of Neyveli fly ash (NFA) collected from Neyveli Lignite Corporation, India, was different from other FAs. It is mainly due to the presence of a high amount of calcium oxide (CaO) in fly ash (NFA). It is interesting to see that FA retains Pb^{2+} ions even though it has limited specific surface area (SSA). The presence of spherical shaped hollow pockets, called cenospheres, in FA particles, acts as a storage house for most of the contaminants (Fomenko et al. 2011; Paul 2007).

5.5.3 Contaminant Retention Characteristics of Bentonite–Fly Ash Mixes

Figure 5.7 shows the Pb^{2+} retention characteristics of bentonite (B) and B-FA 50 mixes. As expected, there is a drastic increase in the retention of blends as

Fig. 5.6 Lead retention studies of fly ashes (modified after Deka and Sreedeeep 2017)

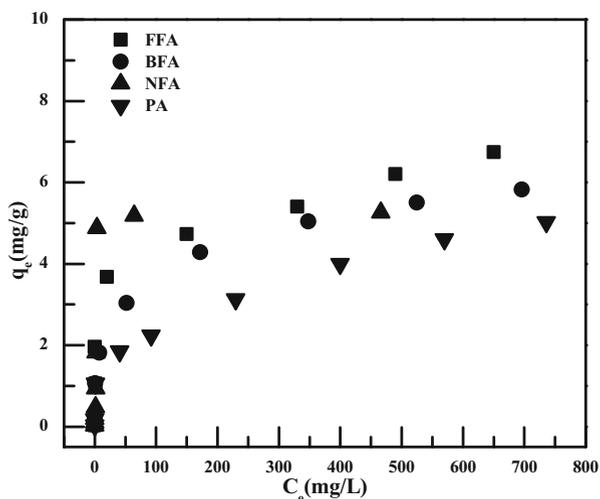
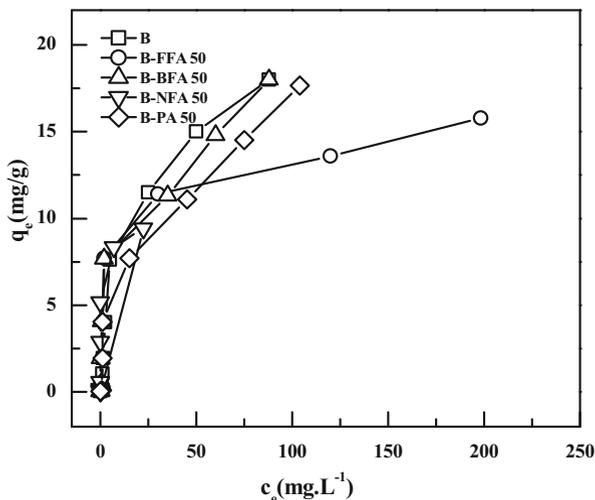


Fig. 5.7 Lead retention studies for bentonite B and FA-B mixes (modified after Deka and Sreedeeep 2017)



compared to FA alone (Deka and Sreedeeep 2017). This can be attributed to the high SSA of B. For the concentration range investigated in this study, the results of B-FA mixes were close to the effects of B. This indicates that there is not much influence of FA in the B-FA 50 mix and most of the retention was predominantly governed by high specific surface area of B.

5.5.4 Percentage Removal of Pb^{2+} by FA and FA-BI Mixes

The removal of Pb^{2+} ions by fly ash, and its blends were studied at various initial metal ion concentration (Figs. 5.8 and 5.9). It was observed that the metal removal efficiency decreased with the increasing initial metal ion concentrations. A drastic fall in the percentage removal efficiency was observed for the range of initial concentrations 100 mg.L⁻¹ to 500 mg.L⁻¹. Above 500 mg.L⁻¹, there is not much change in removal efficiency. The removal efficiency of FFA, BFA and NFA were comparable while PA exhibited the lowest removal. A minimum of 30% to 35% removal was observed in FAs for the maximum initial concentration of around 1000 mg.L⁻¹. This low value of percentage removal would be still significant while using FA for waste containment liners in place of sand (Deka and Sreedeeep 2017). This is mainly because sand is an inert material and do not have any potential to remove heavy metals. Thus FA offers an additional advantage of contaminant removal from landfill leachate. It is worth noting that a good removal efficiency (> 90%) was observed for all the B-FA mixes.

Fig. 5.8 Percentage (%) removal of Pb^{2+} by FAs (modified after Deka and Sreedeeep 2017)

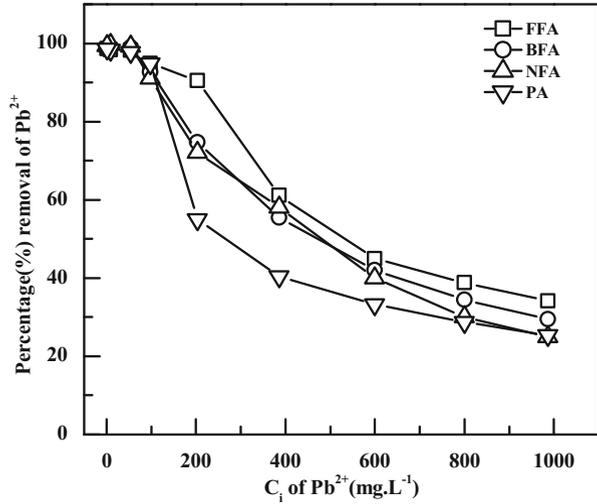
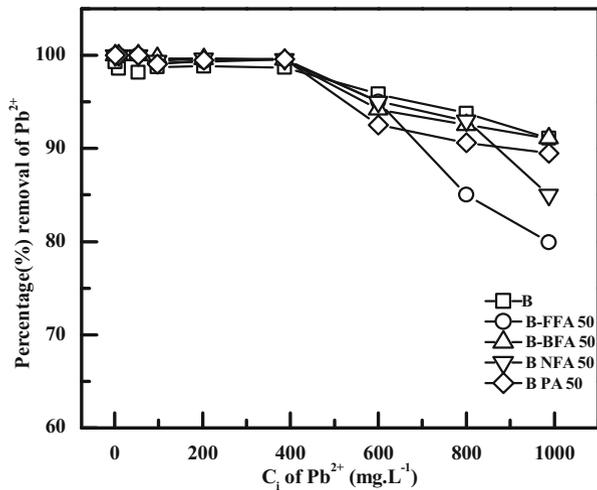


Fig. 5.9 Percentage (%) removal of Pb^{2+} by B-FA mixes (modified after Deka and Sreedeeep 2017)



5.5.5 Hydraulic Conductivity of Expansive Soil Fly Ash Mixes

Falling head test was used to determine the hydraulic conductivity of fly ash-expansive soil mixes for different water content and at various compaction state. Three points were chosen on the standard proctor curve presented in Table 5.4 for the hydraulic conductivity determination: optimum moisture content (OMC), dry of optimum, and wet of optimum (Younus and Sreedeeep 2012).

Figure 5.10 shows the variation of hydraulic conductivity and void ratio at different fly ash content. It can be observed that for all the three compaction states,

Table 5.4 Compaction states of samples used for hydraulic conductivity determination

Mix	Dry of OMC		OMC		Wet of OMC	
	γ_d (g/cc)	w (%)	γ_{dmax} (g/cc)	w (%)	γ_d (g/cc)	w (%)
B100-F0	1.55	27.97	1.57	29.66	1.49	32.83
B80-F20	1.53	20.80	1.56	24.22	1.44	29.42
B60-F40	1.54	20.48	1.55	22.04	1.46	26.35
B50-F50	1.52	18.03	1.54	21.01	1.48	24.55
B30-F70	1.46	16.22	1.48	19.66	1.42	23.16
B0-F100	1.32	14.27	1.38	19.66	1.34	24.89

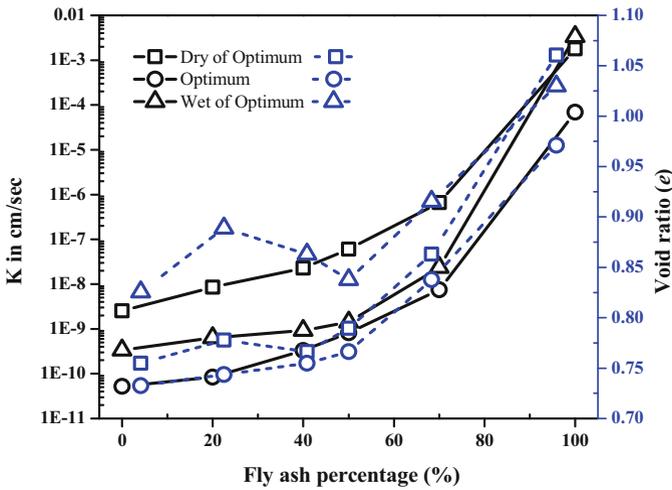
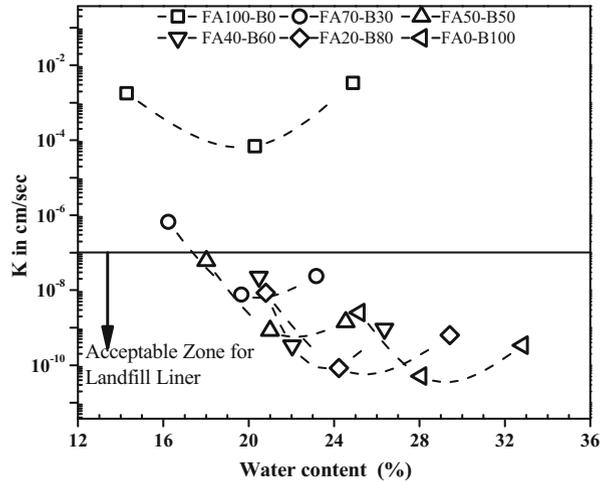


Fig. 5.10 Variation of hydraulic conductivity and void ratio with fly ash percentage (modified after Gupt et al. 2019)

hydraulic conductivity increases with an increases in fly ash percentage. It can be due to the presence of coarser cohesionless particles of fly ash as compared to expansive soil (ES) (e.g. bentonite). With the inclusion of 30% (wt) ES in fly ash, a decrease in the hydraulic conductivity (approximately by four orders) was observed. Further, the minimum hydraulic conductivity (corresponding to compaction state) was observed at optimum moisture content followed by wet of optimum and highest for dry of optimum for a particular mix. For a particular mix at three compaction state, hydraulic conductivity is function of void ratio. Thus, the aforementioned study will led to analyze the potential utilization of fly ash (FA) and its mixes with expansive soil (ES) for landfill liners.

From Fig. 5.11, it can be observed that hydraulic conductivity (K) value for all the mixes decreases from dry of optimum point to OMC and further increases when wet of optimum point is considered. Except fly ash, the minimum K value for bentonite-fly ash mix is obtained at water content ranging from 0.5 to 1.6% (which is more than the OMC value). Generally, the lowest hydraulic conductivity of clayey soil is

Fig. 5.11 Variation of hydraulic conductivity of mixes with varying water content (modified after Younus and Sreedeeep 2012)



achieved when the soil is compacted at water content slightly higher than the optimum water content (Daniel and Benson 1990). This is due to the development of a diffuse double-layer around expansive soil (ES) particles, which causes the swelling of clayey particles exerting pressure against/onto the surrounding particles. Consequently, the effective pore size reduces, resulting in lowering of the hydraulic conductivity. For the potential utilization of a material as landfill liners, the compacted layer should have K value $\leq 1 \times 10^{-7}$ cm/s (Daniel 1984; Benson and Trast 1995). Figure 5.11 shows that except fly ash, all the bentonite–fly ash mixes compacted corresponding to OMC, yields K value less than the acceptable value.

5.6 Future Perspective and Challenges

Fly ash based liner materials have emerged as an alternative landfill liner material for replacement of costly naturally occurring materials (like sand and locally available soils). However, it is limited by a numerous factors such as long-term interaction of fly ash with the geomaterials, leaching property of the fly ash, and mineralogical alteration of the material in the long run. Thus, it is necessary to focus on the compatibility of suitable geomaterials when fly ashes are mixed with the expansive soils and its effect on the contaminant retention characteristics (time effect or aging effect) before its application in the field.

For the practical applicability about the contaminant retention characteristics of fly ash-expansive soil mixes as landfill liner, it needs to be checked with the other heavy metals too. For this, a column test have to performed with the single and multiple contaminants. Fly ash based liner materials also possess a good shear strength when mixed with suitable expansive cohesive material. It not only reduces the cost of the construction, but also reduces the thickness of the liner of the landfill

due to self-retention capacity of the fly ash. The limitations together constitute the hierarchy of mineral composition of the fly ashes to be used as liner materials, further protecting the geoenvironment. However, continuous efforts should be performed for finding an alternate liner material so that the natural occurring material (e.g., sand and locally available soil) can be saved for agricultural purpose. In this regard, waste-based liner materials should be a better and sustainable alternative for the mitigation of ground water pollution as well as for the geoenvironment.

5.7 Conclusions and Recommendation

The present chapter summarized the potential of bentonite–fly ash mixes for its utilization in compacted landfill liners via hydraulic conductivity and contaminant retention as the two prime qualifying parameters at the laboratory scale. The chapter reported the valorization of solid-waste fly ash generated from the thermal power plant for the waste containment projects. This has not only solved many of the environmental issues which arises after disposing of fly ash but also saves the costly natural materials like sand. The ranges of water content and dry unit weight have been examined for bentonite–fly ash (class F) mixes for satisfying the qualifying parameters. Further, the bentonite–fly ash mixes compacted at optimum moisture content satisfied the regulatory requirements of landfill liners. As the fly ash alone cannot be used as compacted liners, the maximum weight percentage of fly ash that can be mixed with bentonite was reported up to 70%.

The laboratory results discussed in this chapter would be quite handy for deciding the appropriate bentonite–fly ash mix to be evaluated at field scale. The retention characteristics of the fly ashes, bentonite, and fly ash–bentonite mixes were studied using heavy metal (Pb^{2+}) as the model contaminant in the batch equilibrium. For all the different types of fly ashes viz., NFA, FFA, BFA, and PA, NFA (class C) fly ash was found to be more capable for the contaminant retention while the PA showed the least retention. The retention mechanism of NFA was predominantly governed by precipitation rather than sorption due to the variation in pH associated with the calcium content. Though the fly ash did not have much influence on the retention characteristics of the 50:50 fly ash–bentonite mix, but more than 90% of heavy metal removal was achieved at a maximum initial concentration of 1000 mg.L^{-1} . Henceforth, the potential of using fly ash–bentonite instead of sand in the construction of landfill liners is demonstrated and recommended. Advocating the use of fly ash in such voluminous projects will further ensure its efficient re-utilization, reducing the amount of land required for its storage along with the other environmental and sustainable advantages.

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Chapter 6

Application of Visual MODFLOW in Groundwater Flow Modeling at the Left Crescent of the Ganga River, Varanasi, India



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Abstract Groundwater flow modeling is a significant tool for conceptualizing the hydro-geological processes and forecasting the groundwater pollution. To simulate the groundwater flow direction and pollutant fate, Visual MODFLOW and MODPATH are used popularly. Present study focuses on the application of Visual MODFLOW to study the groundwater flow direction, groundwater flow path lines and to predict the leachate contamination from the open unsecured MSW dumping site at the left crescent of the Ganga River in Varanasi, India. Simulation of the model is done for one year by giving input value to the flow setting and transport setting database of the software to know the groundwater flow direction and flow velocity in the study area. Linear isotherm (equilibrium-controlled) with no kinetic reactions is assumed for contaminants transport modeling.

The simulated result indicates that the groundwater is flowing from higher heads (water table) to lower heads (towards Ganga River) in the study area. The maximum velocity of groundwater flow is calculated to be $5.7E-06$ m/s (5.7×10^{-7} m/s). Simulated groundwater table was ranged from minimum 58 m to maximum 74.93 m. This result is validated with the field monitoring data of water table which was also observed to be between 61.96 m and 78.85 m. TDS transport model results indicate the movement of TDS pollutant towards the groundwater flow direction. TDS

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transport modeling showing a distinct pollutant path line from MSW dumping site to nearest observed heads (wells) and its path lines are congruent with the groundwater flow direction. This study would be helpful for site-suitability index for landfill strategy makers and the government authorities to safeguard groundwater pollution from potential risk from the landfill.

Keywords Ground water modeling · MODFLOW · MSW · TDS

6.1 Introduction

The groundwater model is a software generated model to make a prediction of future hydro-geological behavior of the aquifer system. Models are used because it is easier to work with a conceptualized system than with the actual system. Wang and Anderson (1982) and Anderson et al. (2015) defined a model as “designed to represent a simplified version of reality.” The hydro-geologic condition, hydraulic properties, and water budget determined the input data for a groundwater modeling (Vishal et al. 2014). Groundwater models give the information about natural as well as anthropogenic process that affect the aquifer system. Largely, spatial distribution of geological properties and temporal behavior of groundwater system is determined by groundwater flow model. In general, an analytical solution can be obtained under many simplifying assumptions, such as unidirectional velocity field, a set of uniform transport properties, and pattern of the sink and source distribution (Kresic and Mikszewski 2007). Groundwater models can be used for three general purposes. (A) To predict the expected change in aquifer. (B) To describe the system in order to analyze various assumptions about its nature and dynamics. (C) To generate a conceptual system that will be used to study principles of groundwater flow associated with various general or more specific problems.

Visual MODFLOW is a well-established tool to study the groundwater flow and contaminants transport modeling due to its user-friendly interface. Srivastava and Ramanathan (2018) studied the movement of trace metals in groundwater around the landfill by using visual MODFLOW and MT3D. The calibration and validation of model showed more than 90% model validation with 95% confidence. Atta et al. (2015) studied the groundwater flow around the MSW landfill site. A three-layer steady-state calibrated model was constructed by using MODFLOW 2000 around the MSW landfill site and found the chance of contamination by leaching of landfill leachate in the same direction as the flow of the water bodies (Atta et al. 2015).

Two-dimensional groundwater flow and transport model is very helpful for analyzing the aquifer response to various pumping strategies and for long-term sustainability of vital groundwater resources (Rejani et al. 2008). Contaminant migration and path lines can be predicted up to 20 years in a two-layered model of groundwater by flow and mass transport modeling (Tiwary et al. 2005).

The threat to the groundwater from the unlined and uncontrolled landfills is of great concern in many parts of the world, particularly in the underdeveloped and developing countries where the hazardous industrial waste is also co-disposed with municipal waste. The migration phenomenon is mainly through advection rather than dispersion. Particle path lines also had been computed to trace the movement of contaminants by using Visual MODFLOW. Therefore, to understand the

groundwater system behavior, to predict the future risk, and take a decision for remediation measures, Visual MODFLOW can act as a reliable tool.

The objective of this study is to develop the groundwater flow and pollutant flow path from the open uncontrolled MSW dumping site using visual MODFLOW.

6.2 Study Area

To accomplish the objective of this study, Ramna MSW dumping site is selected which is very near (2.64 km.) from the bank of River Ganga, located in between N $25^{\circ}14'38.3''$ latitudes and E $83^{\circ}00'15''$ longitudes of rural areas of Varanasi city which is in the eastern part of the state of Uttar Pradesh in the middle Ganga valley of North India. Varanasi has a humid subtropical climate with high variation between summer and winter temperatures. The average temperature is $32\text{--}46^{\circ}\text{C}$ in summer and $5\text{--}15^{\circ}\text{C}$ in winter. The average annual rainfall is 1110 mm. Geologically, the study area is covered by alluvial sediments of the Pleistocene period which is most vulnerable for leaching (Kovacevik et al. 2016).

The sandy study area located near to the drainage courses (channels) of the river Ganga and is prone to flood which deposits a carpet of fresh silt, clay, and loam. So that chemical alteration of solid waste highly takes place and has a chance to leach to subsurface water. The study area and its environs are located at an average height of about 76 m above the mean sea level and have largely even topography (Janardhana Raju et al. 2011). There is a great possibility of groundwater pollution in the study area from the MSW dumping site due to leachate percolation during the rainy season (Fig. 6.1).

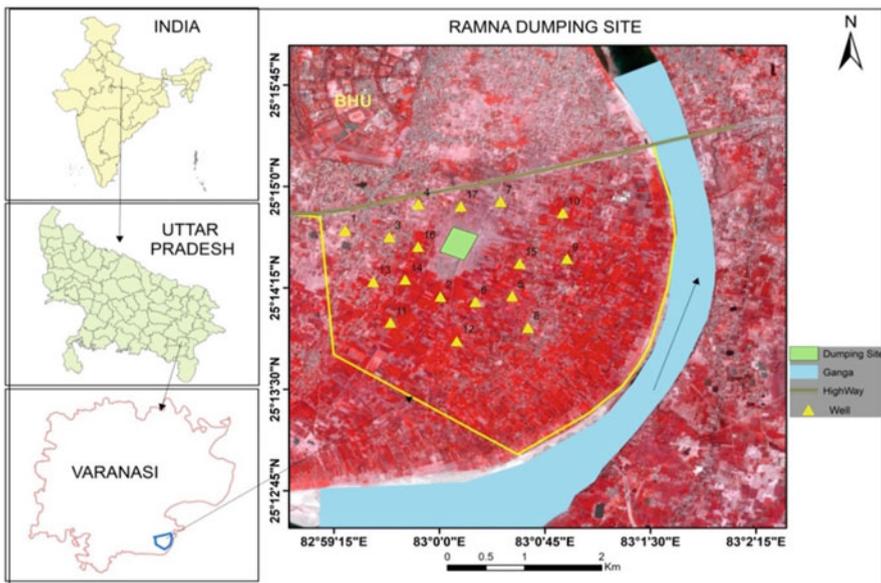


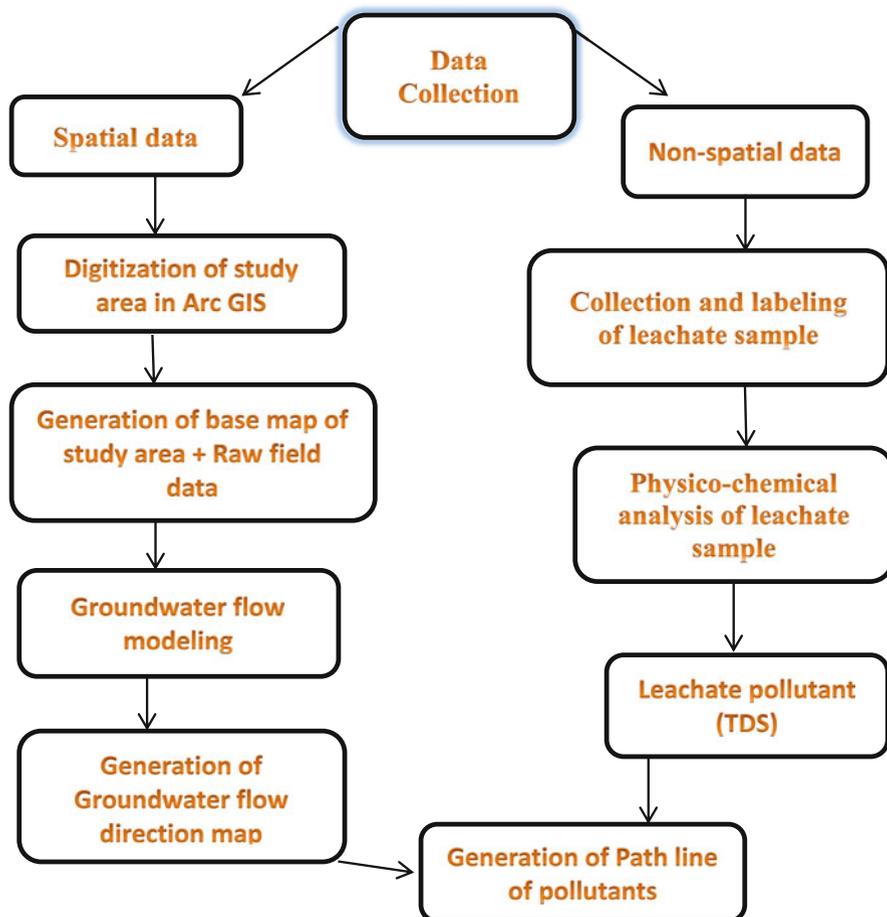
Fig. 6.1 Study area map

6.3 Materials and Methodology

Physico-chemical analysis of MSW leachate samples was carried out to know the leachate characteristic. The leachate sample was collected randomly from leachate pond near the Ramna open dumping site after the rainy season in October and November month of 2014. 500-mL reagent bottle was used for sampling then this sample was immediately transported to the laboratory and kept at 4 °C for physico-chemical analysis of parameter, i.e. temperature, pH, electrical conductivity, TDS, DO, chloride, hardness, nitrate, total alkalinity, BOD₅, COD, Ca, Mg, Na, K, F⁻, Cr, Zn, Cu, Cd, Pb, Fe, Ni, Mn, As, and PO₄³⁻.

Visual MODFLOW software was used for groundwater modeling which is used for predicting the groundwater flow direction and path line of leachate contaminant. This developed model was calibrated and validated with observed field data.

Stepwise methodology is briefly shown in the following flow chart.



Following equation is involved in groundwater flow modeling:

$$\frac{\partial}{\partial x} \left(K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial h}{\partial z} \right) \pm W = S_s \frac{\partial h}{\partial t}$$

K_{xx} , K_{yy} , and K_{zz} are hydraulic conductivities along the x , y , and z coordinate axis, h indicates the potentiometric head, W is a volumetric flux per unit volume, i.e. indicates sources and sinks of the water, S_s is the specific storage of the porous material, and t is the time.

MT3D, a modular three-dimensional transport model is used for simulation of advection, dispersion, and chemical reaction of contaminants in groundwater flow system; it solves the transport equation after the flow solution has been gained from the groundwater flow model (MODFLOW). The general advection-dispersion equation described the fate and transport of species in three-dimensional transient groundwater flow system.

$$\begin{array}{ccccccc} \frac{d}{dt}(\theta c^k) & = & \frac{d}{dx_i} \left[\theta D_{ij} \frac{dc^k}{dx_j} \right] & - & \left(\frac{d}{dx_i} \theta v_i c^k \right) & + & q_s \cdot c_s^k + \sum R_n \\ \downarrow & & \downarrow & & \downarrow & & \downarrow \\ \text{Dispersion-term} & & \text{Advection-term} & & \text{Sink-term} & & \text{Reaction-term} \end{array}$$

where C^k = Dissolved concentration of species k , θ = Porosity of the subsurface medium, t = time. x_i = Distance along the respective Cartesian coordinate axis, D_{ij} = Hydrodynamics dispersion coefficient tensor, V_i = Seepage or linear pore water velocity. It is related to specific discharge, q_s = Volumetric flow rate per unit volume of aquifer representing the fluid source and sink, c_s^k = Concentration of source and sink flux for species k , $\sum R_n$ = Chemical reaction term

6.4 Input Data for Model Preparation

(a) Observation Wells

A total of 56 wells were identified around the Ramna MSW dumping site for initial head value. Their x , y coordinates and ground elevation were recorded using DGPS (Sokkia GRX2).

The groundwater level (piezometric heads) data from 56 observation wells were calculated using a meter tape. The difference between ground elevation and depth of observed well indicates the groundwater table.

(b) Base map of the study area.

(c) Location of observed wells (x , y coordinates and elevation).

(d) The water table of observed wells.

(e) Hydraulic conductivities of soil (K_x , K_y , K_z). Conductivity data used to simulate the flow rate through the sediments.

- (f) Porosity, effective porosity.
 (g) Specific storage (S_s) and Specific yield (S_y), taken from secondary sources.
 (h) Pumping rate calculation.

Pumping rate data calculated from the population and population density data of the Varanasi city.

Per capita water uptake in Varanasi city is approximately 180 L/day (Varanasi Municipal Corporation)

$$\text{Studied Area} = 21 \text{ km}^2$$

Water demand in study area = population density of village \times village area \times water uptake per capita

$$\begin{aligned} &= 1711.858 \times 21 \times 180 \\ &= 6,470,882.14 \text{ L/day} \\ &= 6470.88214 \text{ m}^3/\text{day} \end{aligned}$$

Total no of assumed pumping wells for modeling in study area = 150
 Therefore, per well water uptake

$$\begin{aligned} &= 6470.88214/150 \\ &= 43.13 \text{ m}^3/\text{day} \end{aligned}$$

Average pumping rate of tube well for rice crop in July month = 100 m³/day
 while in monsoon period = 10 m³/day

Average pumping rate of tube well for the wheat crop in winter season = 60 m³/day (Food and Agriculture organization data)

- (i) Recharge rate calculation

Krishna Rao gave the following empirical relationship in 1970 to determine the groundwater recharge in limited climatological homogenous areas.

$$R = K (P - X) \quad (R = \text{recharge}, P = \text{precipitation})$$

$$R = 0.20 (P - 400) \text{ for areas with } P \text{ between } 400 \text{ and } 600 \text{ mm}$$

$$R = 0.25 (P - 400) \text{ for areas with } P \text{ between } 600 \text{ and } 1000 \text{ mm}$$

$$R = 0.35 (P - 600) \text{ for areas with } P \text{ above } 2000 \text{ mm}$$

where R (recharge rate) and P (precipitation) are expressed in millimeters

In Varanasi, the average precipitation between 2012 and 2017 year was 961.14 mm/year, so recharge rate calculated as:

Table 6.1 Lithology input data (Morris and Johnson 1967; Anderson et al. 2015)

Layers	Lithology	K_x, K_y	K_z	S_s	S_y	Total porosity	Effective porosity
Horizon 1	Coarse sand	9×10^{-6}	9×10^{-7}	0.0011	0.06	0.42	0.21
Horizon 2	Sandy clay	3×10^{-5}	3×10^{-6}	0.008	0.32	0.55	0.35

$$R = 0.35 (P - 600)$$

$$R = 0.35 (961.14 - 600)$$

$$R = 0.35 \times 361.14$$

$$R = 126.39 \text{ mm/year}$$

These lithological data were calculated from the soil testing data shown in Table 6.1.

6.5 Results and Discussion

Ramna MSW leachate shows the high quantities of organic and inorganic constituents with some of toxic heavy metals concentrations. This physico-chemical characteristic result shows that the leachate is of higher strength in their pollutant concentration. It was observed that TDS is high in concentration in both the samples (L_1 and L_2) and its mean value is more than leachate standard value. Therefore TDS is selected for the transport modeling analysis for Ramna study area. Simulation of the model is done for one year by giving input value to the flow setting and transport setting database of the visual MODFLOW software to know the groundwater velocity and flow direction in the study area. To develop model there are several steps that explain briefly in the following headings (Tables 6.2 and 6.3).

6.5.1 Grid Design of Flow Model

Grid module helps to explain and discretize the modeling domain. The geographic boundaries of the model grid are covering about 40 km^2 of the study area. The base map of the model grid was discretized into 78 rows and 78 columns and vertically

Table 6.2 Input parameters for river (Morris and Johnson 1967; Anderson et al. 2015)

Riverbed thickness (m)	River width (m)	Riverbed conductivity (m/s)
3	800	3×10^{-4}

Table 6.3 Results of physico-chemical analysis of leachate samples of Ramna dumping site, 2014

S. No	Parameters	Average value (L_1)	Average value (L_2)	Mean	Leachate disposal standard for inland surface water (MoEF 2000)	Leachate characteristics, generated from MSW in developing countries (Diaz 2005)
1	Temperature	27.0	24.9	25.9	NM	NM
2	pH	8.3	9.3	8.8	5.5–9.0	4.5–9
3	EC	3.46	5.65	4.55	NM	NM
4	TDS	2024	2632	2338	2100	0–42,300
5	DO	7.6	7.8	7.7	NM	NM
6	Chloride	1202	1420	1311	1000	100–5000
7	Hardness	800	780	790	NM	0–22,800
8	NO_3^-	60	72	66	50	0–25
9	Total alkalinity	2200	1815	2007	NM	300–11,500
10	BOD_5	1344	1327	1335	30	20–40,000
11	COD	8350	8319	8332	250	500–60,000
12	BOD_5/COD	0.16	0.15	0.16	NM	NM
13	Ca	360	340	350	NM	10–250
14	Mg	127	275	201	NM	40–1150
15	Na	875	616	745	NM	50–4000
16	K	1337	1155	1246	NM	10–2500
17	Fluoride	2.1	0.2	1.7	2	NM
18	Cr	1.42	1.30	1.36	2.0	NM
19	Zn	ND	ND	ND	5.0	0.03–120
20	Cu	0.34	0.24	0.29	3.0	4–1400
21	Cd	ND	ND	ND	2	NM
22	Pb	ND	ND	ND	0.1	8–1020
23	Fe	5.5	3.7	4.6	NM	3–2100
24	Ni	ND	ND	ND	3.0	NM
25	Mn	ND	ND	ND	NM	0.03–65
26	As	ND	ND	ND	0.2	NM
27	PO_4^{3-}	42.3	18.5	30.4	NM	0.1–30

All value in mg/L except Temp ($^{\circ}\text{C}$), EC (mS/cm), and pH

^aND not detectable, NM not mention

the grid distinct in two layers of the aquifer system. Each small cell of the grid is equivalent to 8 m^2 of the study area (Fig. 6.2).

The surface layer is used to make model layer for that the data is being imported. The model layers that are ground surface (top of layer 1), second layers, and a third layer made by incorporating. DEM file downloaded from USGS site (Figs. 6.3 and 6.4).

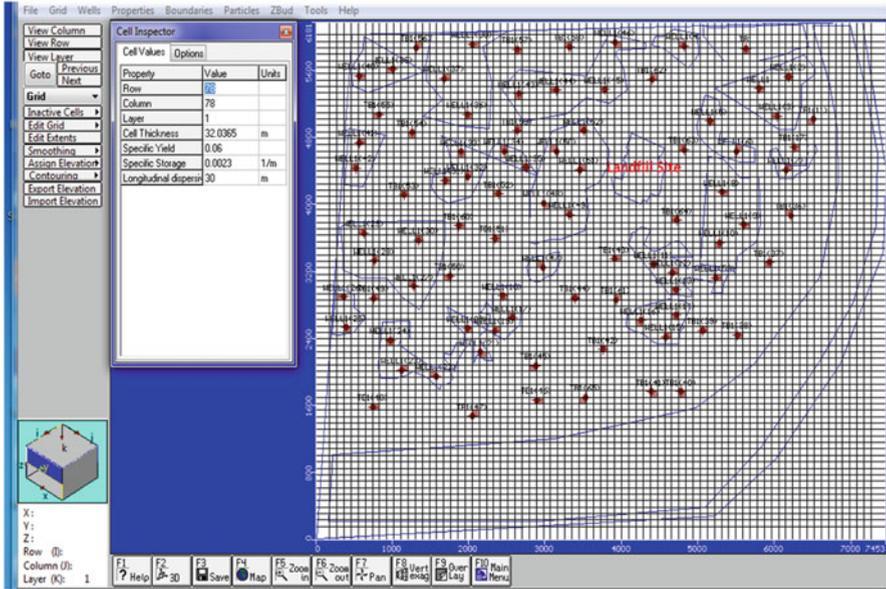


Fig. 6.2 Model grid showing study area

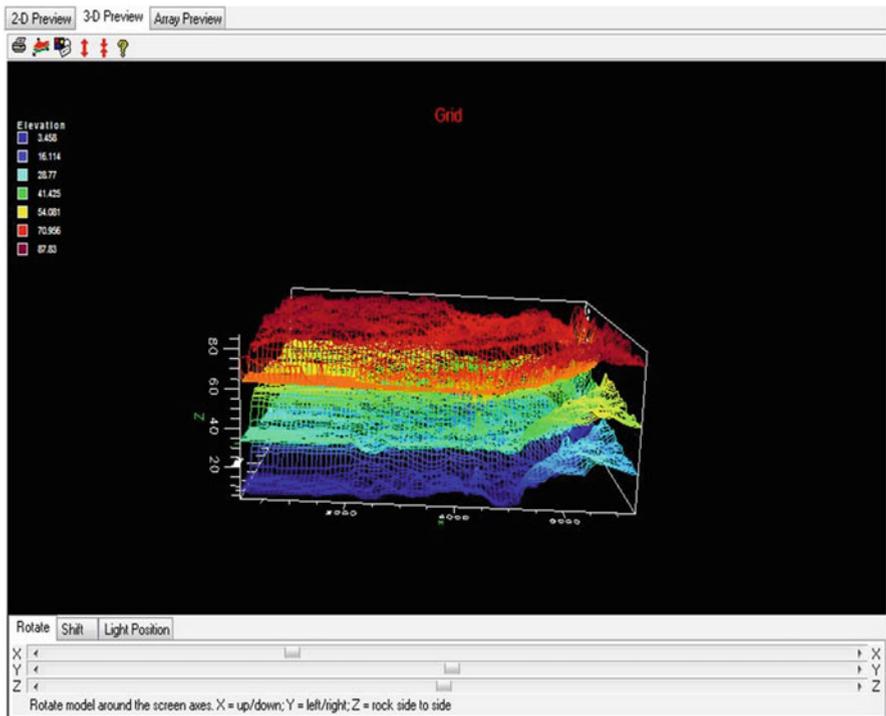


Fig. 6.3 3D view of the model grid

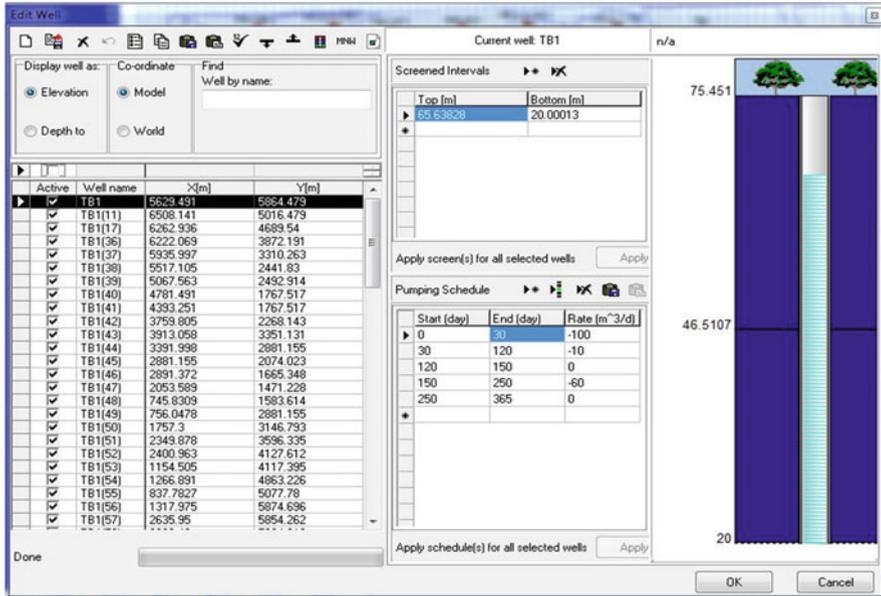


Fig. 6.4 Pumping schedule database for rice and wheat crop in Ramna study area

6.5.2 Assigning Pumping Well Data

Pumping rates value for specified time periods was assigned for the each tube wells and open wells in pumping schedule database as shown in Fig. 6.5.

6.5.3 Assigning of Head Observation Data

56 head observation data of pre- and post-monsoon period were assigned in head observation database of the software for calibration and simulation. Wells location and their head value incorporated through .xls file. To simulate the hydro-geological and hydro-geochemical process flow properties such as conductivities (K_x , K_y , K_z), storage (S_x , S_y , P_{eff} , P_{tot}), and initial head were assigned with their respective value for layer one and layer two. These soil properties and their related parameters are assigned in the input screen of each parameter (Figs. 6.6 and 6.7).

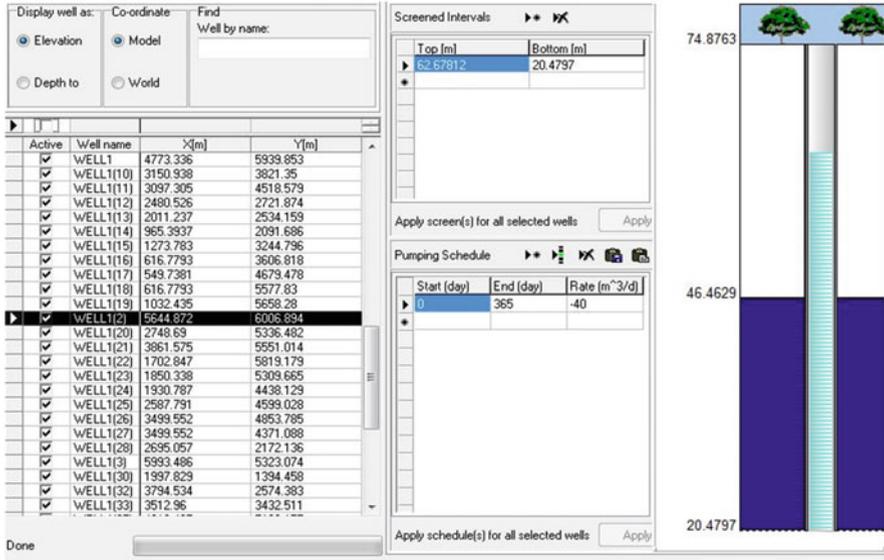


Fig. 6.5 Pumping schedule database for open wells in Ramna study area

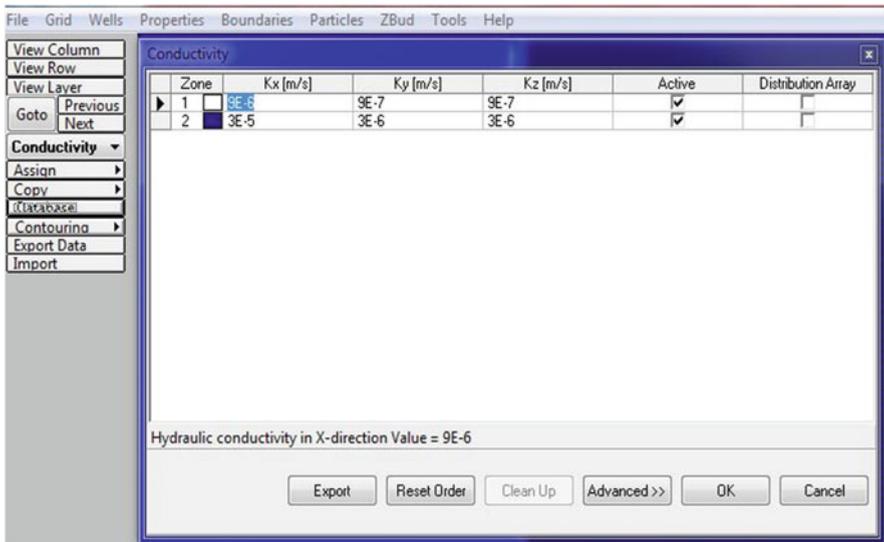


Fig. 6.6 Soil Conductivity data assigned to zone 1 (layer 1) and zone 2 (layer 2)

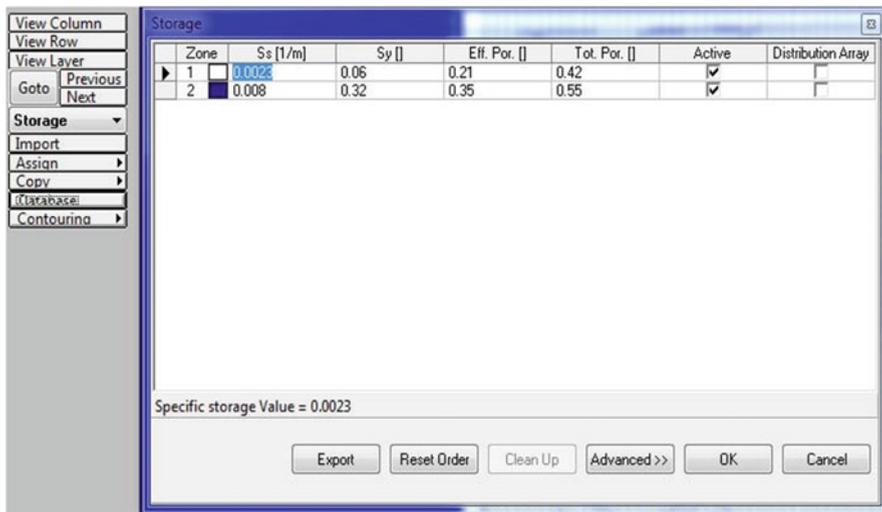


Fig. 6.7 Storage data assigned for zone 1 (layer 1) and zone 2 (layer 2)

6.5.4 Assigning Boundary Conditions

Boundary conditions represent the system’s relationship with the surrounding systems; it defines the exchange of flow between the model and the external system. Eastern and southern parts of the study area have the river, so it was considered as hydrological flow boundary for the model. This river boundary simulated the influence of the Ganga River on the groundwater flow.

Western and northern boundaries have been modeled as a constant head boundary as shown in Fig. 6.8. River Stage (river surface elevation), Riverbed Bottom (river seepage layer elevation), River Conductance (the resistance to cause by riverbed) were assigned as shown in Fig. 6.9. Start time head and stop time head value assigned from pre-monsoon, monsoon, and post-monsoon field observation data of the year.

6.5.5 Assigning Recharge Data

Mostly recharge occurs due to precipitation percolating into the groundwater. Precipitation occurs in the rainy season, so for this period the recharge rate value is assigned as shown in Fig. 6.10 and rest of the period assigned with no recharge value.

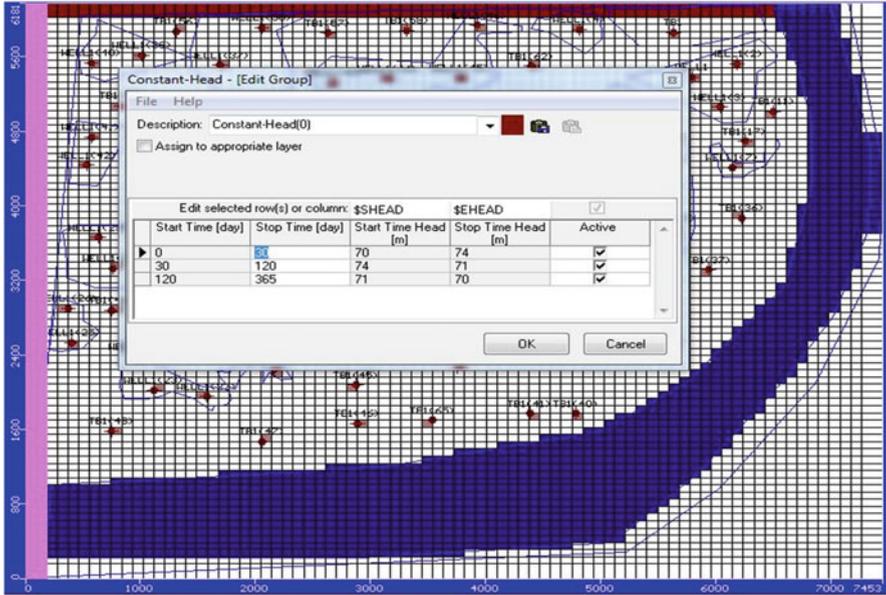


Fig. 6.8 Constant heads assigned as a boundary condition

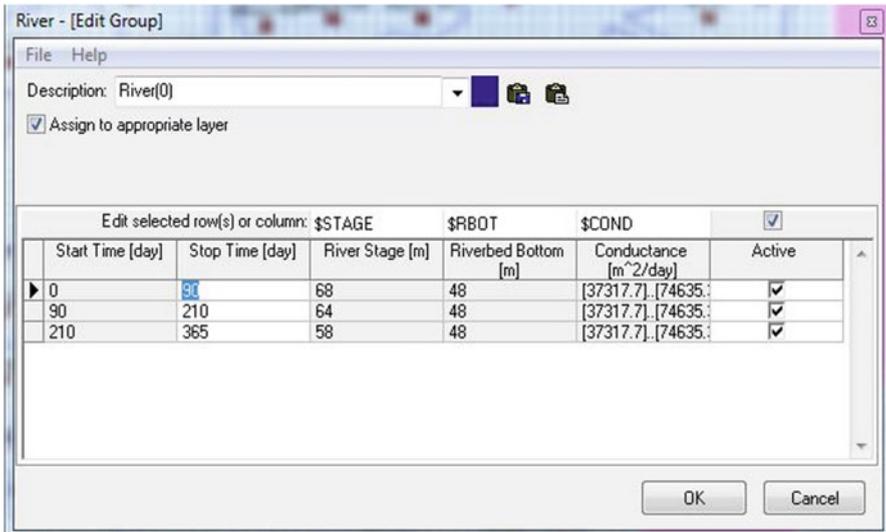


Fig. 6.9 River assigned as a boundary condition

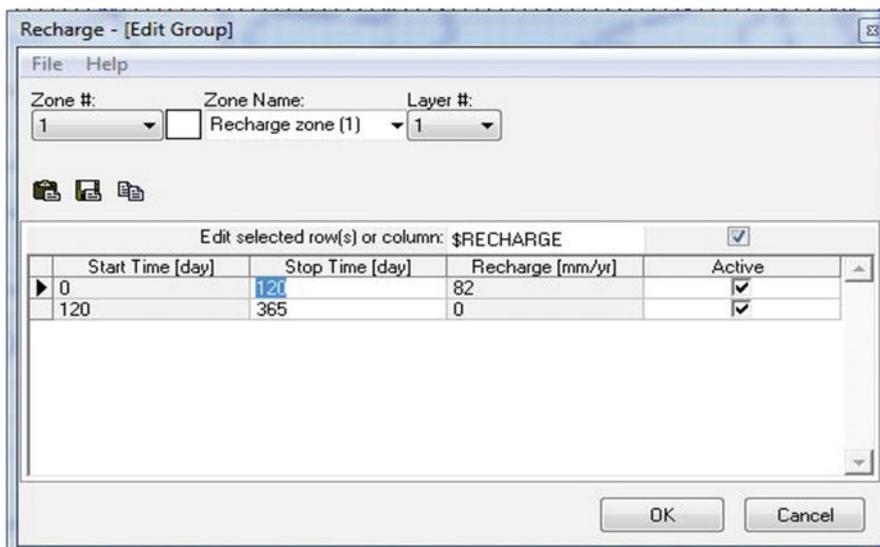


Fig. 6.10 Recharge data assigned in the input database

6.5.6 Run Model

To run the model, transient flow option is selected in run type and USGS MODFLOW 2005 in engine type. The model was run with different inputs for one year. During model running process MODFLOW automatically combined all of the various time period data assigned for each pumping well and boundary condition into the stress period setup. The output result gives a time-dependent groundwater flow simulation (Fig. 6.11).

6.5.7 Output of the Run Model

The outputs of the model simulation are the hydraulic heads and groundwater flow heads, which are in equilibrium with the hydro-geologic conditions like topographical characteristic, hydrologic boundaries, initial and transient conditions. The direction of the groundwater flow of the simulated model shown in Fig. 6.12, which indicates that the groundwater is flowing from higher heads (water table) to lower heads (towards Ganga river) in the study area.

The maximum velocity of groundwater flow is calculated to be $5.7E-06$ m/s (5.7×10^{-7} m/s). The studied area having distinct flow patterns, from west plain to east riverside following the topographical elevation mainly changes in hydraulic gradient responsible for such flow pattern. Therefore, increase in the hydraulic head during the monsoon period may be responsible for the downward and outward flow of groundwater. It may be the cause of groundwater contamination towards riverside (Fig. 6.13).

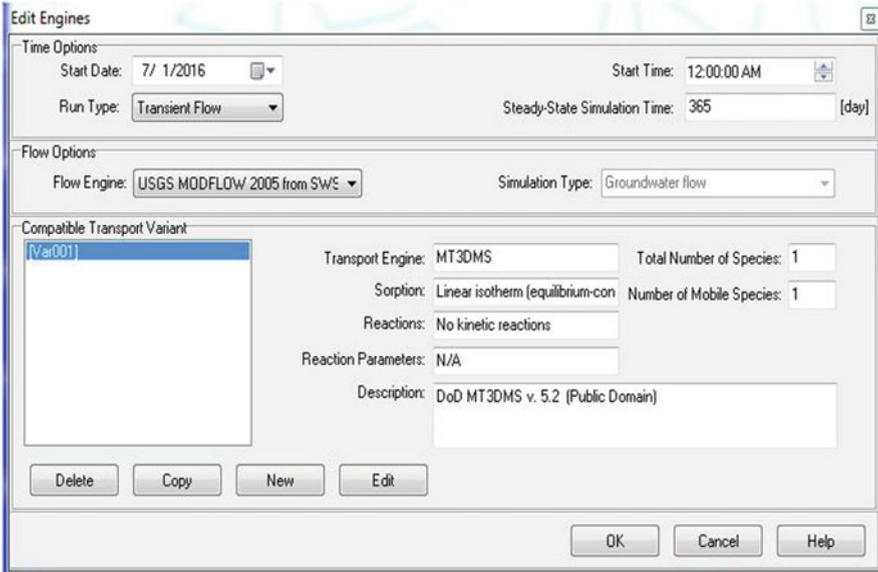


Fig. 6.11 Run engine database

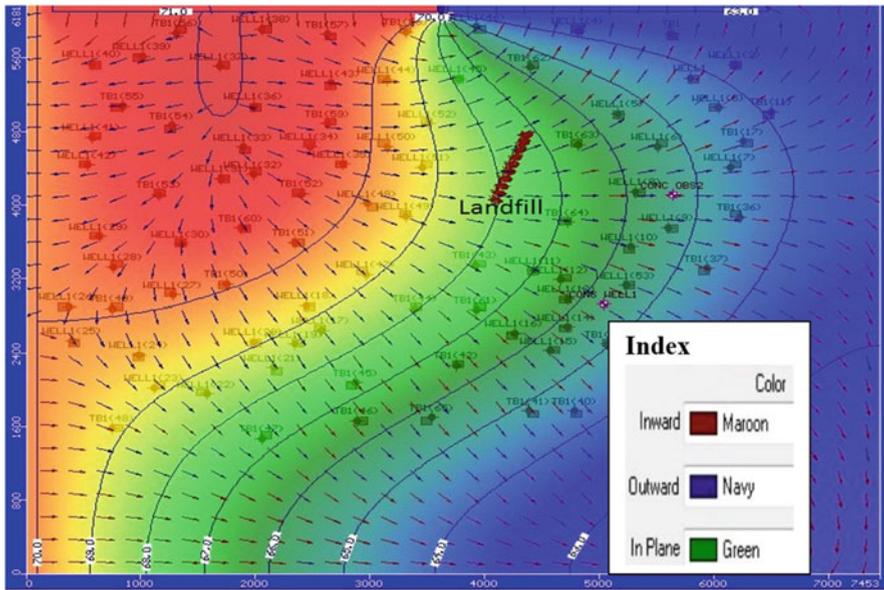


Fig. 6.12 Showing groundwater flow direction in the study area

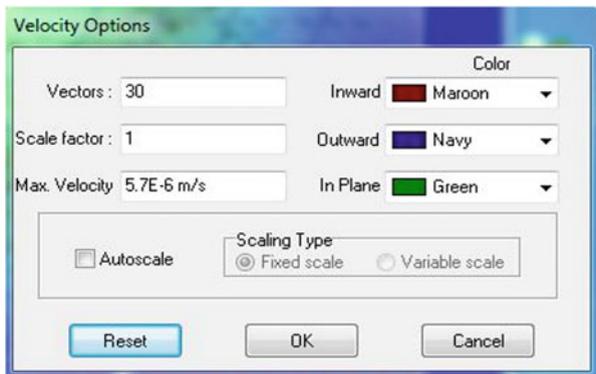


Fig. 6.13 Pore water velocity

Simulated groundwater table was shown in Fig. 6.14, which was ranged from minimum 58.00 m to maximum 74.93 m. This result validated with the field monitoring data of water table which was also observed between 61.96 m and 78.85 m. The hydraulic heads value changes with pre- and post-monsoon period as change in recharge and precipitation value during these periods (Bougioukou et al. 2005).

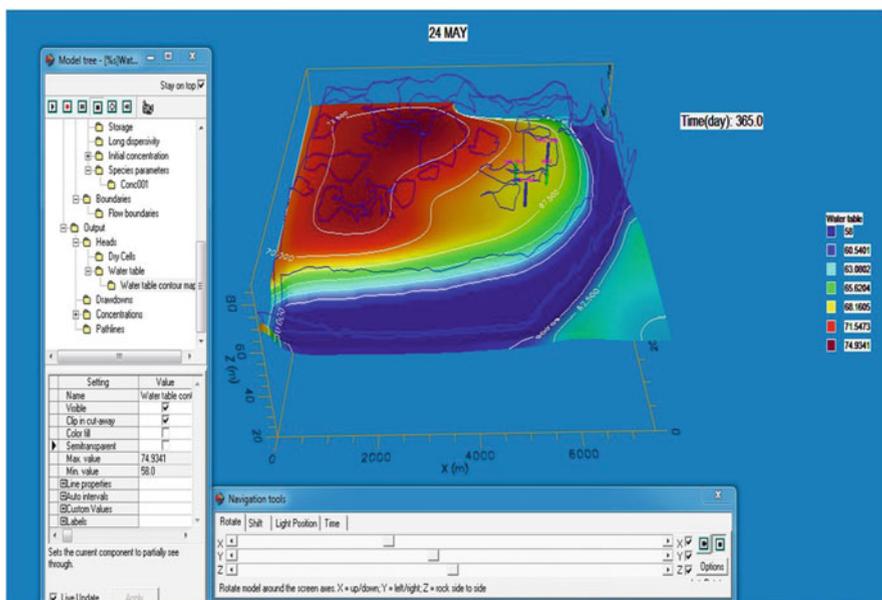


Fig. 6.14 3D view of the simulated groundwater table

6.5.8 Calibration Graph

Model calibration is the very important process in preparing the groundwater flow model because the excellence of the calibration certainly determines the reliability of any decisions made by the simulation results.

Most of the observed point comes under 95% interval. The 95% interval is the interval where 95% of the total numbers of data points are estimated to occur. It means the simulated result will be acceptable for this observed value. Groundwater head varied with the changes in aquifer water levels. Correlation coefficient (r^2) was equal to 0.714 for the calculated and observed head. This represented a good agreement between measured and simulated values.

6.6 TDS Transport Modeling

The transport engine for the running model is MODPATH and MT3DMS. Linear isotherm (equilibrium-controlled) with no kinetic reactions is assumed for TDS transport modeling. The dispersion coefficient $10.15 \times 10^{10} \text{ m}^2/\text{s}$ is assumed and dispersivity value is taken as 0.00033 m from USGS site. TDS concentrations, model boundary, particles tracking algorithm, and advection parameters were adjusted to run the model for 5 year started from 1 July 2016.

Simulation results of TDS transport model indicate the movement of TDS pollutant toward the groundwater flow direction (Fig. 6.15). In future there will be

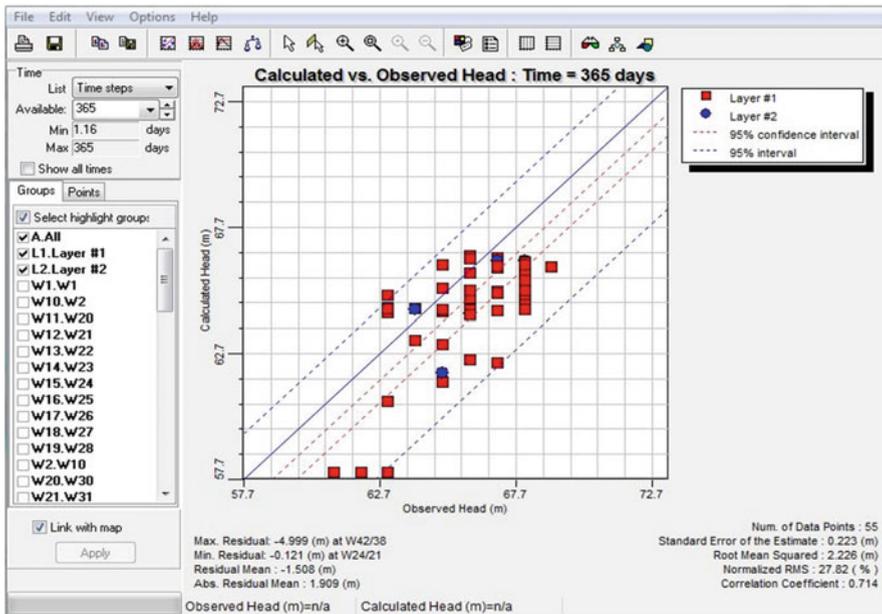


Fig. 6.15 Calibration graph between observation well and the calculated value

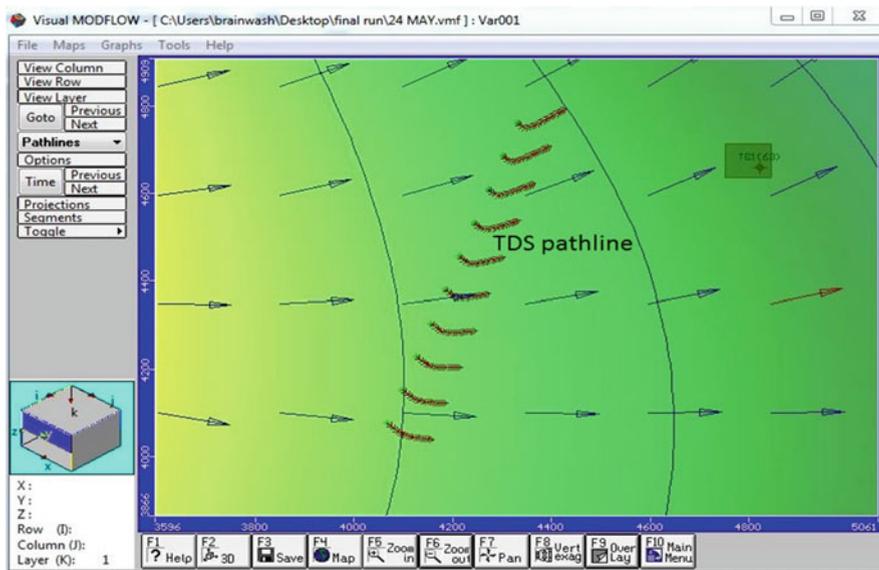


Fig. 6.16 TDS path line showing contamination towards groundwater flow direction

chance to cover more distance and contaminate more open wells nearby the MSW dumping site. Hydraulic gradient inferring the advection process that is one of the main factors that spreading of TDS pollutants. Generally, TDS are measured as a secondary water pollutant (EPA 2001) and it have been related to poor health conditions and no current data on health effects linked with the assimilation of TDS in drinking water; however, early studies inverse relationships were reported between TDS concentrations in drinking water with cancer and heart disease (WHO 1996) (Figs. 6.16 and 6.17).

6.7 Conclusions

Groundwater flow modeling result revealed that increase in the hydraulic head during the post-monsoon responsible for the downward flow of leachate pollutants from the Ramna dumping site and it might be because of groundwater contamination near to the dumping site. Groundwater flow around the Ramna dumping site is significantly influenced by the heads and direction of groundwater flow is observed towards the river. TDS modeling showing a distinct pollutant path line from Ramna MSW dumping site to nearest observed wells and its path are towards the groundwater flow direction.

MSW dumping site should have a designed engineering model to control and minimize the impact of MSW leachate on nearby groundwater quality. Lined

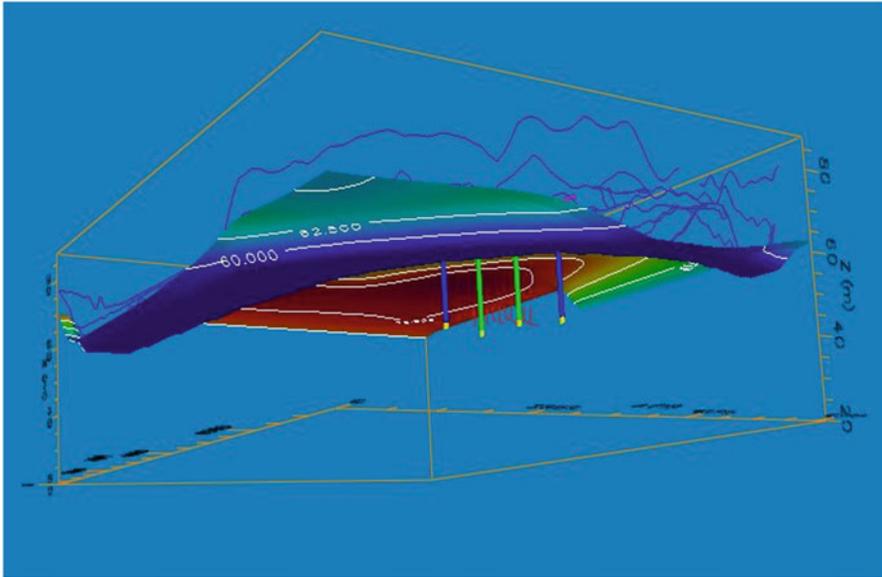


Fig. 6.17 3D view of TDS path line

engineered landfill and leachate collection ponds are the best way to protect the percolation of leachate into groundwater.

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Chapter 7

Recent Developments in Extraction, Identification, and Quantification of Microplastics from Agricultural Soil and Groundwater



Rakesh Kumar and Prabhakar Sharma

Abstract Microplastics have become a threat to the environment in recent years, and its adverse effect has direct impact on animals and human beings because of its accumulation in the environment. This chapter mainly deals with the source and contamination of microplastics in the agricultural soil and groundwater. Moreover, the experimental approach has been adopted to extract and investigate the presence of microplastics in the soil and groundwater and to classify microplastics based on their physical appearances, such as mass, shape, size, color, and chemical properties like diversity of microplastics characterized using Raman spectroscopy as well as Fourier transform infrared spectroscopy. Sources of microplastics have been reported either in the aquatic environment or in the terrestrial ecosystem, which is widely described and noted down with respective experimental techniques for identification and quantification of microplastics in this chapter. Agricultural soils were stated to be dumping sites for waste collected from households in rural, urban, and industrial areas. Therefore, sewage sludge, industrial effluents, paints, discarded plastics, households materials, and fertilizers are common contributors of microplastics in agricultural soils and groundwater either through biological agents or vertical transport into aquifers. This chapter highlights the source, extraction approach, and quantification techniques for microplastics being applied in numerous research across the globe. The presence of microplastics in soil is affecting soil properties such as water infiltration capacity, bulk density, microbial activity, and soil structure. The chapter analytically argues the recent progress in various extraction, identification, and quantification process aims to identify the pertinent gaps in agricultural soils and groundwater and offers possible solutions by briefing the ongoing investigation to preclude these gaps through applicable scientific interventions.

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7.1 Background

Pollution of agricultural soils and groundwater through microplastics (MPs) drawn serious concern recently because of their potential impact on soil ecosystem as well as human health (Koelmans et al. 2017; Rochman 2018). Microplastics drew attention because of their abundance as small size particles having adverse effects in the environment (Scheurer and Bigalke 2018). In agricultural practice, several kinds of plastics are being used for innovative as well as sustainability, such as ethylene-vinyl acetate copolymer (EVA), polyethylene (PE), polyolefin, polypropylene (PP), and polyvinyl chloride (PVC) (PlasticEurope 2018). Recently, Qin (2014) stated that demand and supply in fiber production made significant increase globally. Reasons behind great concern for MPs in recent decades are reported its size (<5 mm) and its abundance, not only in the terrestrial system but also into the freshwater system globally (Ding et al. 2019; Hurley and Nizzetto 2018; Rochman 2018). Studies on the freshwater system described the presence of MPs in many continents such as Europe, North America, and Asia (Free et al. 2014; Sadri and Thompson 2014; Zbyszewski et al. 2014). Besides, recent research in terrestrial ecosystem reported an abundance of MPs and even more than oceans (de Souza Machado et al. 2019; Nizzetto et al. 2016; Rillig et al. 2017b). de Souza Machado et al. (2019) indicated that MPs altered soil properties, along with having an impact on the performance of plants. Separately from this, it has also been reported that MPs present in soil alone more than its availability in the oceans. Mainly, agricultural soils were reported to be dumping sites for urban originated plastics, through sewage sludge, industries effluents, paints, households materials, fertilizers, etc. River deltas, i.e., junction point of freshwater and marine water were reported to be hotspots for the accumulation of MPs, which assured the source for marine pollution (Simon-Sánchez et al. 2019). Recently, the industrial areas were observed to contribute high concentration of MPs in soil, approx 0.03–6.7% of plastics in soil (Fuller and Gautam 2016).

Distribution and consequences of MPs were studied in freshwater systems such as river and lake sediments and agricultural soils (Lehner et al. 2019; Xiong et al. 2018). The extracted particles investigated by the most common technique of density separation and abundance, and features of MPs examined, such as morphology, particle size, mass, color, etc. (Van Cauwenberghe et al. 2015). The biological and physical properties change with the abundance and kind of microplastics present in the soil. Thus, the soil properties such as water infiltration capacity, bulk density, microbial activity, and structure and function are being affected in the presence of polyester, polyacrylic, and polyethylene. Resulting changes in pore space as well as particles interaction in the soil environment (de Souza Machado et al. 2018b). Microplastics were found not only in the marine environment but also in the aquifer

system (Mintenig et al. 2019; Panno et al. 2019). Due to non-persistent properties of plastics, it is challenging to the precise investigation of fate and transport in the soil and groundwater. However, MPs get incorporated into soil matrix by soil management practices (plastic mulch, green plastic hose, irrigation pipes, etc.), bioturbation, water percolation, etc. which contributes to soil pollution. Fate and transport of MPs influenced by spatial variabilities like river flow velocity, wind speed and direction, and tides (Zhang 2017). In addition to the terrestrial system, fate and transport of MPs in the freshwater system as well as in the marine systems were reported across the globe from lake to river. Most interestingly a new methodology was developed by Brown and Cheng (1981) for investigation of MPs from surface water using a net of mesh size 60–100 cm to capture at a depth of 15–35 cm. Liedermann et al. (2018) discussed modified methodology for quantification of MPs transport in Austrian Danube River across vertical depths in river profile using a net-based device having mesh size (in μm) of 41, 250, and 500 μm . Kataoka et al. (2019) analyzed sources as well as inflow of MPs in the river where urbanization and demography of Japan indicated to significant contributors of MPs. MPs reported as substantial transporting agents of contaminants, heavy metals, trace metals, etc., to terrestrial as well as aquatic environment (Ashton et al. 2010; Brennecke et al. 2016; Hartmann et al. 2017; Holmes et al. 2012; Napper et al. 2015; Rochman et al. 2014). Hydrophobic organic chemicals adsorbed on MPs, which can sorb many more organic phases (Lee et al. 2014). Besides this, fate and transport of nano plastics analyzed under batch and column experiments in sandy aquifer soil being investigated using SEM, ICP-MS, ion chromatograph, and organic element analyzer for better understanding. As groundwater system is heterogeneous, fate and transport are unclear about the behavior of micro- or nano-plastics in natural aquifer systems. Hence, background solution and particle size influenced the aggregation of nano plastics onto sandy soil due to organic matters and Ca^{+2} solutions (Song et al. 2019). Plastics, in longer period, release bisphenol A, an endocrine substance and toxic in the soil environment (Sajiki and Yonekubo 2003).

MPs are persistent pollutants, and fate and transport of MPs in environment influenced by flux and its retention in long-term system (Horton and Dixon 2018). Agricultural soils contribute transport of MPs to rivers and even it can be hotspots at soil depth (Zubris and Richards 2005). Agricultural soils can retain MPs for longer duration as compared with urban land because of soil permeability and overland flow (Nizzetto et al. 2016). However, the existing knowledge of agricultural soils and groundwater pollution due to MPs is not competent to draw attention to environmental impacts and mitigation (Brodhagen et al. 2017; da Costa 2018). Whereas studies on MPs in aquatic ecosystems reported since 1970s, MPs pollution in agricultural soils and groundwater ecosystem gained attention recently (Gasperi et al. 2018; Revel et al. 2018; Wright and Kelly 2017).

This chapter aims to review the potential source and the extraction method of MPs from agricultural soils and groundwater. Furthermore, the recent advancement in extraction technologies of MPs is being discussed along with identification and quantification from agricultural soils and groundwater described in the available literature. Besides, this chapter highlights the limitations and future research

opportunities while conducting experiments in agricultural soils and groundwater focused on remediation of MPs.

7.2 Source of Microplastics in the Agricultural Soil and Groundwater

The abundance of MPs in the soil ecosystem and groundwater is a serious environmental pollution. Several studies categorized MPs as per its availability in the environment, into primary and secondary MPs based on the production and degradation from large plastics. Agricultural soils are a significant reservoir for accumulation of MPs. Nizzetto et al. (2016) reported a considerable amount of MPs in farmlands of Europe (63,000–4, 30,000 tons) and North America (44,000–3, 00,000 tons). It has been testified that 80% of the plastics in marine ecosystem generated from the land because the majority of plastics used to dump into landfills later shredded into small particles itself with continuous degradation (Andrady 2011; Fendall and Sewell 2009). Therefore, the transport of MPs contaminants not only to surface water but also to groundwater system and agricultural soils. In developing countries, irrigation and flooding practiced using surface water systems, rivers and streams, which contributes MPs to agricultural soils (Dris et al. 2015b; Eerkes-Medrano et al. 2015). Recent studies quantified the occurrence and extraction of MPs in various types of soil (Lin et al. 2018; Scheurer and Bigalke 2018; Zhou et al. 2018). It was noted that MPs transported to the soil via wind (Rezaei et al. 2019), runoff (Zhang et al. 2015), and biological agents (Lwanga et al. 2017; Rillig et al. 2017b). Plastic debris in agricultural farm observed source of MPs to agricultural soils (Liu et al. 2017). Corradini et al. (2019) stated that MPs accumulated in agricultural soils, which directly incorporated from sewage wastewater disposal. Besides this, there was many more evidence for sewage wastewater as a significant source for transportation and contamination of MPs primarily synthetic fibers (Henry et al. 2019; Horton et al. 2017; Ziajahromi et al. 2017).

Personal care, soaps, toothpaste, and textile materials from domestic use contributed to MPs contamination in sewage (Duis and Coors 2016; Hernandez et al. 2017; Napper et al. 2015; Napper and Thompson 2016). It has been pointed out that sewage sludge in wastewater treatment plants contained MPs (Li et al. 2018c; Mahon et al. 2016; Ziajahromi et al. 2017). Sludge has been described as fertilizer for agricultural soils and pathway for transportation of MPs (Coors et al. 2016; Schmidt et al. 2006; Zubris and Richards 2005). In China, it was stated that MPs were contributed to agricultural soils from plastic greenhouse (Qian et al. 2010), plastic mulch (Liu et al. 2018), runoff as well as soil erosion (Hurley and Nizzetto 2018; Zhang et al. 2015) and degradation through UV exposure and soil abrasion (Song et al. 2017; Zhang and Liu 2018). At household levels, synthetic microfibers released out which are considered as the source of MPs (Hernandez et al. 2017). Besides this, the most vital source of MPs observed as atmospheric fallout. It has

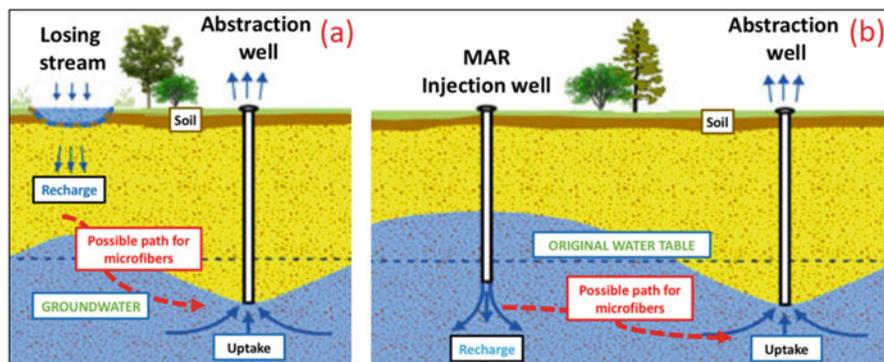


Fig. 7.1 Representation of possible pathways of microfiber in aquifer system: (a) in losing stream and (b) through managed aquifer recharging (MAR) injection well (Blue arrows depicted inflow–outflow to groundwater systems; red arrows representing a possible path of microfibers to supply well) (Adapted from Re 2019)

been reported that the synthetic fibers were characterized as dominant MPs in urban as well as sub-urban sampling sites of France (Dris et al. 2016).

Organic fertilizers were reported as the source of MPs in agricultural soils (Weithmann et al. 2018). Not only organic fertilizers but organic riched sludge also contained with MPs (Hurley et al. 2018). At present, there is limited research performed on abundance and transport of MPs in groundwater systems. The plenty of MPs in groundwater via freshwater systems have also been reported. In the aquifer systems, synthetic microfiber predicted to be present due to the infiltration in soil pores as well as direct inflow of contaminated water through artificial aquifer recharging technique (Re 2019). Figure 7.1 depicted the schematic representation of possible pathways of microfiber in the aquifer system: (a) in losing stream and (b) through managed aquifer recharging (MAR) injection well.

Low concentration of MPs has been investigated in groundwater using μ -FTIR at Germany. Different kinds of MPs, such as polyethylene, polyamide, polyester, etc., were observed having particle sizes between 50 and 150 μm (Mintenig et al. 2019). Although, research on the transport of MPs down to soil profile by earthworm *Lumbricus terrestris* L. raised distress for leaching to groundwater system, which could be the source of MPs in groundwater (Yu et al. 2018). Microplastics were reported in groundwater due to contamination of aquifer system, and source of MPs was observed to septic effluent in the USA (Panno et al. 2019), groundwater well in Germany (Mintenig et al. 2019), and drinking water and raw water having MPs supplied by wastewater treatment plants in the urban areas of Czech Republic (Pivokonsky et al. 2018). However, limited literatures are available on groundwater contamination; nevertheless, groundwater contaminated with MPs is dangerous because, in many parts of the world, it is possible to access directly as drinking purpose.

7.3 Comparative Analysis and Physical Properties of Microplastics from Agricultural Soil and Groundwater

The subsurface soil contains MPs more than the ocean which threatens the soil ecosystem and contaminates the groundwater system. As the subsurface system is composed of several minerals and organic matter, MPs present in the soil matrices mix with minerals as well as organic matter present in it. Therein abundance of MPs makes soil matrices more complex and challenging for extraction from the soil sediments. Although, the collected soil sediments from various sources investigated for identification and separation of MPs from soil (Blaesing and Amelung 2018; Claessens et al. 2013; de Souza Machado et al. 2018a; Lwanga et al. 2017; Rillig et al. 2017b; Zhou et al. 2016). An earthworm, *Lumbricus terrestris* L. transports MPs polyethylene beads in soil profile down from the surface at different layers ($P < 0.001$). The study was accompanied by incorporating MPs into soil biota via egestion and adherence on earthworm, resulting in the potential abundance of MPs at different depth with the function of residential time and possible present of MPs into groundwater (Rillig et al. 2017b). Besides, Lwanga et al. (2017) also assessed the transport of MPs by *Lumbricus terrestris* in the soil where the treatment studies under five concentrations of 0%, 7%, 28%, 45%, and 60% of low density polyethylene in soil surface litter. Hence, the highest content of MPs was recorded for 60% of MPs on the burrow wall, which might cause contamination of groundwater system.

A new technique was developed for the extraction of MPs from soil sediments using elutriation method followed by density separation technique in sodium iodide (NaI) aqueous solution, resulting in optimum extraction efficiency of fibers (98%), granules (100%), and PVC (100%). NaI solution has a maximum density of 1.6 g/cm³, which is maximum among saturated salt solution and is applicable to MPs separation (Claessens et al. 2013). An alternative technique is utilized for the extraction of MPs using sodium bromide (NaBr) solution to investigate different types of MPs obtained from different varieties of soil, such as farmland, paddy, yellow-brown soil, and floodplain soil in Shanghai. It observed extraction efficiencies of MPs in the range of 85–100% followed by μ -Fourier transform infrared (FTIR) analysis for identification of abundance of different categories of MPs in soil. The comparative analysis was investigated in solutions of NaCl, NaBr, and CaCl₂ for extraction of MPs. Out of the three saturated salt concentrations, NaBr indicated maximum extraction efficiencies of MPs compared to other salt solution, i.e., NaCl and CaCl₂. Floodplain soil has a maximum abundance of MPs, $256.7 \pm 62.2 \text{ kg}^{-1}$ with the mean size of MPs, 1549.4 μm followed by paddy soil, yellow-brown soil, and farmland soil (Liu et al. 2019).

Furthermore, improved methods were adopted in which sediments from North Sea Island Norderney were analyzed for extraction of MPs in a two-step process, where the sediments were analyzed in air-induced overflow method for fluidization in NaCl followed by sodium iodide solution for subsequent floatation. Polyethylene

(PE), polypropylene (PP), polyvinyl chloride (PVC) and polyethylene terephthalate (PET), polystyrene (PS), and polyurethane were extracted, having extraction efficiency between 91 and 99% (Nuelle et al. 2014). Similarly, the extraction of MPs at Caofeidian, Hebei Province investigated coastal soil in two steps using airflow flotation separation technique followed by density separation with NaI solution (having density 1.8 g/cm^3). Moreover, MPs were counted using Nano Measurer 1.2 along with size measurement and morphological properties were investigated using scanning electron microscope-energy dispersive spectrometer (SEM-EDS) (Zhou et al. 2016). It has been observed that plastic greenhouse was contributing MPs in vegetable and buffer soil at southwestern China. The abundance of MPs having a size less than 1 mm reported to exist in majority (95%). Results revealed that 72% of plastic particles aggregated with soil. The extraction of MPs was conducted using density separation through NaI, having a concentration of MPs investigated with mean 18,760 particles per kg (Zhang and Liu 2018).

MPs were extracted from agricultural soil due to the implication of sludge as fertilizer through flotation technique with Whatman No. 42 filter paper and therein MPs were counted through statistical ANOVA test (>95%) and classified by the microscope. The morphological characteristics of MPs reported, have sharp geometry with a shiny surface and dark-colored particles. Five different types of polymer MPs (acrylic, polyester, nylon, LDPE, and PVC) were evaluated, in which the majority of them have reported fibers (acrylic, polyester, and nylon). The study was assessed on seven sludge samples, in which fiber content in sludge and soil was found to be 90% and 97%, respectively. The concentration of MPs was found to be 18–41 particles per gram in sludge. Besides this, it was observed that 1.1, 1.6, 1.7, 2.3, and 3.5 particles of MPs per gram of dry soil were found in 1–5 sludge application (Corradini et al. 2019). While Liu et al. (2018) observed that the average concentration of MPs was 22.7 ± 12.1 particles per gram in sewage sludge, having only 63% of fiber out of fibers, fragments, and films contained in sludge in China. Soil samples were collected at shallow and deep depth, analyzed triplicate from 20 farmland soil samples, and performed density separation using saturated NaCl, digestion (using 30% H_2O_2), and micro-FTIR. Sizes and abundance of MPs reported 20 μm to 5 mm and 78.00 ± 12.91 particles per kg for topsoil and 62.50 ± 12.97 particles per kg deep soil. Majority of MPs obtained were less than 1 mm in size, having either black or transparent color. In Ireland, MPs acquired from seven wastewater treatment plants were extracted using elutriation column technique with ZnCl_2 and characterized using attenuated total reflectance, SEM and FTIR. The abundance of MPs observed 196–15,385 particles per kg from bio-solids with majority of them was found fibers (75.8%) followed by fragments, films, and others. MPs classified into HDPE, polyethylene, acrylic, polyethylene terephthalate, polypropylene, and polyamide. HDPE MPs were observed in different colors, such as red, blue, and black, whereas others were uniform in color (Mahon et al. 2016).

As MPs were observed to be found in sewage plants, the extraction efficiencies of MPs have been studied from three consecutive wastewater treatment plants (WWTPs) sewage samples, primary (capacity of 1.54 MPs/L), secondary (capacity of 0.48 MPs/L), and tertiary (capacity of 0.28 MPs/L), treatment plants using NaI in

the laboratory. The result shows that the least content of MPs was received in final treated effluent, lastly with reverse osmosis. The abundance and classification of MPs were examined based on shape using FTIR, resulting in 92–99% extraction of irregular polystyrene using 25–500 μm mesh size screen. In WWTPs (A) sample, the majority of MPs were found to be PET fibers (80%) as well as PE (20%), identified as shiny green, white, and transparent MPs. While 70% of plastic particles were identified as MPs in WWTPs (B), including primary PET and PE. Majority of MPs observed in WWTPs (C) were white and blue and investigated to classify as PE, PET, PS, and PP (Ziajahromi et al. 2017). Similar outcomes were produced in Paris, where fibers content were dominant as compared with plastics (Dris et al. 2015a) and 50% of MPs were reported fibers from secondary effluent in Sweden (Magnusson and Norén 2014). Wang et al. (2018) extracted MPs from bio-solids as well as soil using ZnCl_2 density separation along with H_2O_2 digestion and quantified using UV-Vis spectrometer and gravimetric techniques. It was reported that the extraction efficiencies of large-sized beads (100 μm) were 100%, whereas 20% for small-sized average efficiencies from bio-solids and soils. Here, MPs having beads larger than 1 μm showed extraction more than 75% of extraction efficiencies; however, low efficiency for beads having size 0.05 and 1.0 μm extracted (<30%).

Light density MPs were extracted from soils and analyzed under 130 °C for 3–5 s. MPs were identified using microscope pre- and post-heating for distinguishing organic matter and fibers and quartz reported the change in fibers after heat but quartz and the organic matter remained the same. Floatation technique was applied for detecting LDMPs, such as PE and PP in soil. It was reported that combined floatation, as well as heating techniques, has significant results for the extraction and quantification of LDMPs (Zhang et al. 2018). As of another separation technique, the magnetic separation of MPs was investigated by application of hydrophobic iron nanoparticles which bind plastic particles. Hydrophobization was conducted using iron nanoparticles having hydrophobic tails due to attaining –Si–O–Si– spectral band of hexadecyltrimethoxysilane (HDTMS) made it attached with plastic particles. It has been observed that 92% of PE and PE beads having size <20 μm and 93% of PE, polyethylene, polystyrene, polyurethane, PVC, and PP having size >1 mm were extracted using iron nanoparticles. However, 81% recoveries of MPs were detected for size 200 μm –1 mm (Grbic et al. 2019). The MPs concentration were studied under organic matters, such as dissolved organic nitrogen, ammonia (NH_4^+), nitrates (NO_3^-), dissolved organic phosphorus, and phosphates ions (PO_4^{3-}). The greater MPs content considerably enriched the dissolved organic content. Further organic materials, MPs facilitated not only to humic acid but also activated pool for the growth of organic C, N, and P (Liu et al. 2017).

Most interesting fact that has been reported is that the wind is not the only source for particulate matters, because of tillage and soil erosion but also transportation agents for lightweight MPs for longer distances (Bento et al. 2017; Rezaei et al. 2019). Rezaei et al. (2019) conducted comparative analysis for assessment of the MPs abundance in soil and eroded sediments found to be 6.91 mg/kg and 20.27 mg/kg using flotation method, respectively, represented eroded soil sediments enriched with MPs. The study was conducted in triplicate to collect soil samples from 11 sites,

followed by determining physical as well as chemical properties such as soil moisture content and soil texture and pH, soil organic carbon and calcium carbonate equivalent, respectively. The classification and validation of MPs were conducted using FTIR for distinguishing various types of MPs contaminated in soils and water systems. Here, the thermo-gravimetric analysis (TGA) performed on PA, PE, PP, PS, PVC, and PET for investigating mass loss percentage in the range 60–700 °C, followed by FTIR analysis for identification of changes in bands as a function of temperature. The TGA couple FTIR analysis identified PVC and PS in soil, seawater, and bivalves. However, the identification of characteristic bands of PVC and PS was not reported for soil, while olefins and alkanes absorption bands were identified (Yu et al. 2019). Correspondingly, the MPs were identified directly without separating it from soil with image processing as well as chemometric techniques. MPs were computed using hyper spectral images between 0.5 and 1 mm, characterized by white and black PE MPs. The supervised classification of images was performed to conduct algorithm such as maximum likelihood, Mahalanobis distance, and support vector machine. It was reported that 84% of plastics in size of 1–5 mm and 77% of plastics in the size of 0.5–1 mm PE MPs were identified (Zhao et al. 2018). MPs in groundwater were investigated using the filtration method in drinking wastewater treatment where water directly collected from wells. Raw and drinking water analyzed under compressed air for 24 h and processed through 0.2 µm Whatman filter, followed by density separation for extraction of iron oxide using ZnCl₂. FTIR analysis was investigated for the determination of PE, polyamide, PE, and PVC in the range of 50–150 µm particles size (Mintenig et al. 2019). From Karst aquifer, fibers were extracted using 0.45 µm and dried for 24 h at 75 °C and identified using microscope (Panno et al. 2019).

7.4 Approaches and Techniques Adopted for Characterization of Microplastics

7.4.1 *Experimental Techniques Adopted for Microplastics Extraction from the Complex Environment*

Separating the MPs particles from the complex soil environment is a crucial process. The most common method for isolating MPs particles from the soil is density separation, based on density differences among plastic particles and minerals present with soil in an aqueous solution. The lighter plastic particles float over the salt-saturated solution. As the density of plastic ranges from propylene (0.85 g/cm³) to polylactic acid (1.43 g/cm³), the density of the salt solution is kept higher than that of plastic density for efficient separation (Lambert and Wanger 2018). The density separation technique followed by agitation is operated using saturated salt solution, NaCl, NaBr, NaI, etc. (Claessens et al. 2013; Van Cauwenberghe et al. 2015; Zhang and Liu 2018; Zhou et al. 2016). As NaCl is non-toxic and cheaper; NaCl could not

extract heavy MPs particles having density higher than that of saturated salt solution (i.e., the density of NaCl is 1.2 g/cm^3) and lighter particles which agglomerated with minerals present in soil. However, agglomeration can be possible to reduce by continuous agitation or shaking with a magnetic stirrer (Van Cauwenberghes et al. 2015). The density for different salt solutions was as follows: sodium chloride (NaCl, 1.17 g/cm^3), sodium bromide (NaBr, 1.37 g/cm^3), sodium iodide (NaI, 1.57 g/cm^3), zinc bromide (ZnBr_2 , 1.71 g/cm^3), and zinc chloride (ZnCl_2 , 1.8 g/cm^3), out of which ZnBr_2 and ZnCl_2 have maximum extraction of MPs than NaCl. ZnBr_2 and ZnCl_2 reported being severely hazardous and toxic as compared to NaCl, whereas NaI is reported as poison to water (Nuelle et al. 2014; Quinn et al. 2017). Further for extraction of MPs, new methods were adopted as sediments were analyzed in a two-step process, where the sediments were studied in air-induced overflow technique for fluidization in NaCl followed by sodium iodide solution for subsequent floatation, reported extraction efficiency of PE, PP, PVC, etc., between 91 and 99% (Nuelle et al. 2014). Similarly, the extraction of MPs was investigated in two steps using airflow floatation separation technique followed by density separation with NaI solution (Zhou et al. 2016). Majority of research on soil sediments were based to distinguish MPs using density separation. Sujathan et al. (2017) utilized 30% peroxide oxidation (H_2O_2) at 70°C for reduced reaction time, 12 h (Sujathan et al. 2017). The modified approach adopted by Hurley et al. using 30% H_2O_2 at 60 and 70°C , Fenton's reagent and NaOH solution and 10% KOH solution at 60°C were applied for comparative analysis to validate extraction of MPs from organic-rich soil sediments (Hurley et al. 2018).

A method was developed by Fuller and Gautam (2016) for extraction of MPs based on pressurized fluid extraction, which optimizes the extraction of MPs from 85 to 94% recovery rates. In this method, methanol was used at an initial stage for removal of semi-volatile organic compounds followed by pressurized fluid extraction at 180°C (Fuller and Gautam 2016). In the magnetic separation of MPs, hydrophobization was conducted using iron nanoparticles having hydrophobic tails due to attaining $-\text{Si}-\text{O}-\text{Si}-$ bond of HDTMS made it attached with plastic particles, having recovery rate of 81% observed for particles size $200 \mu\text{m}-1 \text{ mm}$ (Grbic et al. 2019). In the groundwater system, MPs were investigated using the filtration method for characterization and its quantification (Mintenić et al. 2019).

7.4.2 Identification and Quantification Techniques for Extracted Microplastics

Plastics are comprised of different polymers and thus characterized by identification of their specific properties. MPs were sorted using a microscope without FTIR and Raman which makes it unable for the identification of kinds of MPs (Hidalgo-Ruz et al. 2012; Löder and Gerdt 2015). Visual identification with a microscope can be able to describe structural as well as surface morphology of MPs using scanning

electron microscope (Mahon et al. 2016). SEM with energy dispersive spectroscopy technique is utilized for identification of elemental compounds along with particles size (Zhou et al. 2016). Characterization of MPs was conducted using IR spectroscopy for the identification of specific polymer material present in samples. The bands of vibrations produced by materials using IR spectroscopy and compared with reference vibrations for identification. The absorption of specific vibrational bands depicted properties of polymers. Thompson et al. (2004) utilized FTIR for identification of C=O bonds present in polymers. Extraction efficiencies of MPs followed by micro-FTIR spectroscopy analysis identified different types of MPs in soil (Liu et al. 2018, 2019; Mahon et al. 2016; Yu et al. 2019). Correspondingly, different kinds of MPs, PE, polyamide, polyester, etc., were observed using μ -FTIR in groundwater system (Mintenig et al. 2019). Besides, the identification of single particles of MPs was investigated using pyrolysis with gas chromatography coupled mass spectroscopy (Dümichen et al. 2015; Fries et al. 2013). Dümichen et al. identified MPs using thermal analysis coupled with gas chromatographic along with mass spectroscopy for distinguishing PE, PP, and PS in the soil complex (Dümichen et al. 2015, 2017). Thermal GC-MS technique was developed for large amount of samples analysis to tackle with issues coming in pyrolysis GC-MS (Dümichen et al. 2017; Löder et al. 2015). Morphology and analytical properties of MPs were identified using TEM and pyrolysis based GC/MS analysis in loamy soils and within soil fractions which distinguished polymers from soil organic matters. It was observed that MPs were present in the soil since the past 10 years as amended in the form of compost to soils (Watteau et al. 2018).

The amounts of MPs were determined either by FTIR or by counting using the microscope and SEM. Polarized light microscopy was utilized for quantification as well as the identification of synthetic fibers in the soils (Zubris and Richards 2005). The FTIR applied for quantification of distinguishing plastics or non-plastics using characteristics bands as applied for separation of non-plastics out of samples (Liu et al. 2018). Plastic particles $>20 \mu\text{m}$ in soil sediments were quantified using FTIR (Löder et al. 2015; Mintenig et al. 2017). Zhou et al. (2016) counted MPs using Nano Measurer 1.2 along with size measurement (Zhou et al. 2016). Löder et al. (2015) quantified that 1.4% of plastics were synthetic polymers out of extracted plastics from the beach and marine sediments using focal plane array (FPA) detector based micro-FTIR spectroscopy. The number, shape, and size of MPs obtained from WWTPs were investigated under SigmaScan 5 software, resulting in different size and classified based on their shape into fibers, spherical, and fragments described using SEM. Raw water and treated water samples were collected from three WWTPs, reported major abundance of MPs in the range of 1–5 μm . The content of MPs in treated water ($m 338 \pm 76$ to 628 ± 28 particles L^{-1}) observed to be significantly less than raw water (1473 ± 34 to 3605 ± 497 particles L^{-1}) approximately 83% (Pivokonsky et al. 2018).

7.5 Potential Concern for Pollution and Damage to Soil Biota Caused by Microplastics

Several studies reported that the ecological destruction has been observed by enhancing biological exposure to the environment (Bour et al. 2018; Li et al. 2018a; Su et al. 2018). MPs presence in the environment for long term resulted into evolutionary changes in soil biota as well as changes in soil properties, such as soil structure, surface charges, host biota, etc. (Rillig et al. 2019; Yoshida et al. 2016). As a result, this evolutionary pressure may cause changes in genotypes of the population either by selection or by evolution (Rillig et al. 2019). The degradation of MPs was observed; however, it is a slow degradation process either through UV radiation or physical abrasion in soil (Song et al. 2017). It has been revealed that 0.4% mass of PP degraded after one year, whereas no degradation reported for PVC for 10–35 years (Ali et al. 2014; Arkatkar et al. 2009; Santana et al. 2012). No degradation in PE films and PET observed after 3 years buried in sandy soil (Selke et al. 2015). MPs have sorption potential to substance, such as antibiotics, heavy metals, and xenobiotics which establish negative consequences on soil biota and soil properties (Brennecke et al. 2016; Li et al. 2018b; Rillig et al. 2019).

Additionally, MPs change the physical properties of soil, viz. stability in soil aggregation being contributed by soil biota due to the presence of microhabitats may drastically affect aggregation surface, formation and disintegration of aggregates (Lehmann et al. 2017; Rillig et al. 2017a). Besides this, changes in soil physical properties such as structural changes and formation of pores in soil lead to microhabitat loss along with resulting into changes in the water holding capacity as well as bulk density (de Souza Machado et al. 2018b; Veresoglou et al. 2015). It was observed that soil microbes interacted with and ingested polystyrene beads, as well as earthworms, have been reported as transporting agent of MPs to the soil profile. As consequences of microbial interaction with MPs lead to the formation of complex host-symbiont response in soil (Lwanga et al. 2018; Zhu et al. 2018). de Souza Machado et al. (2018b) explained the impact of MPs in soil biophysical environment and their alteration in soil structure as well as properties, such as infiltration capacity, bulk density, and its function as presented in Table 7.1. Not only to the physical environment but also biological environs affected due to the presence of MPs such as water holding capacity, bulk density, microbial activities, and functional changes occurred with polyester, polyacrylic, and PE. The changes in biophysical properties observed in contaminated soil as compared with soil samples,

Table 7.1 Representing the influence of MPs in soil physical environment (de Souza Machado et al. 2018b)

Types of MPs	Water holding capacity	Soil bulk density	Soil microbial activity	Soil structure and function
Polyester	Increase	Decrease	Decrease	Functional change
Polyacrylic	No clear trend	Decrease	Decrease	Functional change
Polyethylene	No clear trend	Decrease	No clear trend	Functional change

where water holding capacity increases with polyester; however, no trends reported with polyacrylic and PE. Apart from this, bulk density and microbial activity have been observed to decrease as compared with control soil in all three cases, except microbial activity has not shown any trends in polyethylene. However, functional changes in soil were observed to be increase and decrease in both ways at the same instant (de Souza Machado et al. 2018b).

The positive evidence for soil restoration using earthworm, *Lumbricus terrestris* has been reported as they contributed to decay LDMPs within 4 weeks (Lwanga et al. 2018). The potential decay of plastics has been observed by microorganisms, such as *Brevibacillus borstelensis* and *Rhodococcus ruber* decayed CH₂ plastics as well as PE, the analysis was performed for 3–9 months (Hadad et al. 2005). It was stated that MPs either affect the survival status and fitness of organism or accumulate into casts, resulting in the transport of MPs down to soil profile as well as leaching to groundwater. The growth and reproduction of *Lumbricus terrestris* were performed under different concentration of MPs. Reduction in growth and loss in weight with high dose of MPs (w/w), such as 28, 45, and 60% in litter for 60 days; however, MPs in 7% w/w MPs sample reported not any significant changes in growth and weight loss (Lwanga et al. 2016). Presence of MPs in the soil for long run formed nanoparticles, which can easily be transferred and accumulate in plants, which leads to altering the ecological and behavioral changes in plants by affecting the growth and photosynthesis of plants. The residues of mulch films and PE have an adverse result on vegetative as well as reproductive parts of the wheat, either above or below ground (Qi et al. 2018). Not only this, however, mulch film reduced crop production as well as soil quality (Hegan et al. 2015; Jiang et al. 2017; Zhang et al. 2016).

7.6 Conclusions

This chapter highlighted the consequences of MPs in agricultural soil and groundwater. The consequences of MPs to soil biota were investigated; however, the degree is not precise. Several experimental pieces of evidence reported adverse effects on soil structure and microbial activities in the agricultural soil, which may have the potential to impact crop productivity and soil health. The current review explains first about the spatial distribution of MPs in agricultural soils and groundwater across the globe. Secondly, the paper described the removal and characterization of MPs extracted from agricultural soils and groundwater. In the third section, the extraction techniques, identification, and quantification revealed which had been utilized in previous research. We discussed experimental explanation of recent research on agricultural soils and groundwater and suggested upcoming research objectives. There were certain limitations for extraction, identification, and analytical quantification of MPs from soils and groundwater. As MPs extracted using salt-saturated solution, such as NaCl, NaBr, NaI, ZnCl₂, ZnBr₂, etc., utilized; however, NaI, ZnBr₂, ZnCl₂ were reported expensive as well as dangerous for the experiment as

it pollutes soils and groundwater after analysis. Whereas NaCl is not efficient for the extraction of heavy density MPs except LDMPs. As degradation of MPs in soil were reported; however, the degree of degradation is not clear. Besides, the degradation of MPs through UV radiation and abrasion process is quite slow and does not provide exact information about complete degradation. As quantification and identification were analyzed using microscope only, it will not provide clear information about the kinds and properties of MPs. Risks for misidentification will be high as quantified by microscopy; however, FTIR or Raman spectroscopy analyzed differentiation in kinds of plastics as well as size. The identification of MPs by content and polymer types present in soil complex is quite difficult because Vis-NIR spectral bands vary with soil types. Despite, the detection of MPs either by visualization techniques or in the laboratory can be methodological imitations. Hyperspectral images were utilized for identification of MPs as soil surface with MPs, not in-depth soil profile. The future research will be identification and quantification of MPs using hyperspectral images deep under soil profile. There are several methods available for extraction of MPs from soil sediments either from terrestrial or from aquatic environment; however, no such uniform and exact methodologies have been defined for extraction of MPs from aquifer, i.e., groundwater system with optimum recovery efficiency available yet. Microplastic pollution is a global concern; however, majority of research has been carried out in Europe, USA, and UK. Only few research on MPs was available from Asia, Australia, Africa, etc., on soil sediments. There is no such technology available to combat MPs pollution. Since pollution through MPs reached an alarming situation, there is only way to tackle problem by public awareness and through industrial policy to reduce production.

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Chapter 8

Monsoonal Rainfall Time Series (1901–2002) Analysis of Uttarakhand, India



Deepak Kumar, Pankaj Kumar Gupta, Ajay Rawat, and Ankit Bajaj

Abstract Uttarakhand is mostly a hilly state, which is located at the foothills of the Himalayan mountain ranges. Monsoon is an important phenomenon, which controls the regional climate of Uttarakhand. Thus, an effort has been made to investigate the trends of monsoonal rainfall using descriptive statistical analysis, rainfall variability index (RVI) followed by frequency and trends analysis. District-wise RVI has been developed to identify the numbers of normal, dry, very dry, wet, and very wet years. Gumbel's extreme-value distribution and Mann–Kendall test have been used for frequency and trends analysis, respectively. The results show that lesser Himalayan district at low altitude has reported with highest magnitude of monsoonal rainfall. Further, the number of wet and very wet monsoonal years has decreased during 1951–2000 as compared to 1901–2000 in the study area. Even so, interestingly, for all districts of both regions, the number of dry and very dry years surpasses the number of wet and very wet years for the last 20 years of study. The climate of Uttarakhand is significantly controlled by monsoon and analysis of monsoon rainfall for a period of 101 years (1901–2002) reveals a decreasing trend in southwest monsoon rainfall. The outcomes of this study may help water management practices and agricultural planning in Uttarakhand.

Keywords Monsoon · Time series analysis · Rainfall variability index · Uttarakhand

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8.1 Introduction

The spatial and temporal patterns of surface-water and groundwater availability are significantly affected by rainfall (Batelaan and De Smedt 2007; Taxak et al. 2014). Variability in the rainfall pattern deserves systematic and instant attention as it affects agricultural production and natural resources. In India, monsoon is the most significant meteorological phenomenon controlling the regional climate by contributing rain in two seasons viz., southwest monsoon (June–September) and northeast monsoon (October–December) (Thomas and Prasannakumar 2016). Generally, the commencement of southwest monsoon over Uttarakhand state is during mid-June and withdraws during mid/late-September (Attri and Tyagi 2010). The variability and quantity of rainfall during the monsoon season have profound impacts on the agricultural practices in lesser Himalayas of Uttarakhand. Thus, a better understanding of trends and changes in monsoonal rainfall has a vital role in natural resource management.

In recent years, many research has been done to investigate the trends in annual and seasonal rainfall over India (Guhathakurta and Rajeevan 2008; Rajeevan et al. 2008; Singh et al. 2008; Basistha et al. 2009; Joshi and Pandey 2011; Jain and Kumar 2012; Patra et al. 2012; Wasson et al. 2013; Duhan and Pandey 2013; Kundu et al. 2014; Pingale et al. 2014; Taxak et al. 2014; Suryavanshi et al. 2014; Murumkar and Arya 2014; Yadav et al. 2014; Ganguly et al. 2015; Pingale et al. 2015, 2016; Vidya et al. 2015; Kumar et al. 2016, Kumar and Jaswal 2016; Nandargi et al. 2016; Sharma et al. 2016; Agnihotri et al. 2017; Thakural et al. 2018; Parveen and Sreekesh 2018). Spatio-temporal variations in rainfall budget and a decreasing trend in the annual as well as southwest monsoon rainfall have been reported by the analysis of rainfall data of the last century. Only a few efforts have been made to study the trends of rainfall over entire Uttarakhand (Basistha et al. 2008, 2009; Yadav et al. 2014; Nandargi et al. 2016).

Descriptive and index based time series analysis has been carried out on annual and seasonal rainfall trends analysis at national or international levels. Oguntunde et al. (2006) investigated hydrological variability and trends in the Volta River over the period 1901–2002. They have used rainfall variability index, Mann–Kendall trend analysis, and non-parametric Sen's slope on hydro-climatological records. Their result suggested that rainfall variability index was highest for the year 1968 and lowest for 1983. Mandal et al. (2015) analyzed 16-year rainfall data of Daspalla region in Odisha state. Probability distribution functions and Markov chain model were used to forecast the probable dates of arrival and departure of monsoon and occurrence of dry spells, respectively. They found that log Pearson type III and Gumbel distributions were best-fit probability functions for prediction of monsoon and post-monsoon rainfall. Thomas and Prasannakumar (2016) analyzed rainfall data using trends and wavelet for a period of 141 years (1871–72 to 2011–12), which reveals a decreasing trend in southwest monsoon and increasing trends for post-monsoon-, winter-, and pre-monsoon-rainfall in Kerala state. Likewise, Taxak et al. (2014) tested spatial and temporal rainfall trends using CRU TS 3.21 gridded data on

annual and seasonal scales in Wainganga river basin located in Central India during 1901–2012. Similar research work on Uttarakhand has also been done by Sarkar and Garg 2018, Negi et al. 2018, Singh and Bharti 2019, Kumari et al. 2019, Kedia et al. 2019.

Particularly in Uttarakhand, a decreasing trend in rainfall and increasing 1-day rainfall events especially after 1970 have been reported and suggested the vulnerability to water resources by Nandargi et al. (2016). Similarly, Basistha et al. 2008, 2009 investigated rainfall trends using ordinary kriging, splines, inverse distance weighted, and polynomial interpolation techniques. Both studies indicated that the most probable year of change in annual as well as monsoon rainfall is 1964. Further, they reported an increasing trend in rainfall up to 1964, followed by a decreasing trend in 1965–1980. These studies were conducted with limited data and techniques. Hence, a better understanding of rainfall trends is required for effective implementation of water resources management plans.

8.2 Study Area

The study area is Uttarakhand state of India, which is located between coordinates $28^{\circ}42'N$ to $31^{\circ}28'N$ and $77^{\circ}35'E$ to $81^{\circ}05'E$. It is mostly a hilly state, having international boundaries with Tibet in the north and Nepal in the east. Uttarakhand is divided into two divisions, namely Garhwal and Kumaon division, as shown in Fig. 8.1. There are a total of 13 districts, in which Garhwal division has seven districts, namely Pauri, Haridwar, Dehradun, Tehri Garhwal, Rudraprayag, Uttarkashi, and Chamoli. While six districts, namely Udham Singh Nagar, Nainital, Almora, Champawat, Bageshwar, Pithoragarh are part of Kumaon division.

Uttarakhand receives about 90% of its rainfall in monsoon (July–September) season (Nandargi et al. 2016). In this state, spatially average rainfall varies from 92 cm in Srinagar to 250 cm in Nainital. The amount of rainfall generally high in low altitudes and gradually decreasing with increasing altitude. The regions of higher altitudes are cold throughout the year. The north part of state is covered with snow and glaciers, while mountainous forest is dominating in rest of the part. Figure 8.2 shows the land use pattern of state. It has a varied hydrogeological set-up and can be divided broadly into two distinct hydrogeological regimes, viz. the Gangetic alluvial plain and the Himalayan mountain belt. It has also major catchments like Yamuna, Bhagirathi, Alaknanda, Mandakini, Pindar, and Kali. Two major rivers of India, viz. the Ganga and Yamuna originate from the glaciers of Uttarakhand. According to soil resources vary from the deep, alluvial and fertile soils of the Tarai tract to the recently laid down alluvium of the doon valley; the thin fragile soil of the Shivalik hills; the black soils of the temperate zone.

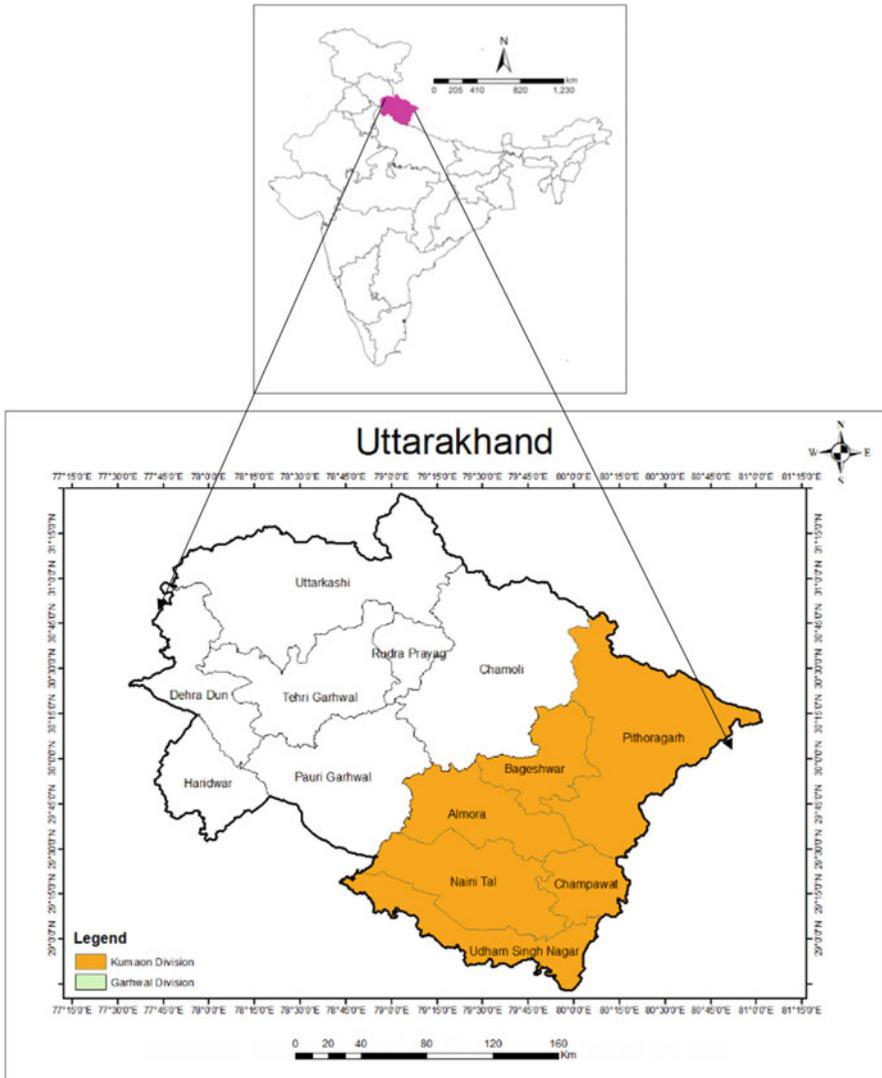


Fig. 8.1 Study area showing Kumaon and Garhwal division of Uttarakhand state

8.3 Data Collections

Monthly rainfall data used in this study was taken from India water portal (available at <http://www.indiawaterportal.org>) for the duration of 1901–2002, for all the district of Uttarakhand. Data was downloaded from Climate Research Unit (CRU) TS2.1 dataset of the Tyndall Centre for Climate Change Research, School of Environmental Sciences, University of East Anglia in Norwich, UK. Dataset consists of

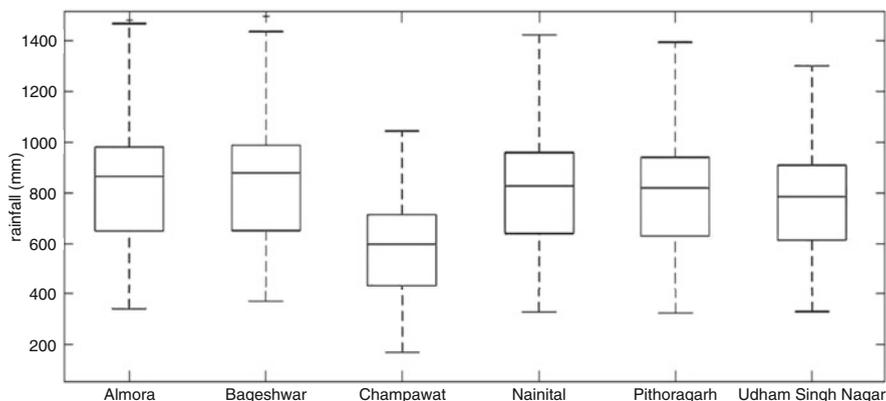


Fig. 8.2 Box plot of monsoonal rainfall distribution during 1900–2002 for Kumaon division

interpolated (on a 0.5° latitude–longitude grid) global monthly rainfall from 1901 to 2002 (Mitchell and Jones 2005). The district-wise rainfall data was obtained by simple linear averaging from the gridded data of the CRU dataset. A simple approximation was used to get the data for each district having a data gap of less than 25% of the district area.

8.4 Methodology

Time series for total monsoon rainfall, i.e., sum of rainfall during July, August, and September for all districts were considered in this study. Following techniques were used to analyze the monsoon rainfall trends in study area.

8.4.1 Statistics of Rainfall Data

The statistic of the sample data has been studied using arithmetic mean, median, standard deviation, and coefficient of variance, whose formulas are summarized in Table 8.1.

In Table 8.1, \bar{x} is arithmetic mean, x_i is sample data, n is the sample size, P_{50} is 50th percentile of the dataset, S is standard deviation, CV is coefficient of variance.

Table 8.1 Statistic used for rainfall data

S. no.	Statistic	Formula
1	Mean	$\bar{x} = \sum_{i=1}^n \frac{x_i}{n}$
2	Median	$P_{50} = x_{\frac{n+1}{2}}$, if n is odd $P_{50} = \frac{1}{2}(x_{n/2} + x_{n/2+1})$, if n is even
3	Standard deviation	$S = \sqrt{\sum_{i=1}^n \frac{(x_i - \bar{x})^2}{n-1}}$
4	Coefficient of variance	$CV (\%) = \frac{s}{\bar{x}} \times 100$

8.4.2 Rainfall Variability Index (RVI)

In the present study, rainfall variability index is used as the standardized rainfall departure. Based on RVI, several climatic regimes, such as normal year, wet year, very wet year, dry year, very dry year, have been distinguished. Equation (8.1) (Oguntunde et al. 2006) has been used for it.

$$\delta_i = \frac{(P_i - \mu)}{\sigma} \tag{8.1}$$

where δ_i is rainfall variability index for year i , P_i is annual rainfall for year i , and μ and σ are the mean and standard deviation of annual rainfall for the study period. When δ_i is within ± 0.5 , the year is characterized as a “normal year”; when δ_i is between $+0.5$ and $+1$, it is characterized as a “wet year”; when $\delta_i > +1$, it is characterized as a “very wet year.” Similarly, when δ_i is between -0.5 and -1 , the year is characterized as a “dry year,” when $\delta_i < -1$, it is characterized as a “very dry year” (Oguntunde et al. 2006).

8.4.3 Gumbel’s Method

Many rare and extreme events like extreme rainfall, snowfalls, and floods, high wind speeds, extreme temperatures, large fluctuations in exchange rates, etc., can have very negative consequences. Extreme-value theory, a branch of statistics, endeavors to model or find the probability of occurrence of such extreme events. Gumbel’s distribution is one of the most widely used probability distribution functions for extreme values in hydrologic and meteorologic studies for prediction of flood peaks, maximum rainfalls, maximum wind speeds, etc.

Gumbel’s distribution (Machiwal and Jha 2012) gives probability of occurrence of an event equal to or greater than a value x_o as

$$P(X \geq x_o) = 1 - e^{-e^{-y}} \quad (8.2)$$

in which, y is a dimensionless variable given by Eqs. (8.3)–(8.6)

$$y = \alpha (x - a) \quad (8.3)$$

$$a = \bar{x} - 0.450005\sigma_x \quad (8.4)$$

$$\alpha = \frac{1.2825}{\sigma_x} \quad (8.5)$$

Thus,

$$y = \frac{1.285 (x - \bar{x})}{\sigma_x} + 0.577 \quad (8.6)$$

where \bar{x} = mean and σ_x = standard deviation of the variate X . In practice, it is the value of X for a given P that is required and as such Eq. (8.2) can be written as

$$y_p = -\ln[-\ln(1 - P)] \quad (8.7)$$

Introducing return period $T = 1/P$ and designating y as a function of return period

$$y_T = -\left[\ln \cdot \ln \frac{T}{T-1}\right] \quad (8.8)$$

or

$$y_T = -\left[0.834 + 2.303 \log \cdot \log \frac{T}{T-1}\right] \quad (8.9)$$

Now rearranging Eq. (8.7), the value of the variate X with a return period T is

$$x_T = \bar{x} + K\sigma_x \quad (8.10)$$

where

$$K = \frac{(y_T - 0.577)}{1.2825} \quad (8.11)$$

Equations (8.8) and (8.9) constitute the basic Gumbel's equations and are applicable to an infinite sample size (i.e., $N \rightarrow \infty$). Since practical annual data series of extreme events such as floods, maximum rainfall depths, etc., all have finite lengths of record Eq. (8.9) is modified to account for finite N .

8.4.4 Mann–Kendall Test

The Mann–Kendall test is a non-parametric test for identifying trends in time series data. The test compares the relative magnitudes of sample data rather than the data values itself. One benefit of this test is that the data need not conform to any particular distribution. This method is applicable for only one data value per time period. The data values are evaluated as an ordered time series. Each data value is compared to all subsequent data values. The initial value of the Mann–Kendall statistic, S , is assumed to be 0. If a data value from a later time period is lower than a data value sampled earlier, S is decremented by 1. The net result of all such increments and decrements yields the final value of S (Mondal et al. 2012).

Let x_1, x_2, \dots, x_n represent n data points, where x_j represents the data point at time j . Then the Mann–Kendall statistic (S) is given by Eq. (8.12).

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^n \text{sign}(x_j - x_k) \quad (8.12)$$

where

$$\text{sign}(x_j - x_k) = \begin{cases} 1 & ; \text{ if } x_j - x_k > 0 \\ 0 & ; \text{ if } x_j - x_k = 0 \\ -1 & ; \text{ if } x_j - x_k < 0 \end{cases} \quad (8.13)$$

The variance of S (as mentioned in Eq. (8.14)), Variance, $\text{VAR}(S)$, is calculated by the following equation:

$$\text{VAR}(S) = \frac{1}{18} \left[n(n-1)(2n+5) - \sum_{p=1}^g t_p(t_p-1)(2t_p+5) \right] \quad (8.14)$$

where n is the number of data points, g is the number of tied groups (a tied group is a set of sample data having the same value), and t_p is the number of data points in the p th group.

A normalized test statistic Z is calculated as follows:

$$Z = \begin{cases} \frac{S - 1}{[\text{VAR}(S)]^{1/2}}; & \text{if } S > 0 \\ 0 & ; \text{if } S = 0 \\ \frac{S + 1}{[\text{VAR}(S)]^{1/2}}; & \text{if } S < 0 \end{cases} \quad (8.15)$$

The probability associated with this normalized test statistic is calculated. The trend is said to be *decreasing* if Z is negative and the computed probability is greater than the level of significance. The trend is said to be *increasing* if the Z is positive and the computed probability is greater than the level of significance. There is *no trend* if the computed probability is less than the level of significance.

8.5 Results and Discussion

The present study has comprehensively presented the overall monsoon rainfall behavior of all the districts of Uttarakhand during the time span of 1901–2002. First of all, a descriptive statistics of rainfall in monsoon has been analyzed, followed by a discussion on stationarity of the time series data. Thereafter, results of trend analysis have been discussed. Finally, results on rainfall frequency analysis have been discussed in this section.

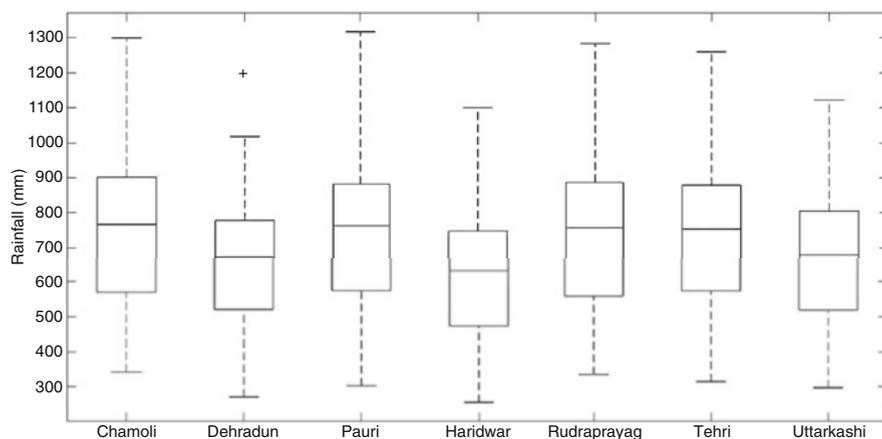
8.5.1 Rainfall Statistical of Uttarakhand

Due to significant variability of landforms in Uttarakhand, the rainfall pattern is also diverse here. Even the total monsoonal rainfall during the months of July, August, and September is significantly diverse.

A brief rainfall statistic of each district of Uttarakhand is also shown in Table 8.2. As per Table 8.2, Champawat has lowest average rainfall of 590 mm and Bageshwar has the highest average rainfall of 836 mm. The average rainfall of Almora, Nainital, Pithoragarh, and US Nagar is close to 800 mm. The coefficient of variation of average monsoonal rainfall is highest for Champawat. 33% variation can be seen for Champawat district. Rest of the districts of Kumaon division has coefficient of variation ranging from 26% to 28%. While in Garhwal division, Pauri has the highest magnitude of monsoonal rainfall of 1317 mm, followed by Chamoli and Rudraprayag. The coefficient of variation in the monsoonal rainfall is near to 27% for all the district of Garhwal division. The distribution of monsoonal rainfall for Kumaon and Garhwal division during 1900–2002 has also been shown using box plot in Figs. 8.2 and 8.3, respectively.

Table 8.2 Rainfall statistics of Kumaon and Garhwal divisions

District	Minimum rainfall (mm)	Maximum rainfall (mm)	Mean rainfall (mm)	Median rainfall (mm)	Standard deviation (mm)	Coefficient of variation (%)
<i>Kumaon division</i>						
Almora	340	1478	821	864	230	28.03
Bageshwar	370	1492	836	878	229	27.43
Champawat	170	1044	590	598	195	33
Nainital	328	1421	800	828	224	27.95
Pithoragarh	323	1392	797	820	208	26.15
US Nagar	329	1299	760	785	203	26.74
<i>Garhwal division</i>						
Chamoli	342	1300	747	767	200	26.7
Dehradun	271	1195	657	674	169	25.7
Haridwar	256	1101	621	763	163	26.6
Pauri	303	1317	736	631	196	26.3
Rudraprayag	335	1284	740	757	197	26.6
Tehri	315	1261	733	754	189	25.7
Uttarkashi	298	1123	672	680	176	26.2

**Fig. 8.3** Box plot of monsoonal rainfall distribution during 1900–2002 for Garhwal division

In Fig. 8.2, central rectangle spans the first quartile to the third quartile (the interquartile range or IQR). A segment inside the rectangle shows the median and “whiskers” above and below the box show the locations of the minimum and maximum. From Fig. 8.2, it can be depicted that for Almora, Bageshwar, Nainital, and Pithoragarh, the minimum and maximum monsoonal rainfall is almost same. It can also be observed that the median rainfall of every district is close to upper (or third) quartile of the box plot. The box plot shown in Fig. 8.2 also depicts the distinct rainfall behavior of Champawat district. Figure 8.3 depicts the box plot of

each district of Garhwal division. From this figure it can be observed that Dehradun and Haridwar received lower magnitude of monsoonal rainfall during 1900–2002. The rainfall pattern of Chamoli, Pauli, Rudraprayag, and Tehri is almost the same.

8.5.2 District-Wise Rainfall Variability Index (RVI) Analysis of Monsoonal Climatic Regime

8.5.2.1 Kumaon Division

Rainfall variability index is usually computed as the standardized precipitation departure and helps to separate the available rainfall time series into different climatic regimes such as “very dry monsoonal year,” “normal monsoonal year,” “wet monsoonal year,” “very wet monsoonal year,” “dry years,” and “very dry years.” In this section, based on RVI results, rainfall climatic regime of all districts of Uttarakhand has been discussed. Rainfall climatic regime, in the present study, has been compared between the rainfall data between 1901–1950 and 1951–2000. For Almora district, average rainfall during the study period is 821 mm and standard deviation in the rainfall data is 230 mm. Hence from the definition of RVI, year having rainfall in the range of 706–936 mm is said to be normal monsoonal rainfall year. Similarly, a wet year has rainfall in the range of 936–1051 mm. A very wet rainfall year has rainfall greater than 1051 mm. Dry years of monsoonal rainfall has a range of 591–706 mm, and very dry monsoonal rainfall has monsoonal rainfall less than 591 mm. As observed from Table 8.3, the number of very dry years during 1951–2000 has increased as compared to 1901–1950. Similarly, number of dry years has also increased during 1951–2000 as compared to 1901–1950. Table 8.3 also

Table 8.3 Monsoonal rainfall climatic regime of Kumaon Division during 1901–2000

Division	District	Period	No. of normal years	No. of wet years	No. of very wet years	No. of dry years	No. of very dry years
Kumaon	Almora	1901–1950	37	12	8	8	7
		1950–2000	22	6	4	9	9
	Bageshwar	1901–1950	15	12	8	7	8
		1950–2000	22	6	5	7	10
	Champawat	1901–1950	13	11	11	7	8
		1950–2000	14	13	5	9	9
	Nainital	1901–1950	14	13	8	6	9
		1950–2000	21	9	4	8	8
	Pithoragarh	1901–1950	15	13	8	9	7
		1950–2000	21	8	4	8	9
	Udham Singh Nagar	1901–1950	16	13	7	4	10
		1950–2000	19	11	4	7	9

depicts that as a consequence of dry periods, number of wet years and very wet years during 1951–2000 has decreased as compared to 1901–1950. Number of normal years has increased after 1950.

Further Table 8.3 also depicts that for Bageshwar district, the number of wet years and very wet years has significantly decreased during 1951–2000. From 1901 to 1950, number of wet years was 12, but during 1951–2000 it has reduced to only 6. Numbers of very dry years have also increased during 1950–2000. As far as normal monsoonal year is concerned, it has significantly increased after 1950. At Champawat, although numbers of wet years have increased (Table 8.3) during 1951–2000, but numbers of very wet years have significantly decreased from 11 to 5 during 1951–2000. Number of dry years and very dry years has also increased during 1951–2000. Number of normal years of monsoonal rainfall is almost the same in the pre- and post-1950. Rainfalls of 688 mm and 912 mm set the lowest and highest limit for a normal monsoon rainfall year for Nainital. Years with rainfall exceeding 1024 mm were tagged as very wet years, while the ones with rainfall values dipping below 577 mm were said to be very dry years. Table 8.3 suggests that number of wet and very wet monsoonal years has reduced during 1951–2000 as compared to 1901–1950. As a consequence of this, number of dry monsoonal year has increased post-1950. Number of normal monsoonal years has increased post-1950 up to 2000.

At Pithoragarh district, in accordance with RVI, years with rainfall values below 588 mm and above 1005 mm were classified as very dry and very wet years, respectively. Normal monsoonal rainfall years were the years with rainfall values between 693 mm and 901 mm. As shown in Table 8.3, number of wet and very wet monsoonal rainfall has significantly decreased during 1951–2000 as compared to 1901–1950. For Udham Singh Nagar district, rainfall values from 557 mm to 658 mm and 861 mm to 963 mm marked the limits for dry and wet years, respectively. As depicted in Table 8.2, number of dry years has increased post-1950, but the number of very dry monsoonal rainfall has decreased post-1950 as compared to pre-1950. Number of wet and very wet monsoonal years has decreased during 1951–2000 as compared to 1901–2000.

8.5.2.2 Garhwal Division

In Chamoli district, rainfall in the range of 647–846 mm is said to be normal monsoonal rainfall year. Similarly, a wet year has rainfall in the range of 846–946 mm. A very wet rainfall year has rainfall greater than 946 mm. Dry years of monsoonal rainfall have a range of 547–647 mm, and very dry monsoonal rainfall has monsoonal rainfall less than 547 mm. As observed from Table 8.4, the number of normal and very dry monsoonal rainfall years increased during post-1950, while the number of wet years dipped during the same period. Number of very wet and dry years remained almost the same. Table 8.4 also depicts the monsoonal climatic regime of Dehradun district. According to RVI, for Dehradun, a year with annual monsoon rainfall lying between 573 mm and 741 mm was considered as normal

Table 8.4 Monsoonal rainfall climatic regime of Garhwal during 1901–2000

Division	District	Period	No. of normal years	No. of wet years	No. of very wet years	No. of dry years	No. of very dry years
Garhwal	Chamoli	1901–1950	16	12	7	7	8
		1950–2000	21	5	6	7	11
	Dehradun	1901–1950	17	8	8	9	8
		1950–2000	16	11	6	6	11
	Pauri	1901–1950	15	13	7	7	8
		1950–2000	16	11	6	9	8
	Haridwar	1901–1950	16	11	6	6	11
		1950–2000	18	5	12	8	7
	Rudraprayag	1901–1950	15	10	9	8	8
		1950–2000	19	8	5	6	12
	Tehri	1901–1950	16	10	9	8	7
		1950–2000	15	11	6	7	11
	Uttarkashi	1901–1950	16	9	10	8	7
		1950–2000	17	9	6	5	13

monsoon rainfall year. Years with rainfall less than 488 mm and greater than 826 mm were said to be very dry monsoonal rainfall year and very wet monsoonal rainfall year, respectively. In this district, three out of five decades in post-1950 did not register any very wet years. Very dry years on the other hand increased and occurred evenly across the same duration. The wet years increased by the same number as the dry years decreased from pre- to post-1950.

Further, at Pauri district, in accordance with RVI, years with rainfall values below 540 mm and above 932 mm were classified as very dry and very wet years, respectively. Normal monsoonal rainfall years were the years with rainfall values between 638 mm and 834 mm. As shown in Table 8.4, although a number of very dry years remained accidentally the same from pre- to post-1950 but rise in dry years could be seen. Both the number of wet and very wet years dwindled across post-1950 period. Rainfalls of 540 mm and 703 mm set the lowest and highest limit for a normal monsoon rainfall year for Haridwar. Years with rainfall exceeding 784 mm were tagged as very wet years, while the ones with rainfall values dipping below 458 mm were said to be very dry years. Table 8.4 suggested that number of very dry years decreased during post-1950 accompanied by an increase in number of dry years. Similarly, number of wet years decreased but number of very wet years increased by the same amount from pre- to post-1950. For Rudraprayag district, rainfall values from 544 mm to 642 mm and 838 mm to 937 mm marked the limits for dry and wet years, respectively. Also (Table 8.4), the number of very dry years in post-1950 period outnumbered those in pre-1950 period by the same amount as the very wet years slumped during the same period. The wet and dry years also witnessed minor decrement, along with a noticeable increase in normal years. The RVI calculations for Tehri district resulted in rainfall values of 639 mm and 827 mm

as the range for normal year, and the rainfall values of 544 mm and 921 mm as the limiting values for dry and wet years. Table 8.4 suggested that normal years, very wet years, and dry years decreased from pre- to post-1950 either in a more or less minor way.

For Uttarkashi, a year with monsoon rainfall reception in between 584 mm and 760 mm was, as dictated by RVI, said to be a normal year. Years with rainfall values falling short of 496 mm were called very dry years, while the ones exceeding 848 mm were called very wet years. From Table 8.4, it is evident that although the number of dry years decreased from pre- to post-1950, the number of very dry years increased twice that of the aforementioned decrease, accompanied by a considerable decrease in the number of very wet years. Normal and wet years remained almost the same. Also, similar to the queer fact observed for the Kumaon region, the number of dry and very dry years always outnumbered wet and very wet years in the last decade of this study (1991–2000) for all districts of Garhwal region.

8.5.3 Monsoonal Rainfall Frequency Analysis of Uttarakhand

Gumbel's extreme-value distribution has been used for frequency analysis of both divisions of Uttarakhand. Figure 8.4 shows the scatter plot of the predicted monsoonal rainfall (using Gumbel's method) and actual monsoonal rainfall for each district of Uttarakhand. Figure 8.4a–f suggests that coefficient of determination is above 0.9 for all districts of Kumaon division. Coefficient of determination for Almora, Bageshwar, Champawat, Nainital, Pithoragarh, and Udham Singh Nagar is 0.946, 0.953, 0.943, 0.938, 0.958, and 0.926, respectively. Thus, coefficient of determination is lowest and highest for Udham Singh Nagar and Pithoragarh, having its values of 0.926 and 0.958, respectively. The results of these R^2 values suggest that Gumbel's method of frequency analysis can conveniently be used for all districts of Kumaon division. Using the Gumbel's extreme-value distribution, the magnitude of monsoonal rainfall for a defined return period has been estimated. Table 8.5 shows the magnitude of monsoonal rainfall for the return period of 30, 60, 90, 120, and 150 years for each district of Kumaon division. For Almora, monsoonal rainfall of 1360 mm, 1493 mm, 1571 mm, 1627 mm, and 1669 mm is expected with a return period of 30, 60, 90, 120, and 150 years. Similarly, monsoonal rainfall of 1372 mm, 1505 mm, 1583 mm, 1638 mm, and 1680 mm is expected with a return period of 30, 60, 90, 120, and 150 years for Bageshwar district. For Almora district, a monsoonal rainfall of 1360 mm, 1494 mm, 1571 mm, 1627 mm, and 1669 mm can return in 30 years, 60 years, 90 years, 120 years, and 150 years, respectively. In a similar fashion, magnitude of monsoonal rainfall for other districts is listed in Table 8.5. While Bageshwar and Almora have the highest expected rainfall for every return period considered, Champawat has the lowest.

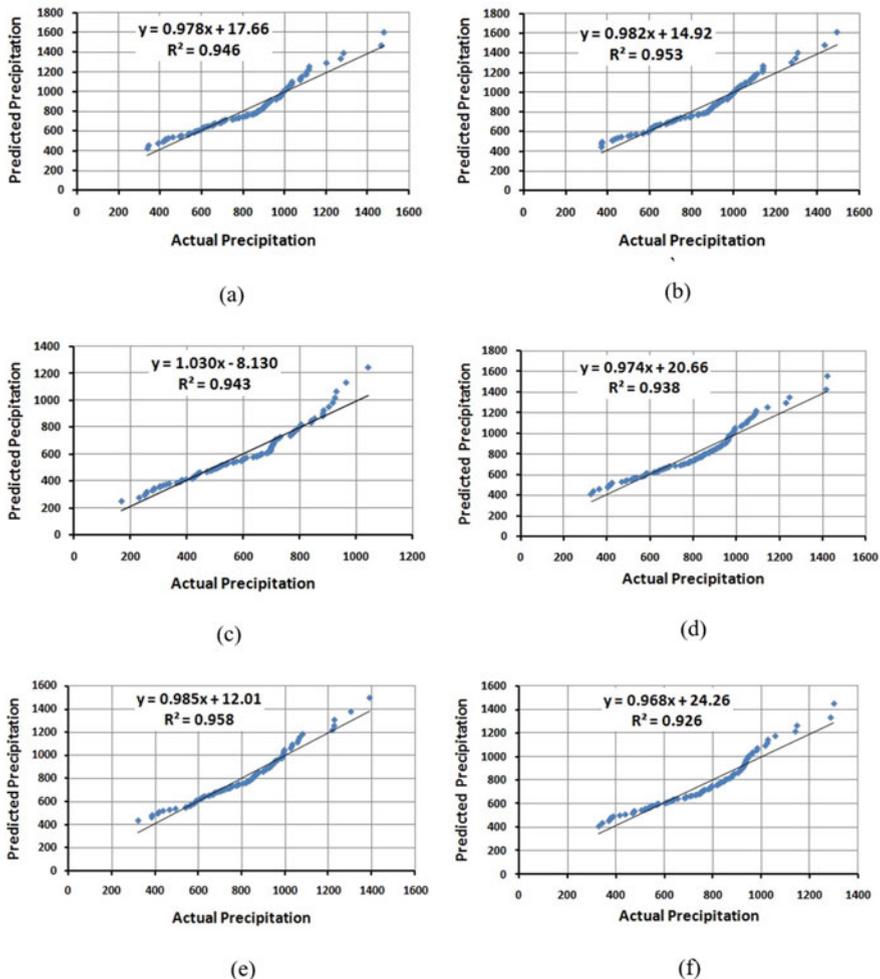


Fig. 8.4 Scatter plot of Gumbel’s predicted monsoonal rainfall versus actual rainfall for Kumaon. (a) Almora. (b) Bageshwar. (c) Champawat. (d) Nainital. (e) Pithoragarh. (f) Udham Singh Nagar

In Fig. 8.5a–g, scatter plot of the predicted monsoonal rainfall (using Gumbel’s method) and actual monsoonal rainfall for each district of Garhwal division has been shown. The coefficient of determination, which when expressed as a percent, represents the percent of variation in the dependent (predicted) variable y that can be explained by variation in the independent (explanatory or actual) variable x using the regression (best-fit line), is greater than 0.93 for all the districts of Garhwal division. Coefficient of determination is highest for Chamoli (0.958). The correlation coefficient, the square of which gives us coefficient of determination, and which provides a measure of strength and direction of the linear association between the independent and dependent variable will have even higher values (>0.96) for all the

Table 8.5 Magnitude of monsoonal rainfall (mm) corresponding to its return period for Uttarakhand

District/return period	30 years	60 years	90 years	120 years	150 years
<i>Kumaon division</i>					
Almora	1360	1493	1571	1627	1669
Bageshwar	1372	1505	1583	1638	1680
Champawat	1045	1158	1224	1271	1307
Nainital	1324	1454	1530	1584	1625
Pithoragarh	1285	1406	1477	1527	1565
US Nagar	1236	1354	1423	1471	1509
<i>Garhwal division</i>					
Chamoli	1214	1330	1397	1445	1482
Dehradun	1052	1150	1207	1247	1279
Haridwar	1003	1098	1153	1192	1222
Pauri	1194	1308	1374	1421	1457
Rudraprayag	1200	1314	1381	1428	1464
Tehri	1174	1284	1347	1393	1428
Uttarkashi	1084	1187	1246	1289	1321

districts. From Table 8.5, it can be depicted that for Chamoli district, the monsoonal rainfall of 1214 mm, 1330 mm, 1397 mm, 1445 mm, and 1482 mm has a return period of 30, 60, 90, 120, and 150 years. As shown in Table 8.5, Chamoli, being the district in Garhwal region with highest mean monsoon rainfall, has the highest expected rainfall for every return period. Similarly, Haridwar has the lowest expected rainfall values. The comparative low variability of rainfall in Garhwal region is also reflected in the above table. Still, Chamoli, Rudraprayag, Pauri, and Tehri form a group of high rainfall while Uttarkashi, Dehradun, and Haridwar form another group of lower expected rainfall corresponding to any return period.

8.5.4 Trend Analysis of Monsoonal Rainfall of Uttarakhand

Mann–Kendall statistics for Uttarakhand has been shown in Table 8.6. Negative values of Mann–Kendall statistics indicate decreasing trend and positive values of Mann–Kendall statistics shows increasing trend if its normalized test statistic is greater than 0.95 (i.e., 95% significance level). At 95% significance level, Almora, Bageshwar, Champawat, Nainital, and Pithoragarh show decreasing trend, while US Nagar shows no trend. The results suggest that the monsoonal rainfall of most of the districts of Kumaon is decreasing and it is a clear indication of climate change in this region. In Garhwal division, most of the districts show no trend in monsoonal rainfall. Since at 95% level of significance, Dehradun, Haridwar, Pauri,

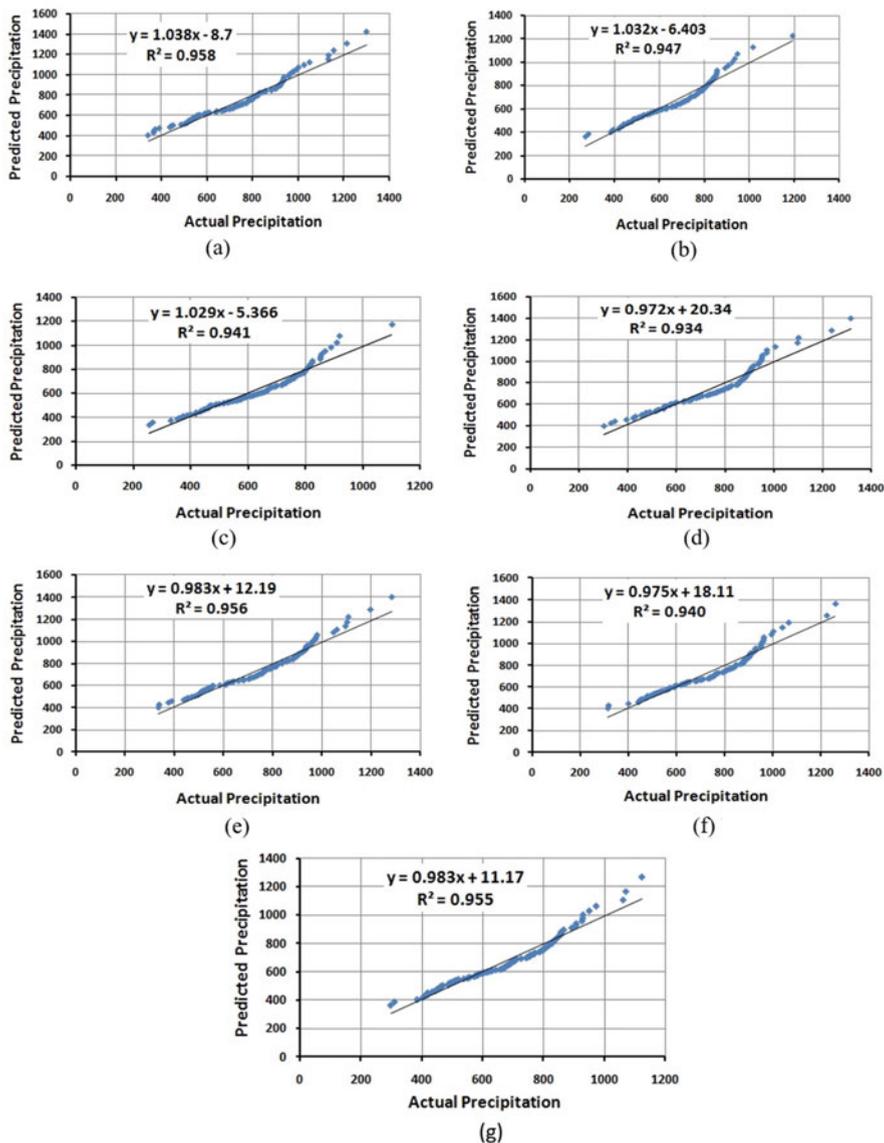


Fig. 8.5 Scatter plot of Gumbel’s predicted monsoonal rainfall versus actual rainfall for Garhwal. (a) Chamoli. (b) Dehradun. (c) Haridwar. (d) Pauri. (e) Rudraprayag. (f) Tehri. (g) Uttarkashi

Rudraprayag, Tehri, and Uttarkashi have probability less than 0.95, hence these districts show no trend during 1901–2002. At 95% level of significance, only Chamoli shows a decreasing trend in monsoonal rainfall during 1901–2002.

Table 8.6 Trend analysis of monsoonal rainfall of Uttarakhand

District	Mann–Kendall statistics (S)	Normalized test statistics (Z)	Probability	Trend (at 95% level of significance)
<i>Kumaon division</i>				
Almora	–628	–1.83	0.97	Decreasing
Bageshwar	–650	–1.90	0.97	Decreasing
Champawat	–620	–1.82	0.96	Decreasing
Nainital	–580	–1.69	0.95	Decreasing
Pithoragarh	–714	–2.09	0.98	Decreasing
US Nagar	–472	–1.38	0.92	No trend
<i>Garhwal division</i>				
Chamoli	–566	–1.65	0.95	Decreasing
Dehradun	–166	–0.48	0.68	No trend
Haridwar	90	0.26	0.60	No trend
Pauri	–330	–0.96	0.83	No trend
Rudraprayag	–504	–1.47	0.93	No trend
Tehri	–398	–1.164	0.87	No trend
Uttarkashi	–456	–1.34	0.91	No trend

8.6 Conclusion

In this study, an attempt has been made to study the monsoonal rainfall experienced by the Uttarakhand state during 1901–2002. The analysis revealed that:

- Lesser Himalayan district viz. Bageshwar (1492), Almora (1478 mm), Nainital (1421 mm) district of Kumaon division has reported with highest magnitude of monsoonal rainfall. While in Garhwal division, Pauri has the highest magnitude of monsoonal rainfall (1317 mm), followed by Chamoli (1300 mm) and Rudraprayag (1284 mm).
- Number of wet and very wet monsoonal years has decreased during 1951–2000 as compared to 1901–2000 in Uttarakhand. Even so, interestingly, for all districts of both regions the number of dry and very dry years surpasses the number of wet and very wet years for the last 20 years of study.
- The randomness (independence) and stationarity using autocorrelation function (ACF) suggest that the monsoonal rainfall time series of each district is stationary in nature. It also suggests that all the monsoonal rainfall time series are strongly random.
- The results from rainfall frequency analysis suggested that Chamoli, Rudraprayag, Pauri, and Tehri of Garhwal division were group of high rainfall district, while Uttarkashi, Dehradun, and Haridwar were group of lower expected rainfall corresponding to any return period (30 years, 60 years, 90 years, 120 years, and 150 years). While, in Kumaon division, Bageshwar and Almora have the highest expected rainfall for every return period considered and Champawat has the lowest.

- The trends analysis showed that the monsoonal rainfall of most of the districts of Kumaon is decreasing. While in Garhwal division, most of the districts show no trend in monsoonal rainfall, except Chamoli, showing decreasing trends in monsoonal rainfall during 1901–2002.
- The results of this study might improve by considering rainfall data from 2003 to 2017. The outcomes of this study may help water management/agricultural planning in Uttarakhand.

Conflict of Interest No any.

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Chapter 9

Hydrological Processes in Subsurface Flow Constructed Wetlands: An Overview for Modeling and Enhanced Remediation



Manik Goel, Abhishek, and Pankaj Kumar Gupta

Abstract Constructed wetlands (CWs) are engineered ecosystems used to treat wastewater and/or polluted subsurface water. In the last decades, the growing literature has been appearing to improve the performance of CWs under varying hydrological conditions. Plant–microbes–geochemical interactions significantly enhance the (1) physical and chemical properties of polluted sites; (2) nutrient supply by root exudates; (3) the aeration by transfer of oxygen; (4) the enzymatic transformation of pollutants; (5) resistant to the migration of pollutants/pathogens. Such biogeochemical interactions accelerate the “biodegradation process” of pollutant by native microbes that cause significant removal of pollutants. Furthermore, biodegradation can be improved by controlling favorable conditions, like temperature, nutrients supply, microbes, nanoparticles, and so on. Most of the research performed in the past are focused on performance evaluation of CWs in laboratory scale, pot scale, and/or large scale sites. However, only a few research work has been performed to understand the biogeochemical and hydrological conditions controlling the performance of CWs. Thus, an effort has been made to present current knowledge on understanding the biogeochemical and hydrological conditions controlling the performance of CWs. Literature review clearly indicates that (1) only few research has been performed to understand the role of geochemical processes on the performance of CWs under varying subsurface conditions, (2) modeling of CWs required more in situ soil–water characterization to estimate different reactive transport parameters, (3) application of nanomaterials can improve the site condition for in situ removal of pollutants by CWs. This manuscript will help field scientists to

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frame policy for effective implementation of CWs for treatments of polluted sites under different hydrological conditions.

Keywords Constructed wetland (CWs) · Biogeochemical interactions · Hydrological conditions · Polluted sites

9.1 Introduction

Wetland is a geographical area that remains partially or fully saturated either permanently or seasonally and is having a special ecosystem. Since a long time, wetlands are known for their rich biodiversity consisting of various indigenous species of plants, animals, and microorganisms. The wetlands are widely present worldwide and are being utilized for diverse applications, viz. water purification and storage, processing of various minerals and nutrients, stabilization of shorelines, etc. They can also be constructed artificially, termed as constructed or engineered wetlands, for meeting various purposes like treatment of wastewater or graywater, food storage, or land reclamation after mining. Constructed wetlands (CWs) are monitored and optimized in a way to yield a maximum efficiency for the specified purpose. The vegetation, a major basic entity of wetlands whether natural or constructed, plays a key role in maintaining the permeability of filter media and provides habitat to microorganism soil which is further responsible for the treatment of wastewater (say, for example). Subsurface constructed wetlands (SSCW), as depicted by name, are designed as channel or bed (Fig. 9.1) such that water surface is not exposed to atmosphere. The performance disparity of SSCW over free water surface (FWS) constructed wetlands is in terms of the risk reduction of mosquitoes breeding followed by lowered health issues and access of the system to the public.

In general, the SSSC include a barrier below the basin area for preventing the seepage of contaminated wetland water/fluid to the underlying groundwater resources. Polymer materials like PVC, HDPE, or sometimes even the compacted soil (in case of resource scarcity) may be used as barrier in SSSC. Inlet and outlet hydraulic structures are planned and constructed accordingly for ensuring uniform

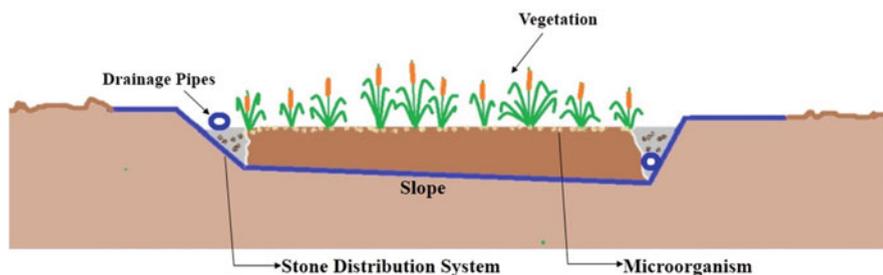


Fig. 9.1 Typical cross-section of subsurface constructed wetland

influent graywater and effluent treated water. Besides the user defined design criteria, the selection of vegetation is a crucial part in the construction of SSCW as it provides medium and oxygen to microorganism's actions. Species generally used for SSCW are *Phragmites australis* (Common reed), *cattail* (*Typha* spp.), *genera Typha* (*angustifolia*, *latifolia*, *domingensis*, *glauca*, and *orientalis*), and *Scirpus* (e.g., *lacustris*, *validus*, *californicus*, and *acutus*) (Vymazal 2011).

In the present scenario, SSCW are known for the cost-effective for both centralized-, decentralized- and on-site water treatment systems (US EPA 2000). The crucial parameters affecting the treatment efficiency of SSCW include porous media properties, vegetation type, hydraulic residence time and temperature. Removal of the organic matter (in particular) in subsurface wetlands is governed by aerobic bacteria residing in plant root zone and also by various hydrological and geochemical processes that primarily include adsorption, absorption, ionization, etc. (Akratos and Tsihrintzis 2007).

9.1.1 Subsurface Constructed Wetland Types

Subsurface constructed wetlands can be broadly classified into two types:

- (a) *Horizontal flow SSCW*: It is primarily a gravel and sand-filled basin planted with vegetation. Contaminants of water or wastewater are filtered out by filter media during horizontal flow followed by degradation by microorganism. Primary treatment of wastewater is required before entering in such wetlands to prevent clogging of filter media. Although most organics are degraded by anaerobic and facultative bacteria yet aerobic bacteria also colonize around the root zone of plants to degrade organics. These wetlands are most suitable for the places with warm climates and readily availability of cheap land.
- (b) *Vertical flow SSCW*: It can be considered as a planted filter bed draining at the bottom. Mechanical dosing system is required to apply the wastewater from above. Filter media in such wetlands goes through various phase of saturation depending upon the dosing period of wastewater. They can be applied efficiently to the communities having their own primary treatment unit (e.g., septic tank). Various processes involved in both types of wetland systems are summarized in Table 9.1. Sometimes, both types of SSCW can also be combined to make a hybrid system in order to get the overall improved efficiency of contaminant removal.

Table 9.1 Various features and processes involved in VF and HF SSCW

Process/features	Horizontal flow SSCW	Vertical flow SSCW
Nutrient removal	Less efficient in nutrition removal	Ability to nitrify due to good oxygen transfer
Area of installation	Requires larger area	Less space requirement
Clogging	Prone to clogging	Less clogging
Energy source requirement	No electrical energy is required	Requires energy source
Operation cost	Lower operating cost	Requires more frequent maintenance than a horizontal SCW
Leaching	Wastewater is less prone to leaching into the subsurface	Long start-up time to work at full capacity
Manpower requirement		Skilled manpower is required for designing and operation, particularly, the dosing system

9.2 Worldwide Scenario of Application of Subsurface Constructed Wetland

Rapid urbanization and increasing population have created stress on the surface and subsurface water resources globally. This stress has led more and more pollution of the available water resources and has created food, water, and energy security issues. Therefore, there is a strict need of finding a sustainable, cost-effective, and green solution to remediate the polluted surface and subsurface water. Among numerous available remediation technologies, the wetlands have proven to be the most effective and environment friendly. Some recent developments in SSCW studies tested for remediating various components of water and wastewater are listed in Table 9.2.

9.3 Hydrological and Geochemical Processes of Subsurface Constructed Wetland

Hydrological and geochemical processes occurring in a wetland should be given due to consideration in designing them for efficient functioning. Hydrological parameters are one of the most vital considerations for efficient performance of any constructed wetland.

Table 9.2 Summary of laboratory and simulation experimental studies reported in the performance of SSCWs

Area of application	Wetland design consideration				Removal efficiency (%)						References
	Scale (m × m × m) (L × B × D)	Vegetation cover	HLR (m ³ d ⁻¹)	HRT (d)	TSS	BOD ₅	COD	TN	TP		
Tartu County, Estonia	1.5 × 0.6 × 0.6	<i>Typha latifolia</i>	0.06	—	—	—	—	20	22.5		
Poland	5 × 1 × 1	<i>Phragmites australis</i>	0.5	—	40.6	90.5	87.5	76.5	40.6	Dąbrowski et al. (2017)	
Juja, Nairobi city, Kenya	7.5 × 3 × 0.6	<i>Cyperus papyrus</i>	—	—	75.27	60.73	42.76	—	42.86	Mburu et al. (2013)	
Peradeniya, Sri Lanka	1 × 25 × 0.6	<i>Scirpus grossus</i> and <i>Hydrilla verticillata</i>	—	18	65.8	65.7	40.8	—	61.2	Tanaka et al. (2013)	
Dhaka, Bangladesh	1.3 × 1 × 0.8	<i>Phragmites australis</i>	624	12.5	55	98	98	—	87	Saeed et al. (2012)	
Ocotlán, Jalisco Mexico	3.6 × 0.9 × 0.3	<i>Srelitzia reginae</i> and <i>Anthurium andreanum</i>	0.128	—	81.66	77.94	76.32	52.78	40.24	Zurita et al. (2011)	
Beijing, China	1.5 × 0.8 × 1	<i>Salix babylonica</i>	0.144	0.75	97	96	—	—	88	Wu et al. (2011)	
Rongcheng, Shandong, China	150 × 30 × 0.5	<i>Phragmites australis</i> and <i>Typha orientalis</i>	20,000	120	71.8	70.4	62.2	—	29.6	Song et al. (2009)	
Egypt	1.1 × 1 × 0.4	<i>Phragmites australis</i>	—	5	82.2	70.3	65.9	36	32.4	Abdel-Shafy et al. (2009)	
Can Tho University, Vietnam	12 × 1.6 × 1.1	<i>Phragmites vallatoria</i>	3,08352	—	79.93	75.10	66.02	51.97	65.96	Trang et al. (2010)	

9.3.1 Hydrological Processes

Subsurface constructed wetlands are shallow open water bodies and hence are strongly affected by the prevailing climate and weather. High flows created either by heavy rain or snowmelt increase the flow velocity and decrease the residence time. Excess runoff through the wetland may alter the contaminant concentration and can lead to flushing of useful microorganism. Wetlands are best suitable for warm climate and as temperature decreases efficiency of wetland tends to decrease.

Evapotranspiration (ET) The total water loss including the plant and soil surface in the form of water vapors is termed as evapotranspiration. It becomes an important factor for SSCW as water is more exposed to atmosphere here due to larger surface area. During high evapotranspiration period, additional water inflow may require in SSCW to provide favorable environment to microbes and for avoiding concentration of pollutant to toxic level.

Groundwater Exchange SCW should be designed with an impermeable barrier to avoid exchange of groundwater between the wetland and subsurface

Water Balance As a general hydrological balance, the difference between the inflow to and outflow from a wetland system will appear as the storage change per unit time. The inflow includes inputs from surface in the form of precipitation or groundwater infiltration (in case of unlined wetlands). The outflow is comprised of evapotranspiration, effluent discharge, and exfiltration to groundwater, if any. The water balance is of prime importance for design and operation of the system as it affects the other hydrological parameters (HLR, HRT) of the system. Water balance of a simple wetland system is described by the equation:

$$S = Q + R + I - O - ET$$

where S storage change, R rainfall, Q total surface flow, I net infiltration, ET evapotranspiration loss, O surface outflow

Hydraulic Loading Rate (HLR) The volume of wastewater applied per unit area of wetland describes the hydraulic loading rate (HLR). Under real field conditions, it is a function of the hydraulic conductivity of the soil stratification under consideration. Higher the hydraulic conductivity of the soil high will be the allowable hydraulic loading rate

Hydraulic Residence Time (HRT) The average time for which wastewater remains in the wetland, represented mathematically as ratio of mean volume to the mean outflow rate is termed as hydraulic residence time (HRT).

9.3.2 Geochemical Process

9.3.2.1 Nitrification

Nitrification is a biological process that converts the ammonia into nitrate and is generally followed by denitrification which involves the reduction of nitrates to nitrogen gas (Fig. 9.2). This sequence of reactions is one of the most important process in SSCW for N-removal followed by sulfate reduction from the soil-water system (Bastviken et al. 2003).

Nitrification can be modeled in two step process using CW2D model of HYDR US by incorporating (1) aerobic growth of *Nitrosomonas* on ammonium ion and (2) aerobic growth of *Nitrobacter* on nitrite ion. In the first step, *Nitrosomonas* consumes ammonium ion (NH_4^+) and oxygen to produce NO_2^- . Inorganic phosphorus along with traces of NH_4^+ is also incorporated in the biomass.

$$r_{\text{step1}} = \mu_{ANs} \frac{C_{O_2}}{K_{ANs,O_2} + C_{O_2}} \frac{C_{NH_4}}{K_{ANs,NH_4} + C_{NH_4}} \frac{C_{IP}}{K_{ANs,IP} + C_{IP}} C_{XANs}$$

Lysis of *Nitrosomonas* produces OM, NH_4^+ , and IP as follows:

$$r_{\text{step1A}} = b_{XANs} C_{XANs}$$

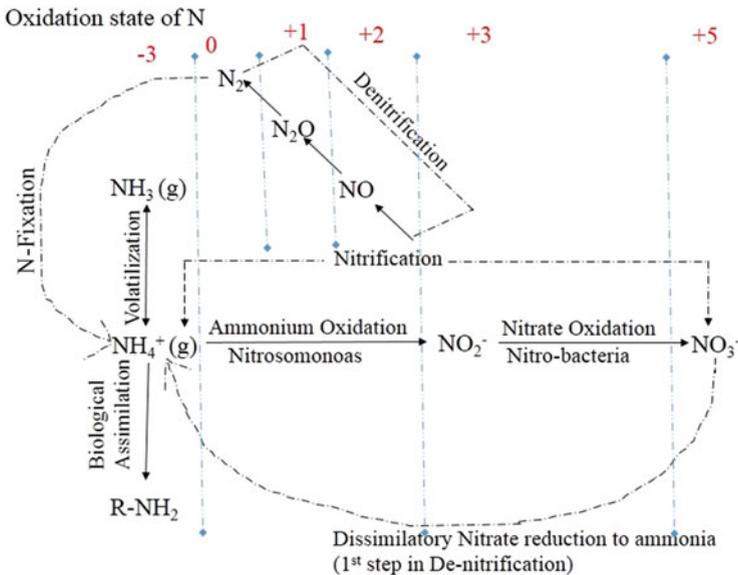


Fig. 9.2 Geochemical pathways of N species in wetland system

In the second step, microbes consume nitrite and oxygen to produce NO_3^- . Ammonium and IP are incorporated in the biomass as follows:

$$r_{C_{\text{step2}}} = \mu_{ANb} \frac{C_{\text{O}_2}}{K_{ANb,\text{O}_2} + C_{\text{O}_2}} \frac{C_{\text{NO}_2}}{K_{ANb,\text{NO}_2} + C_{\text{NO}_2}} \int_{N,ANb} C_{XANb}$$

Modeling of CWs processes involved aerobic growth of Nitrobacter on nitrate followed by lysis of Nitrobacter. In lysis of Nitrobacter OM, NH_4^+ , and IP as follows:

$$r_{C_{\text{step1A}}} = b_{XANb} C_{XANb}$$

9.3.2.2 Denitrification

In denitrification process, nitrate based growth of heterotrophs can be modeled on readily degradable COD. This process consumes NO_3^- and OM and reduces to dinitrogen (N_2).

$$r_{C_{DN-\text{Nitrate}}} = \mu_{DN} \frac{K_{DN,\text{O}_2}}{K_{DN,\text{O}_2} + C_{\text{O}_2}} \frac{C_{\text{NO}_3}}{K_{DN,\text{NO}_3} + C_{\text{NO}_3}} \frac{K_{DN,\text{NO}_2}}{K_{DN,\text{NO}_2}} \\ \times \frac{C_{CR}}{K_{DN,CR} + C_{CR}} \int_{N,DN} C_{XH}$$

While in nitrite based growth of heterotrophs on readily biodegradable COD, the processes consume NO_2^- , OM CR, NH_4^+ , and IP and produce N_2 .

$$r_{C_{DN-\text{Nitrite}}} = \mu_{DN} \frac{K_{DN,\text{O}_2}}{K_{DN,\text{O}_2} + C_{\text{O}_2}} \frac{C_{\text{NO}_2}}{K_{DN,\text{NO}_2} + C_{\text{NO}_2}} \frac{C_{CR}}{K_{DN,CR} + C_{CR}} \int_{N,DN} C_{XH}$$

where lysis produces OM, NH_4^+ , and IP and assumed to represent the sum of all decay and sink processes. Refer Tables 9.3 and 9.4 for values associated with different mechanisms.

$$r_{C_{DN}} = b_H C_{XH}$$

9.3.2.3 Ammonia Volatilization

Ammonia volatilization refers to the general physicochemical process for obtaining the ammonia either from ammonification reactions or from wastewater is transferred from water to the atmosphere. The pH of system plays an important role in controlling this process. For significant mechanism of ammonia removal, pH must

Table 9.3 Components defined in the reactive transport module adapted from Langergraber and Šimůnek (2005)

<i>I</i>	Symbol	Unit	Description
1	O ₂	mg _{O2} L ⁻¹	DO
2	CR	mg _{COD} L ⁻¹	Readily biodegradable COD
3	CS		Slowly biodegradable COD
4	CI		Inert chemical oxygen demand
5	XH		Heterotrophic microorganism
6	XAN _s		<i>Nitrosomonas</i> spp. (autotrophic bacteria 1)
7	XAN _b		<i>Nitrosomonas</i> spp. (autotrophic bacteria 2)
8	NH ₄ N		mg _N L ⁻¹
9	NO ₂ N	Nitrite ion (NO ₂ ⁻)	
10	NO ₃ N	Nitrate ion (NO ₃ ⁻)	
11	N ₂ N	Dinitrogen gas (N ₂)	
12	IP	Phosphorus (inorganic)	

be above 10. Mostly, pH of CWs ranges from 7 to 8.5, thus ammonia volatilization is not a significant parameter in the case of CWs.

9.3.2.4 Hydrolysis

In SSCW, hydrolysis refers to a process by means of which bio-molecules degrade due to reaction with water. It is a first-order kinetics that helps the microorganism to gain energy by breaking the contaminant molecule into daughter ones which ultimately enhance the overall efficiency of the system under consideration. On the contrary, it slightly increases the dissolved COD concentration in the wetlands (Reddy and Angelo 1997).

$$r_{\text{hydrolysis}} = K_h \frac{C_{CS}/C_{XH}}{K_X + C_{CS}/C_{XH}} C_{XH}$$

9.3.2.5 Fermentation

Fermentation is an exothermic and anaerobic process that includes formation of valuable products by reduction–oxidation process. It does not include any external electron acceptor. It is a substrate-level phosphorylation.

Table 9.4 Kinetic parameters (at 20 °C, values in brackets at 0 °C) adapted from Langergraber and Šimůnek (2012)

Parameter		Value
<i>Hydrolysis</i>		
K_h	Hydrolysis rate constant [d^{-1}]	3 (2)
K_x	Coefficient for hydrolysis [$mg_{COD,CS} mg_{COD,BM}^{-1}$]	0.1
<i>Heterotrophic microorganism (aerobic growth)</i>		
μ_H	Maximum growth rate on CR in aerobic conditions [d^{-1}]	6 (3)
b_H	Rate constant for lysis [d^{-1}]	0.4 (0.2)
K_{het,O_2}	Oxygen coefficient [$mg_{O_2} L^{-1}$]	0.2
$K_{het,CR}$	Substrate coefficient [$mg_{COD,CR} L^{-1}$]	2
K_{het,NH_4N}	Ammonium ion coefficient [$mg_{NH_4N} L^{-1}$]	0.05
$K_{het,IP}$	Phosphorus coefficient [$mg_{IP} L^{-1}$]	0.01
<i>Heterotrophic microorganism (denitrification)</i>		
μ_{DN}	Maximum denitrification rate [d^{-1}]	4.8 (2.4)
K_{DN,O_2}	Oxygen coefficient [$mg_{O_2} L^{-1}$]	0.2
K_{DN,NO_3N}	NO_3^{-} coefficient [$mg_{NO_3N} L^{-1}$]	0.5
K_{DN,NO_2N}	NO_2^{-} coefficient [$mg_{NO_2N} L^{-1}$]	0.5
$K_{DN,CR}$	Substrate coefficient [$mg_{COD,CR} L^{-1}$]	4
K_{DN,NH_4N}	Ammonium ion coefficient [$mg_{NH_4N} L^{-1}$]	0.05
$K_{DN,IP}$	Phosphorus coefficient [$mg_{IP} L^{-1}$]	0.01
<i>Nitrification step 1 (Nitrosomonas)</i>		
μ_{ANs}	Maximum growth rate on NH_4^+ , aerobic condition [d^{-1}]	0.9 (0.3)
b_{ANs}	Rate constant for lysis [d^{-1}]	0.15 (0.05)
K_{ANs,O_2}	Oxygen coefficient [$mg_{O_2} L^{-1}$]	1
K_{ANs,NH_4N}	Ammonium ion coefficient [$mg_{NH_4N} L^{-1}$]	0.5
$K_{ANs,IP}$	Phosphorus coefficient [$mg_{IP} L^{-1}$]	0.01
<i>Nitrification step 2 (Nitrosomonas)</i>		
μ_{ANb}	Maximum aerobic growth rate on NO_2^{-} [d^{-1}]	1 (0.35)
b_{ANb}	Rate constant for lysis [d^{-1}]	0.15 (0.05)
K_{ANb,O_2}	Oxygen coefficient [$mg_{O_2} L^{-1}$]	0.1
K_{ANb,NO_2N}	NO_2^{-} coefficient [$mg_{NO_2N} L^{-1}$]	0.1
K_{ANb,NH_4N}	Ammonium ion coefficient [$mg_{NH_4N} L^{-1}$]	0.05
$K_{ANb,IP}$	Phosphorus coefficient [$mg_{IP} L^{-1}$]	0.01

9.3.2.6 Respiration

Respiration can be aerobic or anaerobic or both. Unlike fermentation respiration necessarily needs an external electron acceptor. It is an electron transport-linked phosphorylation.

where DO is dissolved oxygen and COD is chemical oxygen demand.

The term coefficient in the above table signifies for saturation/inhibition coefficient of respective elements.

9.3.2.7 Methanogenesis

Final degradation of organic compounds forming methane by the microbes is known as methanogenesis. It is carried by anaerobic microorganism called as methanogens. It is a dominating pathway for degradation of organic compounds in SSCW due to lack of oxidant in usually water logged soil. In organic matter-rich sediments, the availability of oxygen is limited only to the top few millimeters near the ground surface and near plant roots hence most of the mineralization of organic matter is carried out anaerobically. Purification of wastewater in SSCW is done by the combination of various geochemical processes which in turn governed by the hydrologic design of the wetlands. A summary of CH₄ and CO₂ generation from CWs is listed in Table 9.5. Furthermore, Table 9.6 presents the summary of study reported NO_x from CWs.

9.4 Modeling of Reactive Transport Processes of SSCWs

Having experienced an exponential comprehensive applicability of SSCW as wastewater treatment technique in recent years, it has become indeed necessary to develop mathematical models capable of simulating and predicting the wetland processes as accurately as possible. For a wetland system, a number of simultaneous and inter-related physical, chemical, and biological processes have to be considered. The existing mathematical models can be broadly categorized as

- (a) “Black box” models (e.g., correlation models, fuzzy logic models, etc.) which use the experimental data for the derivation of the model equations and
- (b) process based models which derive the governing equations from the actual processes occurring in the wetland systems. These models are of varying complexity and are primarily using, instead of experimental data in case of “black box” models, the general energy, mass, and charge balance equations. Calibration and validation of the model are also done with the help of field data.

In order to include the highly complex mechanism of SSF WC into a single model, various processes are needed to be understood and included (Langergraber and Šimůnek 2013). The sub-models based on these processes mainly include:

- flow model dealing with the water flow. It includes diffusion in the gaseous phase, convective–dispersive transport in the liquid phase, and adsorption–desorption processes between the solid and liquid phases.
- transport model dealing with the transport of constituents and adsorption and desorption processes.

Modeling complexities for VF wetlands systems are increased further due to the intermittent loading of wastewater. Therefore, the stated two model types are

Table 9.5 Summary of CH₄ and CO₂ from wetland system

Wastewater source	Study site	Plant species	Area (ha)	Carbon dioxide emission (mg m ⁻² h ⁻¹)	Methane flux (mg m ⁻² h ⁻¹)
Domestic	Nykvarn, Sweden	<i>Typha latifolia</i>	0.1	n.a.	1.9
Irrigation activities	Ormastorp, Sweden	<i>T. L. minor</i>	0.7	n.a.	3.1
Domestic	Lakeus, Finland	<i>Phragmites australis</i> , <i>T. latifolia</i>	4.4	108.3	8.4
Domestic	Magle, Hässleholm, Sweden	<i>Juncus effusus</i> , <i>T. latifolia</i> , <i>P. australis</i>	13,000	100	4.8
Peat mining runoff	Kompsasuo, Finland	<i>M. trifoliata</i> , <i>C. lasiocarpa</i> , <i>P. palustris</i> , <i>Sphagnum spp.</i>	1.9	567	16.7
Domestic	Kõo, Estonia	<i>P. australis</i>	0.0128	208	3
Domestic	Skjønhaug, Norway	<i>I. pseudacorus</i> , <i>T. latifolia</i> , <i>S. lacustris</i>	0.4	n.a.	181
Landfill leachate, fresh	Bangkok, Thailand	<i>T. angustifolia</i>	0.0003	n.a.	14.3
Domestic	Miho, Ibaraki, Japan	<i>P. australis</i>	0.0012	n.a.	3
Dairy farm wastewater	Truro, Nova Scotia, Canada	<i>T. latifolia</i>	0.0007	176	10.8

Table 9.6 Summary of study indicating NOx emission from wetland system

Wastewater sources	Study site	Plant species	Area (ha)	Nitrous oxide flux (mg m ⁻² h ⁻¹)
Domestic	Nykvarn, Sweden	Unplanted plots	0.09	0.192
Domestic	Magle, Hässleholm, Sweden	<i>J. effusus</i> , <i>T. latifolia</i> , <i>P. australis</i>	20	0.23
Peat mining runoff	Kompsasuo, Finland	<i>S. papillosum</i> , <i>S. angustifolium</i> , <i>M. trifoliata</i> , <i>Carex spp.</i>	1.9	0.014
Domestic	Ibaraki, Japan	<i>P. australis</i>	0.0012	0.079
Artificial wastewater	Ibaraki, Japan	<i>Z. latifolia</i>	0.000025	0.424
Dairy farm	Truro, Nova Scotia, Canada	<i>T. latifolia</i>	0.00066	0.25

effectively used for design and implementation of horizontal flow wetlands and free water surface wetlands only.

- Bio-kinetic model dealing with the biochemical transformations and degradation processes of the contaminants.
- Plant model describing growth, decay, decomposition, nutrient uptake, root oxygen release, etc.
- Clogging model describing the transport and deposition of suspended particulate matter (SPM). It becomes of great concern for the long run simulation of the model because of the failure risk associated with the clogging.

The two most advanced models are:

- Wetland module of HYDRUS implemented in its simulation software, and,
- COMSOL Multiphysics™ platform with BIO_PORE implemented in it (Samsó and Garcia 2013).

Both of the above models are based on the multi-component bio-kinetic models, i.e., CW2D (constructed wetland 2D) and/or CWM1 (constructed wetland model #1). A brief comparison of the two bio-kinetic model formulations (Langergraber et al. 2009) is summarized in Table 9.7.

Apart from solving the Richards equation for partially saturated flow media and convection advective–dispersion equation for heat and solute transport, the HYDRUS Wetland Module also incorporates an additional sink term for water uptake by plant roots coupled with non-equilibrium (non-linear) reactions between the solid and the liquid phases. In addition to its application with municipal wastewater, it can also be used to model TWs for treatment of combined sewer overflow. Graywater, agricultural runoff, etc. BIO_PORE model was built using COMSOL Multiphysics™ platform to reproduce the dynamic behavior of constructed wetlands

Table 9.7 Brief description of governing process and applicability of the two bio-kinetic models

Model	CW2D	CWM1
Processes	Aerobic and anoxic	Aerobic, anoxic, and anaerobic
Constituents	O ₂ , OM, nitrogen, and phosphorus (12 components)	O ₂ , OM, nitrogen, and sulfur (16 components)
Major suitability	VF CW	HF CW

where OM stands for organic matter present in the system

Table 9.8 Brief of the various sub-models in the two bio-kinetic models, i.e., HYDRUS wetland model and BIO_PORE model

Sub-model category	HYDRUS wetland model	BIO_PORE model
Flow sub-model	Richards' equation, saturated and unsaturated flow	Dynamic water table, saturated flow
Transport sub-model	Advection–dispersion, adsorption	Advection–dispersion, adsorption
Bio-kinetic sub-model	CW2D and CWM1	CWM1
Plant sub-model	Evapotranspiration, plant root uptake of nutrients	Evapotranspiration, plant root uptake of nutrients
Clogging sub-model	Excluded	Included
Applicability	More applicable for VF wetlands	Mainly developed and applied for HF wetlands

over long-term scenarios (Langergraber 2017). A number of process induced sub-models were implemented in both of the models, the summary of which is described in Table 9.8.

9.5 Use of Nanomaterials in CWs

Nanotechnology provides an effective way for in situ remediation without involving excavation of the ground or pumping water from the subsurface (Mustapha et al. 2018; Gupta and Sharma 2019; Gupta et al. 2019, 2020a, b; Gupta and Yadav 2020a, b). This technology implements the nanoparticles into the contaminated zone that either sequester the contaminant or degrade them into harmless products (Khin et al. 2012). Nanomaterials (Table 9.9) that are popularly used in SSCW includes:

Nano Zero-Valent Iron (n-ZVI) These are the most commonly used nanomaterials in SSCW for degrading pollutants like polychlorinated biphenyls (PCBs) and trichloroethene (TCE). Modified nano-particles, like bimetallic nano-particle, are form by coating n-ZVI with another metal such as palladium, [silver](#), or [copper](#). The permeable reactive barrier (PRB) due to ZVI filters out the contaminants

Table 9.9 Category of contaminants removed by nanomaterials

Category of contaminants removed	Target material	Type of nanomaterial
Metal	Arsenic/lead	One dimension TiO ₂ /Fe-doped TiO ₂
Nutrient	Nitrate	Cu/Fe/Ag-doped TiO ₂ , TiO ₂ NPs doped with Bi ³⁺
Organic	2,4,6-Trichlorophenol	Ag-doped TiO ₂
Organic	Polycyclic aromatic hydrocarbons (PAH)	Silica nanoparticles prepared by mixing salicylic acid and hyperbranched poly (propylene imine)
Metal	Removal of Co ²⁺ , Sr ²⁺ , and Ni ²⁺ from the aqueous solution	CNT with iron oxide magnetic composites
Bacteria	Removal of <i>E. coli</i> and <i>S. aureus</i> from contaminated water	CNT with silver ions and copper nanoparticles
Organic	Phenol	TiO ₂
Metal	Pb(II), Cu(II), Cd(II)	Hydrated ferric oxide
Metal removal	Removal of Zn ²⁺ , Cd ²⁺ , Cu ²⁺ , Hg ²⁺ , Ni ²⁺ , Cr ⁶⁺ from wastewater	Nano-carbon colloids and polyethylenimine

in groundwater leaving decontaminated groundwater and dissolved iron on the other side of the PRB.

Titanium Dioxide (TiO₂) TiO₂ is chemically stable, cheap, and insoluble in water. It produces highly reactive hydroxyl radicals on exposure with UV rays (sunlight) that degrades the contaminants. Titanium oxides need sunlight for its activation and hence cannot be used for in situ remediation. It is abundantly used in wastewater treatment or pump-and-treat groundwater remediation.

Metal Oxides (NMO) Nano-scaled metal oxides used for remediation in SSCW include silver, titanium, iron, and gold. They are known for their antibacterial effect against a variety of contaminants. NMO can be synthesis using thermal decomposition, reduction, hydrothermal synthesis technique with high yields (Auvinen et al. 2017). Metal oxides are formed consistent with minimizing surface energy and minimizing system entropy and hence are very effective for the remediation processes.

Carbon Nanomaterial (CNM) Carbon has a unique property of catenation that helps it to form long chain of carbon along with other elements. CNM has several advantages over conventional nanomaterials due to their larger area to mass ratio and unique structure. These properties make them powerful adsorbents, increase their kinetics, and provide selectivity towards aromatic solutes.

Although nanoparticles in SSCW are proving to be a great solution for wastewater remediation yet their proper selection and design are necessary for their effective functioning. Major challenges that incurred during application of nanomaterials are:

- Reaction with non-targeted compounds.
- Formation of unwanted products that may either reduce the effectiveness of nanomaterial or might be more harmful than the parent reactant.
- They may interfere with ongoing biological remediation process.

9.6 Conclusive Remarks and Future Outlook

Conventional treatment of polluted natural resources (wastewater/polluted soil–water) by a treatment plant typically involves primary and secondary processes for removing major contaminants before disposal. However, secondary treatment of wastewater is too expensive, and the infrastructure for domestic wastewater treatment prior to disposal is insufficient in small cities and may be non-existent in the rural and other remote communities. CWs are cost-effective approach to polish polluted sites. In this manuscript, we reviewed biogeochemical processes involved in CWs. The outcome of this research works can support and be useful to design treatment plan for sewage water and wastewater under recent schemes like Smart Cities, Swachh Bharat Abhiyan, Namami Gange of Government of India. A large scale duplex treatment wetland can be the most advanced tool for treating the discharge of wastewater from industrial units, hotels, apartments, and colonies located nearby Ganga. Better implementation of treatment wetland can help to address the problem of eutrophication and nutrient management of Ganga Basin. At household level, construction of treatment wetlands around the septic tank of toilets under these schemes can effectively reduce the pollution of soil–water resources, especially in shallow aquifer regions. One can construct a treatment wetland by planting native plants and supplying domestic wastewater. Biomass produced from the constructed wetland can be used in (vermi-) composting based on the socio-economic acceptance. By implementing such effective techniques with ongoing schemes, one can improve rural sanitation, quality of soil–water resources, and ecotourism.

Conflict of Interest No any.

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Chapter 10

Arsenic Pollution in Groundwater and Its In Situ Microbial Remediation Technologies



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Abstract Surges to combat the risk among the people regarding arsenic pollution and generate the technology for efficient removal for drinking and life stakes purposes is requisite worldwide. Around 105 countries and 226 million people are under potential threat of arsenic contamination. In India, around 90,000 km² area and 50 million people are critically affected by its contamination broadly reported in flood plains of the Ganga river. As concern about adsorption process by nanoparticles for removal of arsenic, very less work is reported in literature in field conditions which will be easily accepted by local population. Sufficient assessment, evaluation, and up-gradation of new and already existing technologies are required to mitigate the problems of its contamination effectively. This study investigates the applicability of different adsorbents and microbes explored for arsenic removal which in further might provide information on evaluating the possible scope of remediation opportunity among scientific community.

Keywords Arsenic · Remediation techniques · Adsorbents · Groundwater

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10.1 Introduction

In India, over the past decades, arsenic contamination from geological origin in sedimentary basin of the Ganga–Brahmaputra–Meghna (GBM) river basin has become most challenging problem for geochemist, environmental scientist, and policy makers to fulfil the safe drinking water demand for growing population (Fendorf et al. 2010). In early 2000s, Chowdhury et al. (2000) identified about 985 villages in West Bengal affected by high As (>0.05 mg/L) contamination in groundwater. In subsequent years (between 2000 and 2005), 9 districts of West Bengal were reported As-affected districts by Chowdhury et al. (2000); Acharyya et al. (2000); Pal et al. (2002); Rahman et al. (2003); Acharyya (2005); Mukherjee et al. (2005). Bhattacharjee et al. (2005) highlighted As-affected 3 blocks of Sahibganj district of Jharkhand, where 25% of samples had high As-concentrations. However, in this period only one study by Chakraborti et al. (2003) reported high concentration of As in Bhojpur district of Bihar state. The extension of As-contamination towards upper/middle Ganga Basin was reported by Ahamed et al. (2006) who investigated three districts i.e. Ballia, Varanasi, and Gazipur of Uttar Pradesh (UP). This study reported 26.7% of samples exceeds the 50 $\mu\text{g/L}$ and 10% of samples exceeds 300 $\mu\text{g/L}$ of As-concentration. In 2008, Chakraborti et al. (2008) reported high As-concentration (up to 502 $\mu\text{g/L}$) in Manipur Valley, Manipur. Although these studies were significant for understanding of spatial distributions of As and related health issues, it has not investigated or incorporated hydrological processes involved in As-distribution in subsurface.

Hydrological processes significantly affect the distribution of pollutant in shallow or deep aquifer regimes. In this direction, Mukherjee et al. (2007a) advances the understanding of regional hydrostratigraphy and groundwater flow modeling in the arsenic-affected areas of the western Bengal basin. In this study, lithological data collected from different sources were used to develop hydrostratigraphy of target area i.e. Delta region (Murshidabad, Nadia, North 24 Parganas, and South 24 Parganas). 3-D Modflow was used to simulate groundwater flow by incorporating hydro-meteorological data and groundwater abstraction. Results of this study indicated that pumping of groundwater containing As-contamination for agriculture increased the total recharge which further carry As from agricultural soil to groundwater in this region. More studies were explored by Mukherjee et al. (2007b) by investigating isotope signature ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of river water, rainwater, shallow and deep groundwater. Similar composition of isotopes in shallow and deep aquifers indicated vertical mixing and recharge by monsoonal rainfall. Vertical mixing of groundwater from shallow aquifers is major driver of As-contamination in deep zone (Mukherjee et al. 2011). Some researchers identified As-contamination zone using color of sediments from subsurface lithology in West Bengal (Pal and Mukherjee 2009; Rahman et al. 2015). Seasonal hydrological effects on As-contamination was investigated by Farooq et al. (2011) which showed dilution effect during monsoon and post-monsoon. However, Oinam et al. (2011) reported high As-concentration

(1–200 µg/L) in post-monsoon than pre-monsoon and monsoon in Bishnupur District, Manipur. Desbarats et al. (2014) investigated As source and movement by incorporating groundwater flow dynamics in West Bengal. This study integrates groundwater flow modeling, reverse particle tracking, and environmental tracers to locate source zone of arsenic. The study indicates that As-concentration measured in a well increases with the thickness of channel fill traversed by the flow path to the well screen. Recent studies observed As-contamination has been extending in upper and middle plains of Indo-Gangetic regions. As of now, the states such as Assam (Das et al. 2017), Bihar (Chakraborti et al. 2016a, b), Chhattisgarh (Singhal et al. 2018), Himachal Pradesh (Rana et al. 2016), Jharkhand (Alam et al. 2016), Punjab (Sharma et al. 2016), Manipur, Uttar Pradesh (Olea et al. 2018), and West Bengal (Bhowmick et al. 2018) are affected with As-contamination.

10.2 Arsenic Related Health Problems

Arsenic as gained considerable attention because of its toxic characteristics and high potential for causing severe health problems. Since last decade, adverse effects of As-contaminated drinking water on the pulmonary, cardiovascular, neuro, renal, hematological, and hepatic system have been reported (Mazumder et al. 1988; Kapaj et al. 2006; Abdul et al. 2015). A clinical examination followed by interview of 6864 participants in West Bengal by Mazumder et al. (2000) shows that skin lesions was high in participants who had >50 µg/L As in drinking water. This study also revealed that the 5 female out of 7 and 6 male out of 14 were contaminated with cough related issues in the areas of As-contaminated groundwater containing concentrations > 500 ppb. Likewise, Chakraborti et al. (2003) performed medical examination of 550 samples (390 adults and 160 children) and reported 13% of the adults and 6.3% of children with skin lesions in West Bengal. This study also reported an increase in fetal loss and premature delivery in the women with the highest concentrations of arsenic in their drinking water. Von Ehrenstein et al. (2006) have indicated a sixfold increase in the risk of stillbirth during pregnancy, as person is exposed to high concentrations of arsenic (i.e. > 200 µg/L). Singh and Ghosh (2012) performed health assessment by estimating average total dose (ATD), chronic daily intake (CDI), cancer risk (CR), and hazard quotient (HQ) along with As-concentration in groundwater in Maner Block, Patna District. Health analysis suggested a high cancer risk of 19–87/1000 children whose average daily As consumption was about 580 µg. Similarly, Singh et al. (2014) conducted similar kind of health investigation in four villages of Vaishali and Bhagalpur District of Bihar. This study indicates high cancer risk was derived as 1–5/1000 people to 5–16/10,000 people in Vaishali, and 7–21/1000 and 5–16/1000 people in Bhagalpur. Most recently, Kumar et al. (2020) performed groundwater and health assessment in Gyaspur Mahaji village, Patna district (the flood plain region of the river Ganga). As-concentration was found up to 826.4 µg/L with 86% of samples highly contaminated (>50 µg/L). This study reported 1% of population with Cancer, 3.10% with

body lump, 42.76% with breathlessness, 75.52% with gastritis and flatulence, 26.9% with anemia, 58.45% with skin problem, 7.5% with Melanosis, and 2.7% with hyperkeratosis in palm and sole. Most of these studies were performed on physical medical examination followed by interview and assessing As-concentration in water and food of participants. One can refer review by Kapaj et al. (2006); Sharma et al. (2014); Abdul et al. (2015); Quansah et al. (2015); Bhowmick et al. (2018) for more details of specific health issues related to As-contaminated groundwater and food.

10.3 Modified Conventional Arsenic Removal Techniques

Arsenic can be removed from contaminated water by physico-chemical as well as biological techniques. Coagulation, precipitation, and Lime softening are processes which chemically transform dissolved arsenic into an insoluble solid which is precipitated. Dissolved arsenic may also be adsorbed on the surface and be co-precipitated with other precipitating species. Suspended/colloidal arsenic may also be separated by coagulation and flocculation. The pH of the process highly influences the efficiency of removal. Commonly used chemicals in this technique are ferric salts, alum, manganese sulfate, ammonium sulfate, copper sulfate, etc.

Modified conventional treatment methods include coagulation with Alum or iron, Fe–Mn oxidation, and lime softening. Dissolved arsenic can form low solubility metal arsenates (e.g. calcium arsenate) upon the addition of appropriate chemicals. This solid, commonly present as a floc, can then be removed by sedimentation and filtration. A large fraction of the larger utilities affected by the new MCL standards have already installed these methods. For them, proposed the lowest-cost As removal method is to remove arsenic and reduce hardness with these conventional methods. But for very small water systems, it is not cost-effective to install a new coagulation or softening process for removing arsenic alone.

10.3.1 *Precipitation by Alum*

Generally, the compound like $\text{Al}_2(\text{SO}_4)_3$ has been reported to be utilized for the removal of arsenic in water. It occurs through the process of co-precipitation. Below pH 5, it is an effective process for the removal of As^{V} as compared to As^{III} . For As^{III} removal, it requires pre-oxidation step. A decrease in half of the arsenic removal capacity has been reported as pH increases to value of 8. After the addition of chlorine, an increase in removal percentage from 50% to 95% has been demonstrated which occur due to the enhancement of oxidation As^{III} to As^{V} . In similar study, the arsenic removal capacity of about 90% was reported during the treatment of arsenic initial concentration of 0.4 mg L^{-1} and alum dose concentration of 30 mg L^{-1} at pH 5. The chloride ions were utilized as oxidizer in this process and an acid for

decreasing the solution pH. Moreover, this method is also requiring post pH adjustment using caustic to make water portable for household usage.

10.3.2 Precipitation by Iron

This process of arsenic removal has been considered as an effective methodology as compared to those of using alum compounds. After exploring this process, the adjustment of pH was not found to be important as reported for alum. It is capable of removing arsenic effectively below the pH value of 8.5. In the pH range of 6.1–7.2, the raw water having the molar ratio of 20:1 for Fe: As lead to removal of arsenic effectively. Further, a fluid bed technology has been reported to be explored for its removal which contains an inert medium such as quartz sand grains. During this process, ferrous ions were allowed to add along with the hydrogen peroxide. This results in the precipitation of iron (oxy) hydroxide onto the surface of sand grains. A dense coating lead in providing the active sites for the binding of arsenic species. The study revealed the sorption of arsenic with the amount of 50 g kg^{-1} onto these granules. The removal mechanisms involve the processes such as addition of chemicals, their mixing, precipitation, and separation of solids and liquids. Several operations occurred within a single reactor, including adding chemicals, mixing, precipitation, and solid/liquid separation.

10.3.3 Lime Softening

This process is successful in removing the As^{V} concentration more than 90% along with the reduction of carbonate hardness. The dominating specie of arsenic in groundwater is As^{III} , as compared to As^{V} . Although, As^{V} can be more readily removed as to those of As^{III} . Using this approach, the optimum pH for the removal of As^{III} and As^{V} has been demonstrated to be 11.0 and 10.5, respectively. At pH 11, the competing ions such as SO_4^{2-} and CO_3^{2-} in inlet water was not found to affect the As^{V} removal. However, a reduction in the removal in presence of carbonates was reported between the pH ranges of 10–10.5. The PO_4^{3-} ions lead to a reduction in arsenic removal below pH 12. Therefore, several efforts are being made in developing the treatment technologies to overcome the problems related to competing ions impact on As removal. Moreover, the presence of iron has been reported to enhance the removal capacities using this process. Nowadays, the research community has focused to explore the multi-component treatment systems involving the different operational processes such as coagulation with alum or iron, precipitation, flocculation, sedimentation, and filtration.

10.3.4 Adsorption and Ion-Exchange Reactions

Some of the adsorbents such as hydroxides of iron and aluminum having the significant affinity for the arsenic species in the aqueous solution. The literature is replete of cases in the utilization of different adsorbents which provide the active sites for interaction during the arsenic removal process. Further, the ion exchange removal process involves the replacement of reversible ions which were adsorbed onto the solid surface by dissolved ions. In general, removal through adsorption has been considered to be cost-effective, easy to operate, and requires less maintenance procedures. These remediation technologies have shown a significant potential for As-removal during their usage in several well sites for providing safe drinking water to local community.

10.3.5 Adsorption by Activated Carbon

Several authors have synthesized commercial available activated carbon and investigated its capabilities for arsenic removal. A combination of GAC and carbon steel wool was explored for arsenic removal, where electrochemical reactions were known to be primary mechanism for its removal Campos, et al. (2002). Further, GAC containing mixture along with Fe, Zr, iron oxide, iron salts have been reported to be utilized for arsenic removal. An approximate of tenfold increase in the removal capacity has been demonstrated for arsenic removal. The optimum pH for As^V and As^{III} has been observed to be 5–7 and 9–11, respectively.

10.4 Worldwide Scenario of Arsenic Removal

Successful removal of arsenic from the water has gained attention from past few decades. Several nanomaterials were known to be synthesized, and examined as adsorbents for contaminants removal from groundwater. Pilot scale study observed the maximum reduction by below 50% of total arsenic by single layer and double layer sand filter at different flow rate (Janjic et al. 1997). Commonly, the water softener were also explored for As removal, but their removal efficiency was found higher only in the basic pH conditions (McNeill and Edwards 1997). Removal by coagulation with ferric chloride and alum was reported slightly above neutral pH (Hering et al. 1997). Significant mechanism involved in removal of arsenic in wetlands is sorption and/or exchange onto organic matter (Sobolewski 1999). The Ultra-filtration process for heavy metals removal in presence of humic substances has also been reported in groundwater (Alpatova et al. 2004). In a fixed bed remediation system, the polymeric cation-exchanger along with inorganic hybrid has been reported to be as most inexpensive and durable technique for arsenic

removal (DeMarco et al. 2003; Cumbal and Sengupta 2005). Cerium oxide coated with carbon nanotubes with high surface area is reported for removal of arsenic but the process is pH dependent and effected by other ions (Peng et al. 2005). A comparative study between the commercially available adsorbents and zirconium oxide was examined by (Hristovski et al. 2008). But, the concern of cost related to the use zirconium based nanoadsorbents raised their applicability in real world scenario. Novel membrane composed of ACF and Ce^{3+} - TiO_2 is used for removal of organic pollutants (Liu et al. 2010). Also, the macro-porous nanocomposite and iron oxide nanoparticles were explored for As removal which have shown the negligible common ion effect (Savina et al. 2011). Hence, continued up-gradation of the technology was reported for removal of arsenic and trace organics from water.

Enhanced adsorption is reported by using granular iron oxide metal nanoparticles impregnated with activated carbon at neutral pH (Nieto-Delgado and Rangel-Mendez 2012). Nano-powder of TiO_2/Al_2O_3 metal oxides coated with chitosan (a polysaccharide) was explored for removal of arsenic (Yamani et al. 2012). Layered double hydroxide from Cu/Mg/Fe/La is reported for arsenic removal with limiting factor of common ion effect and dependence on pH (Guoa et al. 2012). So many metal nanoparticles impregnated with organic compounds are reported in literature for removal of arsenic by adsorption (Arcibar-Orozco et al. 2012; Jiang et al. 2012; Zhu et al. 2012).

Recently, LDH/graphite oxide and functionalized nanomaterials due to its efficiency and degeneration capacity gained attention as adsorbents. Metal nanoparticles incorporated with organic matter show efficient removal due to their high surface area and good adsorption capacity. Use of $ZrO(OH)_2$ /graphite oxide shows good adsorption capacity at wide range of pH without common ion effect reported by (Luo et al. 2013). Carbon/hydroxides based nanoparticles have shown a higher adsorption capacity for As-removal, compared to those of discussed materials along with insignificant common ion affect (Vitela-Rodriguez and Rangel-Mendez 2013). Carbon nanotubes/iron oxide nanoparticles have 3D-graphene structure with mass production and high surface area shows effective removal of arsenic (Vadahanambi et al. 2013). The mesoporous structure of zirconium oxide has been reported the enhanced surface area synthesized along with the use of naturally available material i.e. agar (Cui et al. 2013).

The studies demonstrating the utilization of nanoadsorbents along with the effective designing of treatment plants for arsenic removal in the areas of Bangladesh and West Bengal has been known to be reported from the begining of twenty-first century. Use of batch mixed iron treatment plant for arsenic removal was reported (Ramaswami et al. 2001). In regard to the use of local available plant as adsorbent, *Garcinia cambogia* was explored through batch and column experiments (Kamala et al. 2005). Various natural adsorbents with their efficiency, stability, usage, desorption capacity, and sources of biomaterials for further implications were reviewed extensively in the literature (Mohan et al. 2007). Sarkar et al. (2010) have explored the efficiency of hydrated ferric hydroxide (HFO) and activated alumina (HAIX) in a filtering unit as adsorbents for Indian conditions. Electrochemical Arsenic Removal (ECAR) technology study reported for the

removal of arsenic up to $<10 \mu\text{L}$ shows enhanced coagulation of HFO particles (Gadgil et al. 2010) 28. The As removal in presence of trace organics by electro-coagulation technique has been explored for both laboratory and field conditions of Bangladesh (Wana et al. 2011). A 99.9 % As removal efficiency was observed in this study. Carbon based porous bi-metal doped multifunctional adsorbents with very high surface area was reported by (Kumar et al. 2011). Phytoremediation technology for arsenic removal is also reviewed with limitations (Vithanage et al. 2012). The As removal through adsorption by different laterites soil for both at laboratory and field (India and Bangladesh) conditions was examined by Maiti et al. (2013).

Fill and draw units, BCSIR Filter Unit, bucket treatment unit, activated alumina unit, use of iron coated sand, unit developed by Stevens Institute Technology, and arsenic removal unit attached to tube-well are commonly used arsenic removal techniques followed by rural people of India (Mukherjee et al. 2012). Removal efficiency of arsenic from groundwater reported in the order of NOIS > red soil > murum > sand can be used as a local adsorbent (Mahanta et al. 2012). The use of *Leucaena leucocephala* seed powder (LLSP) as adsorbent has been reported for As removal from groundwater (Kumar et al. 2013). Nano-cellulose fibers from rice straw were used as adsorbents for removal of cadmium, nickel, and lead ions from aqueous solution with good regeneration capacity (Kardam et al. 2014). An enhanced arsenic adsorption was observed by *Zea mays* cob powder, which was modified chemically and can be explored further as an effective material for field-scale applications (Srivastava et al. 2013).

Initially, biomaterials have not been considered as a good adsorbents because of their drawbacks related to less sorption efficiency and stability, (Pagnanelli et al. 2000). This also restricting their commercial applicability. Then, banana stalk grafted with acryl amide shows enhanced adsorption capacity of mercurous ions (Shibi et al. 2002). Later on biomaterials grafted with co-polymers show special properties including high strength, thermal stability, biodegradability, and non-toxicity (Ramakrishna et al. 2005). In another study, grafted sunflower stalks with acrylo-nitrile using KMnO_4 as redox initiator show good adsorption capacity of copper ions from the solution (Hashem et al. 2006). The copper^{II} nanoadsorbents were also explored for arsenic removal, but their removal was found to be pH dependent (Goswami et al. 2012). A good regeneration capacity of biomaterials (agricultural waste) grafted with co-polymers was reported (Goyal and Srivastava 2009). These nanomaterials were also shown the enhanced sorption efficiency and good regeneration capacity. Thus, grafting improves the adsorption capacity, selectivity, and stability of the biomaterial with good regeneration capacity.

In contrast to Indian conditions, literature showed that the technologies for effective removal of arsenic have been continuously upgraded since past two decades. Poor reliability and ineffectiveness of arsenic removal plants were reported in India due to clogging and high cost of regeneration of adsorbents, etc. (Amir Hossain et al. 2005). The use of biomaterials as adsorbents for As removal has gained a considerable concern in India, because of its easy availability and by local

communities. Also desorption of biomaterials is cost-effective and easily achieved by using soft acids and bases or even by distilled water.

10.5 In Situ Microbial Remediation Technologies

The use of engineered microbes is an attractive remediation technology for the low-cost and efficient removal of arsenic. Bioremediation of different forms of arsenic by microbial community involves their oxidation, reduction, methylation, and intracellular bioaccumulation. Arsenate uptake is mediated by phosphate transporter proteins Pst and Pit whereas arsenite is uptaken by glycerol transporter GlpF. The As(III) is pumped out by the ArsAB-ATPase. Satyapal et al. (2016) reported engineered bacteria, *C. glutamicum*, show increased efficiency for arsenic transformation and could be used as biocontainers for bioaccumulation of arsenic. The isolation and characterization of arsenite-oxidizing, arsenate-reducing bacteria indicate that they belong to the *Acinetobacter*, *Comamonas*, *Pseudomonas*, *Stenotrophomonas*, *Delftia*, *Agrobacterium*, and *Bacillus* species. NT-26 has been reported as the fastest arsenite oxidizer having doubling time of 7.6 h. Bacteria are able to anaerobically utilize arsenate as an electron acceptor and can use oxygen as electron donor and arsenite as electron donor in a chemolithotrophic manner. Some isolated genera have not been previously reported to have direct interaction with the arsenic species, for example, *Aeromonas* and *Exiguobacterium*. The two strains of micro-organisms CA1 and WK6 belonging to the species *Aeromonas* and *Exiguobacterium*, respectively. The CA1 indicates a novel pathway for arsenate reduction as no *arsB* and *arsC* was observed. Whereas, strain WK6 shows *arsB* but not *arsC*, thus indicates an *arsC*-independent pathway. *Chrysiogenes arsenatis* can respire aerobically by using arsenate as a terminal electron acceptor and acetate as electron donor. A recently identified microbial strain MM-7 of oxidizing bacterium from the genus, *Stenotrophomonas* was found to oxidize the AsIII. It can completely oxidize 500 μM of arsenite in 12 h of incubation at pH ranging from 5 to 7. *Pseudomonas lubricans* showed high resistance against arsenite up to 3 mg/mL. Satyapal et al. (2018) found that analysis of the 16S rRNA gene sequence of selected isolates revealed that they belong to the genus *Pseudomonas*. The AgNO_3 test based microplate method revealed that isolates, AK1 and AK9, have potential in transformation of arsenic species. Further, the presence of *aoxR*, *aoxB*, and *aoxC* genes in the both isolated strain AK1 and AK9 was confirmed, which play an important role in arsenic bioremediation by arsenite oxidation. Similarly, microbial reduction can also enhance the solubility of ions like Fe(III) and As(V) by reducing them to Fe(II) and As(III), respectively, and can facilitate leaching from soil. Studies have reported bacteria from different natural aquifers which can transform As (Bachate et al. 2012; Battaglia-Brunet et al. 2002). Pokhrel and Viraraghavan employed *Aspergillus niger* to remove As(V) and As(III) (Pokhrel and Viraraghavan 2006; Kinegam et al. 2008; Chang et al. 2010; Kapahi and Sachdeva 2019). Table 10.1 listed studies reported and utilized microorganisms for As removal from soil or water.

Table 10.1 Microorganisms used to remediate As-polluted soil-water systems

Microorganisms	Arsenic removal mechanisms	Media
<i>Stenotrophomonas</i> sp. MM-7 <i>Bacillus aryabhatai</i> MCC3374 <i>Ralstonia eutropha</i> Q2-8 <i>Exiguobacterium aurantiacum</i> Q3-11 <i>Pantoea agglomerans</i> <i>Rhodococcus</i> sp. <i>Pseudomonas putida</i> KT2440	As ^{III} oxidation	Soil
<i>Anabaena</i> sp. <i>Bacteroidetes</i> and <i>Proteobacteria</i> <i>E. coli</i> JM109	As ^{III} oxidation	Water

10.6 Conclusion

The removal of arsenic from groundwater using through adsorption has been recognized as viable option as compared to conventional technologies due to its easy operation. To provide the potable water in the arsenic effected areas field scale implementation of nanoadsorbents is required. To broaden the usage of nanoparticles based remediation systems, the selection of appropriate methodology for columns studies by employing boundary conditions are prerequisite in evaluating NPs reliability at larger scale applications effectively. The knowledge about the stability, efficiency, and interaction related to synthesis of functionalized nanoparticles by using easily available sources of natural biomaterials as adsorbents leads the research for scrutiny of arsenic removal technologies and selection of biomaterials in synthesis for local acceptance. Reusability of adsorbed materials and study on the management for disposal of sludge through eco-friendly way will be helpful to make the research with magnificent outcomes. Moreover, Indian literature lacks studies examining the utilization of nanoparticles for arsenic removal highlighting their applications in the real world.

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Chapter 11

An Insight into Biological and Chemical Technologies for Micropollutant Removal from Wastewater



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Abstract Over the last few decades, the occurrence of micropollutants (MPs) in wastewater has emerged as a challenging task for the scientific community. Biological treatment technologies (BTTs) are most widely used for MPs removal, including activated sludge, constructed wetland, membrane bioreactor (MBR), aerobic bioreactor, anaerobic bioreactor, microalgae bioreactor, fungal bioreactor, trickling filter, rotating biological reactor, nitrification, and biosorption. Results showed that during biological treatment some of the non-biodegradable MPs are not efficiently

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removed. Chemical treatment technologies (CTTs) including Fenton, ozonation, photolysis, photo-Fenton, photocatalysis, and electro-Fenton process have been widely used. However, the complete mineralization of MPs by CTTs is usually expensive. Therefore, a cost and resource-efficient alternative are to direct biological treatment in combination with a chemical treatment to convert the hazardous pollutants into more biodegradable compounds. This chapter provides an insight into the removal of micropollutants from wastewater treatment plants (WWTPs) by biological, chemical, and hybrid technologies. Further studies are needed for optimizing these processes, especially in terms of technical and economic perspectives.

Keywords Micropollutants · Wastewater treatment · Hybrid systems · Biological treatment technologies · Chemical treatment technologies

11.1 Introduction

Over the last few decades, the available water sources across the world have been depleted rapidly due to climate change, extensive use in agriculture and industries, rise in population, urbanization, and constant consumption of water (Kumar et al. 2016; Manikandan et al. 2016; Goswami et al. 2017a; Dutta et al. 2019). These have resulted in urgent thrive for new water sources to meet the demand, worldwide. Micropollutants (MPs), consist of a group of chemical compounds, present in the environment at trace level concentrations (ng L^{-1} - $\mu\text{g L}^{-1}$) (Sathe et al. 2020; Goswami et al. 2018a). These include pesticides, cosmetics, personal and household care products, industrial chemicals, pharmaceuticals, food additives and detergents, and many other emerging compounds. The low concentration present in the aquatic environment results in the ecological risk due to their intervention with the endocrine system in higher organisms, resistance in microorganisms, and bioaccumulation in soil, plants, and animals (Kushwaha et al. 2017a, b; Bind et al. 2019; Kumar et al. 2019).

According to the European Union (EU) over 100,000 chemical compounds are considered as MPs, out of which 30,000–70,000 are used for daily activities (Schwarzenbach et al. 2005). Also, from 1930 to 2000, the production of chemical substances has increased from 1 to 400 million tons per year, globally (Gavrilescu et al. 2015). The discharge of MPs in the environment has likely occurred for a long time, but have not been documented. The synthesis of new compounds and their disposal generate new sources of these pollutants (<http://www.norman-network.net>). Current wastewater treatment plants (WWTPs) are specifically intended to remove MPs. Thus, many MPs can pass these WWTPs which leads to their persistence in the environment. Besides, no further monitoring and precautions of these MPs have been established in WWTPs (Bolong et al. 2009). Subsequently, many of these compounds are added up in the aquatic environment, resulting in a threat to aquatic life (Pruden et al. 2006; Gupt et al. 2018; Singh et al. 2019). Till date, no standards and guidelines have been implemented for the discharge of these micropollutants.

However, EU has announced a list of 45 priority group of compounds, includes pesticides, metals, polycyclic aromatic hydrocarbons (PAHs), phthalates, and endocrine disruptors chemicals (EDCs). These compounds are of immediate concern due to their persistence and threat to environment and have been specified in Directive 2008/105/EC (Goswami et al. 2018a). Seventeen organic compounds of emerging concern were enlisted in the watch list of substances for wide monitoring by the EU–Decision 2015/495/EU (Barbosa et al. 2016). Other MPs, such as pharmaceutical personal care products (PPCPs) and steroid hormones, are yet to be included in genera pollutants. Furthermore, the scientific community and regulatory organizations should undertake the synergistic and antagonistic impact of MPs, to set the regulatory limit for the micropollutants along with their fate, behavior, and eco-toxicological effects.

In the last few years, various physical, chemical, and biological technologies have already been used for the removal of MPs (Kushwaha et al. 2015). Biological technologies are most commonly used technique for removal of MPs, including activated sludge, constructed wetland, membrane bioreactor (MBR), aerobic bioreactor, anaerobic bioreactor, microalgae bioreactor, fungal bioreactor, trickling filter, rotating biological reactor, nitrification, enzyme treatment, and biosorption (Bind et al. 2018; Goswami et al. 2019a). It has been stated that wastewater also consists of some non-biodegradable MPs which are not removed by biological technologies efficiently. Chemical technologies are also extensively used for the degradation of MPs; these include Fenton, ozonation, photolysis, and advanced oxidation processes (AOPs) such as ferrate, photo-Fenton, photocatalysis, solar drive processes, ultrasound process, and electro-Fenton process. Recently, some hybrid technologies have been used to boost the removal of MPs of varied nature (Yadav et al. 2017; Goswami et al. 2019b, c; Gupta et al. 2020). In this technology, the removal of MPs is carried out by biological treatment trailed by chemical processes or vice versa.

Thus, this chapter principally addresses the contemporary occurrence and fate of various MPs in the environment. Specifically, the chapter delineated the removal of MPs during conventional as well as advanced wastewater treatment processes by various biological, chemical, and hybrid technologies. Further, the chapter focuses on fostering a new challenge-driven approach to R&D needs in the field of biomonitoring and evaluation of the ecological risks of MPs.

11.2 Occurrence and Fate of MPs in the Environment

11.2.1 *MPs in WWTPs*

The concentration of MPs occur in influent and effluent of WWTP depends on production rate, sales and product usage, consumption of water/day/person, metabolism rate, persistence in the environment, change in climate, and elimination efficacy of WWTP processes (Fig. 11.1) (Jelic et al. 2012). The concentration of MPs reaching WWTP also depends on the production and utilization of products

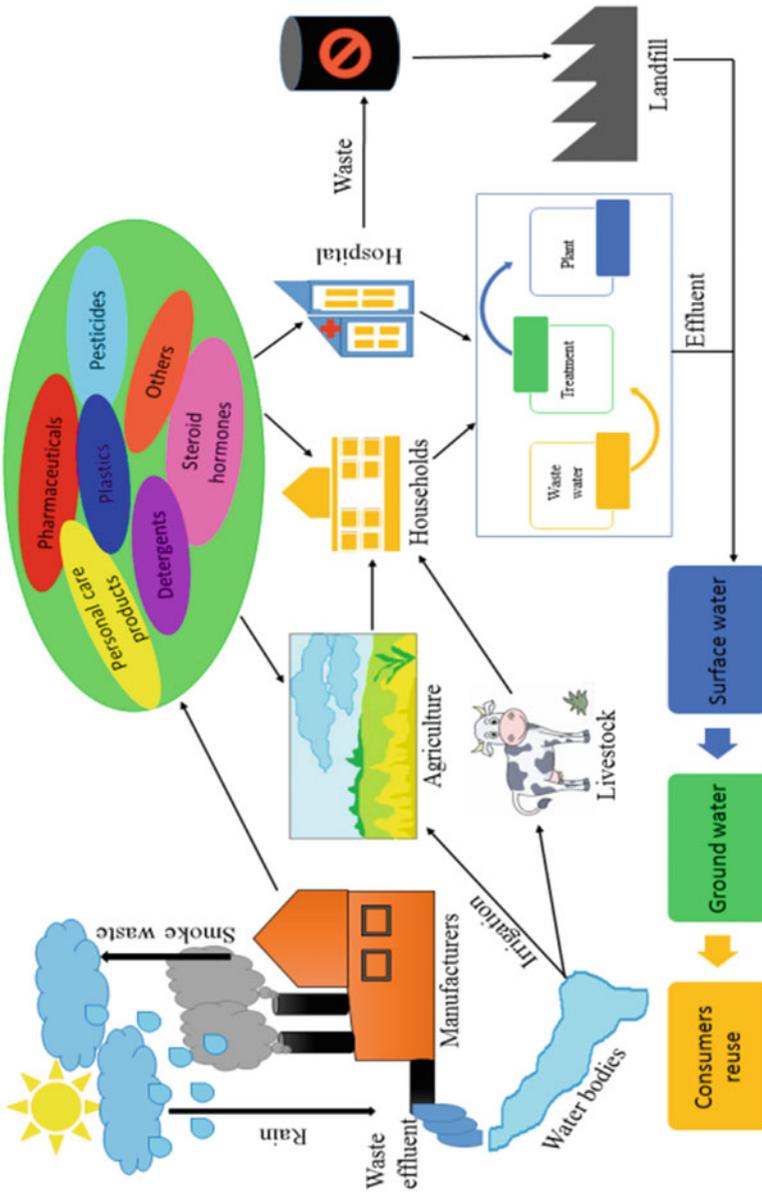


Fig. 11.1 Schematic representation of sources and routes of micropollutants in environment

comprising MPs. Choi et al. (2008) reported that the amount of acetaminophen, carbamazepine, cimetidine, diltiazem, sulfamethoxazole, and trimethoprim depends on their annual manufacture in Korea. Similarly, Kasprzyk-Hordern et al. (2009) also reported that the occurrence of acetaminophen, tramadol, codeine, gabapentin, and atenolol was highest in raw wastewater due to their higher production rate. The investigation also showed that climatic change also affects MPs usage. The use of pesticides can be periodic depending upon the climatic conditions due to the occurrence of pests (Kolpin et al. 2004). Rainfall is another significant aspect that affects the flow of wastewater when a combined sewer system is used. Kasprzyk-Hordern et al. (2009) reported that when the flow was decreased during dry weather then increase in the concentration of PPCPs was observed in raw wastewater.

11.2.2 MPs in Surface Water

The primary source of MPs in the surface water is due to the discharge of WWTP effluent. After treatment processes in WWTPs, MPs undergo natural attenuation i.e. surface water dilution, photolysis, sorption onto sediments and suspended solids and aerobic biodegradation (Pal et al. 2010). In dry weather, the concentration of MPs is significantly increased as compared to wet weather (Gómez et al. 2012). However, rainfall did not always lower the MPs concentration. In some circumstances, rainfall has been involved in increasing the concentration of MPs to surface water. Studies showed that during precipitation, chemicals (biocides and bisphenol A) used in building materials leach out and accumulate to significant levels in roof runoff and consequently result in surface water contamination (Schoknecht et al. 2009; Singer et al. 2010). In general, the densely inhabited water bodies are severely contaminated with MPs due to extensive use of these chemicals. The presence of bisphenol A (BPA), triclosan, and nonylphenol in high concentration has been reported in Guangzhou (one of the largest cities in China) surface water.

11.2.3 MPs in Groundwater

In contrast to surface water, MPs levels in groundwater were found to be low (Loos et al. 2010; Vulliet and Cren-Olivé 2011). The groundwater contamination with MPs is mainly caused by landfill leachate, sewer leakage, livestock breeding, the interaction between surface and groundwater, and intrusion of contaminated water from agricultural lands. Groundwater is mostly contaminated with triclosan, sulfamethoxazole, carbamazepine, and non-steroidal anti-inflammatory drugs. Generally, MPs concentration in septic tank leakage and landfill leachate ranged from 10 to 10^3 ng L⁻¹ and 10 to 10^4 ng L⁻¹, respectively (Lapworth et al. 2012). Usually, subsurface flow and transport such as adsorption, dilution, and travel time result in a decrease in the level of MPs from the source to groundwater (Teijon et al. 2010). The

physicochemical properties of MPs are also important for their mobility to groundwater (Dougherty et al. 2010; Karnjanapiboonwong et al. 2011).

11.2.4 Fate of MPs

The traditional WWTPs comprises primary, secondary, and occasionally tertiary treatment processes. In primary treatment, suspended substances (plastics, oils and fats, settleable solids, sand and grit, etc.) of wastewater are separated (Carballa et al. 2005). MPs removal in this step is accomplished by sorption. Carballa et al. (2004) observed 40% removal of fragrances (tonalide and galaxolide) in primary treatment as a result of a high partition coefficient between the solid and liquid phase. Stasinakis et al. (2013) stated the removal of nonylphenol monoethoxylate (13%) and Bisphenol A (43%) by sedimentation in primary treatment. During secondary treatment, biological (aerobic or anaerobic) degradation of MPs occur. The various biological treatment includes membrane bioreactors, fixed-bed bioreactors, moving bed biofilm reactor, and conventional activated sludge (CAS). Salgado et al. (2012) reported low (<25%) biodegradation of diclofenac while higher (>75%) biodegradation for ibuprofen and ketoprofen during the secondary treatment while Suárez et al. (2010) reported increased (>75%) biodegradation of tonalide, estrone and galaxolide, estradiol. Finally, the tertiary treatment uses several combinations of ozonation, activated carbon adsorption or filtration for the MPs removal from effluent.

Further, the fate of MPs in the subsurface environment is greatly influenced by its physicochemical properties, such as octanol-water partition coefficient (Kow), downgradient (Dow), and solubility in water (Sedlak and Pinkston 2001; Wells 2006) and other environmental conditions. MPs in soil surface drift through the soil zone (Oppel et al. 2004), unsaturated zone, and finally saturated zone (Snyder et al. 2004; Zuehlke et al. 2004). The migration of MPs in the subsurface can be controlled by sorption to clay and organic matter, microbial transformations or degradation, ion exchange in the aquifer.

11.3 Biological Treatment Technologies (BTTs)

11.3.1 Conventional Treatment Processes

11.3.1.1 Biological Trickling Filter (BTF) and Biofilm Reactor

It consists of a three-phase system which comprises fixed biofilm bed. In a bioreactor, wastewater is trickled over a fixed biofilm surface, and air moves upward and downward (Daigger and Boltz 2011). In WWTPs, BTF has been widely used for removal of chemical and biological oxygen demand, decontamination of

pathogens, and odor removal but their use for MPs removal have been limited (McLamore et al. 2008; Naz et al. 2015). BTF was used either alone or in association with other processes (e.g. activated sludge). Depending on the bioprocesses (activated sludge, trickling filter, and aerated lagoons) used, the removal efficiencies vary from complete to no removal. Kasprzyk-Hordern et al. (2009) evaluated the removal of 55 PPCPs, drugs, EDCs during treatment of wastewater from South Wales by trickling filter and activated sludge over 5 months. They found that MPs were more efficiently removed by activated sludge processes than trickling filter beds. Therefore, there is a necessity to modify or develop the current bio-trickling processes for achieving improved removal efficiency for a wide range of MPs. Moreover, Zupanc et al. (2013) studied the removal of pharmaceuticals using a moving bed biofilm reactor. The highest removal was observed for ibuprofen (94%) followed by naproxen (70–80%) and diclofenac (74–85%), but least removal was detected for clofibrac acid (5–28%), ketoprofen (63–73%), and carbamazepine (0–1%).

11.3.1.2 Biological Nitrification and Denitrification

Nitrification is the oxidation (biological) of ammonium to nitrites and nitrite is further oxidized to nitrate, and denitrification is the biological reduction of nitrite/nitrate to molecular nitrogen. This type of process is often applied in association with the membrane bioreactor (MBR) for wastewater treatment. Phan et al. (2014) studied the removal of MPs under nitrifying and denitrifying conditions in MBR. The retention time for sludge was 25 days and autotrophic bacteria carried out the nitrification process under the aerobic condition and anoxic condition denitrification process. These conditions support the growth of both nitrifying and heterotrophic bacteria that efficiently increased the MPs removal.

Phan et al. (2014) found 82–100% removal of PCPs (benzophenone, galaxolide, oxybenzone, salicylic acid, and tonalide) and EDCs (estrone (E1), 17- α -ethinylestradiol (EE2), 17 β -estradiol (E2), estriol (E3), BPA, 4-tertbutylphenol, and 4-tert-octylphenol) by denitrification process. On the other hand, only 8–32% removal was observed for fenoprop and atrazine while 88–98% removal was observed for pentachlorophenol and triclosan. Furthermore, the nitrification process significantly removes EDCs (estrone, 17 α -ethinylestradiol, 17 β -estradiol, galaxolide, tonalide, ibuprofen (IBU), naproxen, erythromycin, and roxythromycin). The removal efficiency by nitrification process of various MPs follows the order: EDCs > PCPs > pharmaceuticals.

11.3.1.3 Biological Activated Carbon (BAC)

In general, activated carbon (AC) especially granular used for MPs removal become saturated with contaminant resulting in loss of effectiveness of AC. Therefore, microorganisms are immobilized on the surface of granular activated carbon (GAC) and these microorganisms dwell inside the pores of the granular carbon

(Gerrity et al. 2011; Reungoat et al. 2012). In comparison with other biofiltration process, BAC filters offer high adsorption capacity, increased removal efficiency along with biofilm development. As compared to other materials (clay, sand, and anthracite) rough surface and high porosity of GAC stimulate microbial growth by providing better attachment (Luo et al. 2014a, b; Sbardella et al. 2018). The use of both biodegradation and adsorption mechanisms simultaneously can remove a wider range of MPs, thereby increasing the potential application of such technology in tertiary treatment (Kalkan et al. 2011; Velten et al. 2011). It has been reported that the BAC process showed better removal efficiency when used after ozonation and coagulation (Kalkan et al. 2011; Zhang et al. 2017). Zhang et al. (2017) reported that removal of pharmaceutically active compounds (PhACs) in surface water was increased to 75% when the BAC process is applied after coagulation and clarification process. Gerrity et al. (2011) studied the removal of PhACs using ultrafiltration (UF) and ozone preceded by BAC and the system effectively decreased the PhACs concentration in WWTP. Sbardella et al. (2018) studied the removal of PhAC using BAF-UF process in tertiary treatment. This treatment effectively removed antibiotics (78%), beta-blockers (89%), psychiatric drugs (83%), and other therapeutic groups (79%). Reungoat et al. (2012) investigated the removal of trace organic chemicals (TOCs) from the effluent of WWTP. They reported the combination of BAC filtration and ozonation could effectively remove >90% of TOCs.

11.3.1.4 Microalgae/Fungi Based Treatment

The treatment of wastewater by microorganisms is a sustainable and cost-effective approach (Goswami et al. 2017b). Microorganisms based system has been showed to efficiently remove MPs by enzymatic degradation (de Wilt et al. 2016; Matamoros et al. 2016). The extracellular enzymes produced by fungi are well-known to degrade MPs having low water solubility (Cajthaml et al. 2009). Several fungal species such as *Trametes versicolor*, *Phanerochaete chrysosporium* is known to have promising PhACs degrading capabilities (Castellet-Rovira et al. 2018). *P. chrysosporium* was investigated for the removal of diclofenac (DCF), ibuprofen (IBU), naproxen (NPX), psychiatric drugs carbamazepine (CBZ), and diazepam in a sterile medium under various operational conditions. In the stirred tank, when the biomass of *P. chrysosporium* was immobilized as pellet with hydraulic retention time (HRT) of 1 day, DCF, IBU, and NPX were completely removed (Rodarte-Morales et al. 2011; Rodarte-Morales et al. 2012). In fluidized bed bioreactor, *T. versicolor* pellet was investigated for removal of CBZ and sulfonamides antibiotics such as sulfamethazine (SMT), sulfathiazole (STZ) and sulfapyridine (SPY), 54% CBZ removal ($200 \mu\text{g L}^{-1}$ initial concentration), and >94% sulfonamides removal (5 mg L^{-1} initial concentration) (Jelic et al. 2012; Rodríguez-Rodríguez et al. 2012).

On the other hand, wide attention has been made for treating wastewater by microalgae (phytoplankton) mainly because of resource recovery of algal biomass, utilized as fertilizer and biofuel (Passos et al. 2014; Matamoros et al. 2015). In some raceway reactors bacteria and microalgae are grown symbiotically for removal of

MPs. In such type of systems, heterotrophic bacteria consume oxygen produced due to micro-algal photosynthesis and degrade organic matter (Passos et al. 2014). Shi et al. (2010) reported the 95% removal of EDCs (E1, E2, and EE2) at $1 \mu\text{g L}^{-1}$ in the algae-based polishing pond. Matamoros et al. (2015) reported 85 and 93% removal of BPA and octylphenol, respectively, by microalgae. de Wilt et al. (2016) performed the batch experiment for removal of CBZ, diclofenac, IBU, trimethoprim, paracetamol, and metoprolol using *Chlorella sorokiniana*. They observed 60–100% removal of IBU, diclofenac, paracetamol, and metoprolol whereas 30 and 60% removal was observed for CBZ and trimethoprim, respectively. Peng et al. (2014) observed approximately, 10% removal of norgestrel and progesterone when dead cell biomass of *Chlorella pyrenoidosa* and *Scenedesmus obliquus* was used for adsorption.

11.3.1.5 Activated Sludge Process (ASP)

Among all conventional wastewater treatment processes, this type of system is most commonly used for the removal of MPs. This process employs the use of bacteria and protozoa for the treatment of industrial and sewage wastewaters. Microorganisms present in system break down organic matter into water, carbon dioxide, and inorganic compounds. EDCs (androstenedione, androsterone, EE2, coumestrol, E3, E1, 2 hydroxy estrone, alpha hydroxyl estrone, progesterone, testosterone, BPA, and octylphenol) showed complete removal (100%) at $15\text{--}700 \text{ ng L}^{-1}$ concentration by ASP (Liu et al. 2009; Semblante et al. 2015).

11.3.1.6 Aerobic, Anaerobic, and Facultative Microbiological Treatment

In the primary and secondary treatment of wastewater, MPs are sorbed on suspended solids and as an outcome they are present in sludge through sedimentation (Stasinakis et al. 2013). The bioreactor based on aerobic, anaerobic, and facultative treatment has been used for sludge stabilization produced from activated sludge (Zhao et al. 2008). The mechanism involves the utilization of MPs by bacteria and converting them into CO_2 . For sludge stabilization anaerobic digestion is one of the utmost used processes. The treated sludge is used for agricultural purposes or discharged in soil (Yang et al. 2016). The degradation of MPs by bacteria depends on several factors such as microbial community, pollutants bioavailability, contact time, etc. (Besha et al. 2017; Grandclement et al. 2017; Kushwaha et al. 2018). Many researchers reported the degradation of a wide variety of MPs (bisphenol A, polycyclic aromatic organics, nonylphenol, and pharmaceutical compounds) by bacteria (Goswami et al. 2017c; Goswami et al. 2020). Depending on the HRT of wastewater and MPs concentration the removal efficiency by these bacteria ranged between 60 and 100%. Roh et al. (2009) studied the biodegradation of MPs (BPA, IBU, and triclosan) in nitrifying activated sludge by *Nitrosomonas europaea*. They observed

that BPA ($0.7\text{--}1.6\text{ mg L}^{-1}$ initial concentration) and triclosan ($0.5\text{--}2\text{ mg L}^{-1}$ initial concentration) were degraded by *N. europaea* but unable to degrade IBU. Some EDCs (BPA, nonylphenol, E2, EE2) were efficiently removed by aerobic degradation process. In aerobic lagoons, 65–100% pharmaceuticals compounds were removed due to increased HRT (Buttiglieri and Knepper 2007; Conkle et al. 2008).

11.3.2 Non-conventional Treatment Processes

11.3.2.1 Membrane Bioreactor (MBR)

Recently, MBR is considered as a contemporary technology for the treatment of wastewater comprising MPs. MBR is a hybrid technology combining activated sludge biological treatment and membrane filtration. Moreover, MBR can efficiently remove an extensive spectrum of MPs including compounds that are resilient in ACP and CWs (Radjenovic et al. 2007). The increased efficiency of MBR is due to the extended solid retention time (SRT) which promote degradation of compounds by microbes. Additionally pollutants with a molecular weight larger than the membranes are retained (Ahmed et al. 2017). The MPs removal in MBR can be affected by various factors, such as the existence of anoxic and anaerobic sections, concentration and age of sludge, wastewater composition, temperature, conductivity, and pH (Kovalova et al. 2012; Luo et al. 2014a, b). Various advantages of MBRs over conventional processes include less space requirement and high effluent quality performance at higher SRT, increased removal rate of MPs, low feed to microorganism ratio (F/M), high biomass and less sludge bulking problem, low-rate sludge production (Le-Clech 2010; Ngo et al. 2012).

MBRs are implemented for varied classes of MPs such as EDCs, PPCPs, pesticides, etc. In comparison to conventional activated sludge (CAS) process which removes 15–80% removal rate, MBR system further reduces the MPs level by 20–50% (Goswami et al. 2018b). However, in the case of pollutants that are highly degraded in CAS or recalcitrant compounds, the MBR system did not show significant removal (Hai et al. 2011). Some authors concluded that removal efficiency of MBR and CAS system is comparable for certain EDCs, pharmaceutical, naphthalene sulfonates, benzothiazole-2-sulfonate, and fragrances (Clara et al. 2005; Joss et al. 2005). Trinh et al. (2012) studied the removal of MPs in the MBR system and observed >90% removal for most of the MPs. However, some MPs (carbamazepine, amitriptyline, diazepam, fluoxetine, diclofenac, gemfibrozil, sulfamethoxazole, omeprazole, and trimethoprim) were moderately removed (24–68%). Kovalova et al. (2012) studied the pilot-scale MBR for hospital effluent. They found only 22% removal of pharmaceutical and metabolites, since a large portion (80%) of the feed was persistent iodinated contrast media. Kim et al. (2007) investigated the removal of hormones and pharmaceuticals in the MBR system. They observed approximately 99% removal of hormones (E3, androstene-dione, and testosterone) and pharmaceuticals (acetaminophen, IBU, and caffeine). Gruchlik et al. (2018)

studied the removal of 15 EDCs (initial concentration 1–5 $\mu\text{g L}^{-1}$) by MBR system. They observed removal efficiency ranged between 92–99% for each EDC compound. Vyrides et al. (2010) observed 99% triclosan, 70–80% beta-blockers, 97% atendol were removed in the MBR system. However, during the removal of pharmaceuticals compounds, the MBR system exhibited mixed performance. For example, 75–95% removal was observed for antibiotics (azithromycin, clarithromycin, erythromycin, ofloxacin, and sulfamethaxazole), analgesics (carbamazepine, citalopram, IBU, lorazepam, metronidazole, primidone, and trazodone), anti-inflammatory drug (acetaminophen), and stimulant (caffeine) in MBR system (Besha et al. 2017). Conversely, other pharmaceuticals were insufficiently removed. The removal efficiency of MPs in MBR system was in the order EDCs > PCPs > beta-blockers > pharmaceutical compounds > pesticides (Le-Clech 2010; Ahmed et al. 2017; Gruchlik et al. 2018).

11.3.2.2 Constructed Wetlands (CWs)

Since, wetlands occurring naturally can eliminate contaminants existing in the water that flows through thereby improving the quality of water. Therefore, to replicate the process artificial wetlands are constructed in more controlled conditions (US EPA 2004). Currently, CWs are used for treating wastewater effluents especially for treating domestic sewage effluents (Gorito et al. 2017). CWs system consists of the substrate, water, plants, and native microflora. The removal of pollutants is achieved by integrated combination of physical (sorption and sedimentation), chemical (oxidation), and biological (biodegradation) processes in association with soil, substrate, and plant (Töre et al. 2012; Zhang et al. 2014; Kushwaha et al. 2019). Soil plays a significant role by providing support for the growth of plant and microbes (Ahmed et al. 2017). Various factors influence the processes that occur during pollutant removal in CWs. For example, volatilization depends on the pollutants vapor pressure, therefore, higher the vapor pressure of pollutant more likely it will volatilize (Suthersan 2002). The physicochemical properties greatly influence the sorption of MPs in the soil. The change in light intensity and absorbance spectrum of specific pollutant influence the photodegradation (Zhang et al. 2014).

Factors like CWs design and operating conditions (substrate/soil matrix, wetland configuration, substrate depth, plant species, HRT and operational mode i.e. batch or continuous) affect the pollutant removal (Zhang et al. 2014; Borah et al. 2019). CWs are categorized as surface flow CWs (SFCWs), horizontal subsurface flow CWs (HS SFCWs), and vertical subsurface flow CWs (VSSFCWs). Gorito et al. (2018) studied the removal of MPs from non-spike freshwater aquaculture effluents and spiked MPs (100 ng L^{-1}) using *Phragmites australis* in VSSFCWs at microcosm level. They found >87% removal of MPs from both non-spiked and spiked microcosms. Töre et al. (2012) observed 75–100% removal of E1, E2, EE2, steroid estrogens, bisphenol A, and phthalates. Rühmland et al. (2015) studied the removal of pharmaceuticals compound and human metabolites in a SFCWs, a pond, and a pond with floating plants. They found that photodegradable pharmaceuticals compounds were

removed more (>70%) in the pond during summer. Zhang et al. (2012) investigated the removal of pharmaceutical compounds in SFCWs and categorized the compounds into three groups depending on their removal efficiency: (1) Compounds (salicylic acid and ketoprofen) that are efficiently removed having removal efficiency >85%; (2) compounds (IBU, naproxen, and caffeine) are moderately removed having removal efficiency between 50% and 85%; and (3) compounds (diclofenac, carbamazepine, and clofibrac acid) that are poorly removed i.e. efficiency <50%. Petrie et al. (2018) studied the removal of MPs (PPCPs and illicit drugs) in HSSFCWs in the presence of *Phragmites australis* and reported >50% removal of MPs.

11.4 Chemical Treatment Technologies

11.4.1 Conventional Oxidation Processes

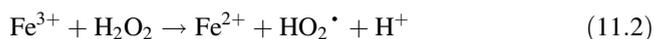
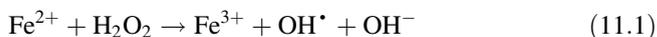
11.4.1.1 Ozonation

Conventional technologies (filtration, chlorination, and coagulation-flocculation) are not appropriate for removing MPs from WWTPs (Saqib et al. 2010). Therefore, ozonation is an efficient technology for removing MPs from WWTPs. Ozone acts as an electrophilic molecule that explicitly reacts with a high electron density molecule in MPs such as aromatic rings and double bonds (Gomes et al. 2017). Sui et al. (2010) examined the efficiency of ozonation for removing diclofenac, carbamazepine, metoprolol, indomethacin, N, N-Diethyl-meta-toluamide (DEET), bezafibrate, trimethoprim, and sulphiride. In general, all MPs were efficiently removed (>95%) except metoprolol and DEET, which were moderately removed while bezafibrate showed the least removal (14%). Hernández-Leal et al. (2011) investigated the removal of MPs (fragrance, surfactant, biocide, and UV-filter) from graywater (biologically treated) by ozonation. They observed >79% removal of all MPs at 15 mg L⁻¹ ozone dose. In another study, Lee et al. (2014) predicted the removal of MPs in hospital wastewater by ozonation. They found two-thirds of MPs present in hospital wastewater are efficiently removed (>80%) with an ozone dose of 5 g O₃ g⁻¹ dissolved organic carbon (DOC). Gerrity et al. (2011) studied the removal of steroid hormones and PPCPs by O₃/H₂O₂ treatment. The treatment removed (>90%) all MPs except tris-(2-chloroethyl)-phosphate and tris-(2-chloroisopropyl)-phosphate was less efficiently removed (<30%) while atrazine and IBU were moderately removed (60–90%). Ahmed et al. (2017) reported that ozonation showed high efficiency in removing EDCs and pesticides. They concluded that the increased efficiency is due to their high octanol-water partition coefficient (K_{ow}). Zhang et al. (2012) reported EDCs were more efficiently removed at lower pH from synthetic secondary effluent by ozonation.

11.4.1.2 Fenton Process

Fenton process has found to be effective in MPs removal. It involves the production of hydroxyl radicals (OH^\bullet) due to the reaction between hydrogen peroxide (H_2O_2) and ferrous ions under acidic condition (Kavitha and Palanivelu 2004; Escher et al. 2006). The advantages of the Fenton process includes: (1) use of environmentally safe reagents; (2) reaction time is short; (3) no energy requirement for activation of H_2O_2 ; (4) easy operating principle; and (5) limitation of mass transfer (Kajitvichyanukul and Suntronvipart 2006; Velásquez et al. 2014). Moreover, the Fenton process can be applied as pre-treatment to enhance the biodegradability of contaminants in wastewater especially recalcitrant contaminants (Tekin et al. 2006; Sanchis et al. 2013).

In solution, OH^\bullet tend to remove the electron from substance and generate hydroxide anion. To compensate the lost atom, OH^\bullet gain hydrogen atom from hydrocarbons. At the first step, the degradation of pollutant is very fast. This can be attributed due to the presence of Fe^{2+} species in solution which rapidly generates OH^\bullet . At the second reaction step, the reaction rate decreases due to depletion of Fe^{2+} and formation of Fe^{3+} . This is due to the reaction between Fe^{3+} and H_2O_2 and results in the generation of perhydroxyl radical (HO_2^\bullet). The resultant HO_2^\bullet is weaker oxidant as compared to OH^\bullet Eqs. (11.1) and (11.2) (de Luna et al. 2013).



Guo et al. (2015) observed 80% removal of amoxicillin when Fenton reaction was used as a pre-treatment process for the conventional activated sludge process. Chi et al. (2013) investigated the removal of EDCs and PPCPs from biologically pre-treated municipal wastewater using heterogeneous Fenton process. They observed 90% and 40% removal of EDCs and PPCPs, respectively. Ifelebuegu and Ezenwa (2011) achieved 95% and 98% removal of E2 and EE2, respectively, by Fenton oxidation process. Li and Zhang et al. (2014) studied the removal of E1, E2, E3, and EE2 from waste activated sludge using Fenton oxidation. They observed the removal efficiencies of E1, E2, EE2, and E3 were 70%, 90%, 84%, and 98%, respectively, under following conditions: 15.62 mmol g^{-1} H_2O_2 dosage; pH 3; 60 min, Fe (II) to H_2O_2 molar ratio = 0.167.

11.4.1.3 Photolysis

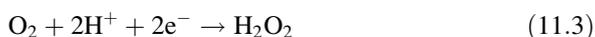
Photolysis has been one of the most broadly investigated processes for treating wastewater. In this process, MPs break down due to absorption of photons (Yan et al. 2015). Though sources of light can vary, UV has frequently used the technique for disinfection of water. Photolysis can be of two types, namely, direct and indirect photolysis. In the direct photolysis, the pollutant directly absorbs photons and gets

degraded while in indirect photolysis, degradation of pollutants occurs in the presence of photosensitizers (Andreozzi et al. 2003; Ahmed et al. 2017). Kim et al. (2009) studied the removal of 41 pharmaceutical compounds by UV and UV/H₂O₂. UV only showed >90% elimination of diclofenac, ketoprofen, and antipyrine while the addition of H₂O₂ increased the efficacy of the process and showed 90% elimination of 39 compounds. De la Cruz et al. (2012) studied the comparative removal of 32 MPs by UV, UV/H₂O₂, Fenton, and photo-Fenton. UV radiation (10 min) showed 46% MPs removal while ketoprofen, diclofenac, diuron, and mefenamic acid was complete. In contrast, UV/H₂O₂ showed 81% removal of MPs and when UV was applied to the Fenton process it showed 97% MPs removal. Further, the photo-Fenton process showed significant degradation of MPs.

11.4.2 Advanced Oxidation Processes (AOPs)

11.4.2.1 Electro-Fenton Processes (EFPs)

EFP is one of the most current AOPs and has been developed to overcome the limitations of conventional technologies for pollutant removal. EFP couples the Fenton's process with electrochemistry. It has been extensively used for treating wastewater and pharmaceutical compounds (García-Montoya et al. 2015). In the first stage, Fenton reagent are added externally and an inert anode material having high catalytic activity are used while in the second stage, only H₂O₂ is added from outside and Fe²⁺ is delivered from iron anodes (Jiang and Zhang 2007). Compared to classical Fenton process, in EFP H₂O₂ is generated and transported in a more controlled way. The incessant supply of H₂O₂ to the solution is performed by reduction of two-electron oxygen in an acidic medium according to Eq. (11.3).

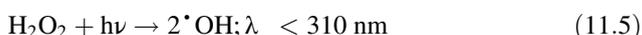


Since, no harmful reagent is used in EFP, it is an environment-friendly approach for treating wastewater (Munoz et al. 2005). However, for complete mineralization of solutions electrolysis requires longer time duration, thus, requires increased energy consumption thereby increasing the EEPs cost (Faouzi et al. 2006; Oturan et al. 2013). Thus, to reduce the cost of the process, the amalgamation of EFPs with biological treatment can reduce the electrolysis time and mineralization is attained by biological treatment (Olvera-Vargas et al. 2016). Sires et al. (2007) studied the removal of chlorophene, triclosan, and triclocarban using EFP. They reported complete removal of triclosan under optimized conditions (60 mA for 45 min and 300 mA for 30 min). The elimination and mineralization of sulfamethoxazole and sulfachloropyridazine were investigated using anodic oxidation and EFP. EFP was more efficient and fast in removal and mineralization of pharmaceutical compounds and their intermediates as compared to the anodic oxidation (Dirany et al. 2010; Dirany et al. 2012). Other researchers also reported the effective degradation of

innumerable categories of pollutants by EFP, such as IBU (Skoumal et al. 2009), salicylic acid (Feng et al. 2013), and paracetamol (Su et al. 2012).

11.4.2.2 Photo-Fenton Process (PFP)

PFP couples the UV light and Fenton reagent (H_2O_2 and Fe^{2+}). The generation of $\cdot\text{OH}$ radicals takes place by two reactions: (1) photo-reduction of Fe^{2+} to Fe^{3+} Eq. (11.4) and (2) photolysis of H_2O_2 Eq. (11.5). The Fe^{2+} produced enters the Fenton process to generate $\text{OH}\cdot$.



de Lima Perini et al. (2013) observed complete removal of ciprofloxacin by PFP within 10 min in the presence of iron citrate or iron oxalate at 4.5 pH. De la Cruz et al. (2012) studied the removal of 32 MPs from domestic wastewater by PFP and observed 98% removal after 30 min of treatment. Klammerth et al. (2013) investigated the degradation of MPs in municipal WWTP effluents. They reported 95% removal of the contaminant at pH 3 but the only drawback was that water has to be acidified before treatment. Matos et al. (2012) reported 70% and 60% degradation and mineralization of abamectin within 60 and 180 min UV radiation, respectively.

11.4.2.3 Photocatalysis

Photolysis is the photodegradation of compounds by the action of the photocatalyst. The photocatalyst accelerates the photoreaction by interacting with chemicals in their ground or excited state (Serpone and Emeline 2002). Generally, the photocatalyst is semiconductor metal oxides having a low bandgap. After absorption of photon energy, excited electrons in catalyst change energy levels. On the contrary, in valence band an electron vacancy (h^+) occurs resulting in migration of electron-hole pair towards photocatalyst's surface where it carries out the redox reaction with compounds (Dalrymple et al. 2007). The reaction between h^+ and water and/or H_2O_2 results in the generation of $\text{OH}\cdot$ which acts as oxidant agent. Photocatalysts used titanium dioxide (TiO_2), zinc sulfide (ZnS), zinc oxide (ZnO), ferric oxide (Fe_2O_3), tin oxide (SnO_2), silicon (Si), and cadmium sulfide (CdS). In the last few decades, due to inert nature, cost-effectiveness, and photostability, TiO_2 has been the most extensively used photocatalyst (Rajeshwar et al. 2001; Gaya and Abdullah 2008). Coleman et al. (2005) studied the effect of platinum and silver metals on the degradation of EDCs using TiO_2 . They observed 98% degradation of 7- α -ethinyloestradiol (0.82 mg l^{-1}) in 3.5 h while no significant effect of platinum and silver metal was observed in the degradation of EDCs. Miranda-García et al. (2011) observed E1, E2, EE2, E3, bisphenol A, and progesterone was degraded up to

100% in stimulated and municipal WWTP effluent using immobilized TiO₂. Elmolla and Chaudhuri (2010) investigated the degradation of antibiotics (cloxacillin, amoxicillin, and ampicillin) in the presence of TiO₂, H₂O₂ under UVA (365 nm) irradiation. Authors observed that addition of H₂O₂ resulted in complete degradation of antibiotics in 30 min at pH 5.

11.5 Hybrid Technologies

Conventional technologies (activated sludge) are not able to efficiently eliminate most of the MPs. As a consequence, hybrid technologies are well appropriate for MPs removal from wastewater. This technology employs a combination of two or more processes. Indeed, a combination of two processes enhances the removal of recalcitrant MPs due to synergistic effects. The removal of poorly biodegradable compounds by adsorption is enhanced when activated carbon is added (Alvarino et al. 2016). The combination of MBR and oxidation process efficiently removes pharmaceutical compounds and EDCs from wastewater. Similarly, the oxidation process with biological system showed nearly 100% removal of Beta-blockers and pesticides from wastewater (Babuponnusami and Muthukumar 2014; Ahmed et al. 2017; Gruchlik et al. 2018). Falås et al. (2013) studied the efficiency of suspended and attached growth hybrid process by a combination of activated sludge and biofilm carriers in removing MPs. The hybrid system significantly removed diclofenac. Casas et al. (2015) investigated the removal of MPs from hospital wastewater by a combination of activated sludge and biofilm and most of the pharmaceuticals were significantly removed. Ooi et al. (2018) studied the removal of pharmaceuticals in pilot-scale plant consisting of bed biofilm reactor (MBBR) in combination with nitrifying and denitrifying processes. They observed 8 compounds were completely removed after 24 h of treatment.

11.6 Biomonitoring and Risk Assessment for Micropollutants

EU Water Framework Directive (2000/60/EC) recognized three monitoring approaches namely surveillance, operational, and investigative monitoring. Surveillance assesses the long-term changes caused by anthropogenic activity, operational monitoring evaluates the status of groundwater bodies being at risk, and investigative assesses the complications arising from the first two. The continued vigilance in evaluating the effects of emerging pollutants is essential to ensure the long-term security and sustainability. The risk assessment can be performed in following four steps: (1) problem formulation, (2) assessment of exposure-response, (3) exposure characterization, and (4) risk characterization (Clarke and Smith 2011). It highlights

the need for a link between R&D for assessing the emerging pollutants and tools for its treatment. Therefore, an integrated approach is necessary for assessing the source and their removal through various treatment and remediation technologies, without neglecting the jeopardies they pose to the environment and humans (Fig. 11.2).

11.6.1 Problem Formulation

Project formulation is the development of the assessment strategy. It is based on four major principles i.e. prevention of pollution, assessing the threshold in the ecosystem, community reclamation, and functional redundancy (Brock et al. 2006). In this key step, scientists and policy-makers have to work together in the establishment of goals: policy-makers should set standards for protecting the ecosystem, an equilibrium between ecological and economic consequences, while scientists should provide sufficient data in support of policy (Brock et al. 2006; Quevauviller 2006).

11.6.2 Hazard Characterization

The hazard characterization is based on the assessment of various endpoints associated with diverse organisms including both humans and nonhumans. The reference value should be based on acute and chronic toxicity, no-effect dose, and permissible daily intake. Along with this, synergistic and additive effects of compounds having the same mode of action should be undertaken. However, identification of pollutants cannot be exclusively based on chemical analyses, since such analyses do not provide evidence about its bioavailability and toxicity (Baun et al. 2006; Schriks et al. 2010). Therefore, the endpoints for emerging contaminants are based on quantitative structure-activity relationship (QSAR) approach. Also, the biodistribution of compounds can be assessed based on pharmacokinetic models (Geissen et al. 2015).

11.6.3 Exposure Characterization

The exposure characterization in the case of emerging pollutants is difficult due to the scarcity of information on both environmental exposure and response, which leads to difficulty in building conceptual models. Thus, it is important to take into account the human metabolism, the efficiency of various WWTPs, and concentration of pollutants in the environment (Lamastra et al. 2016).

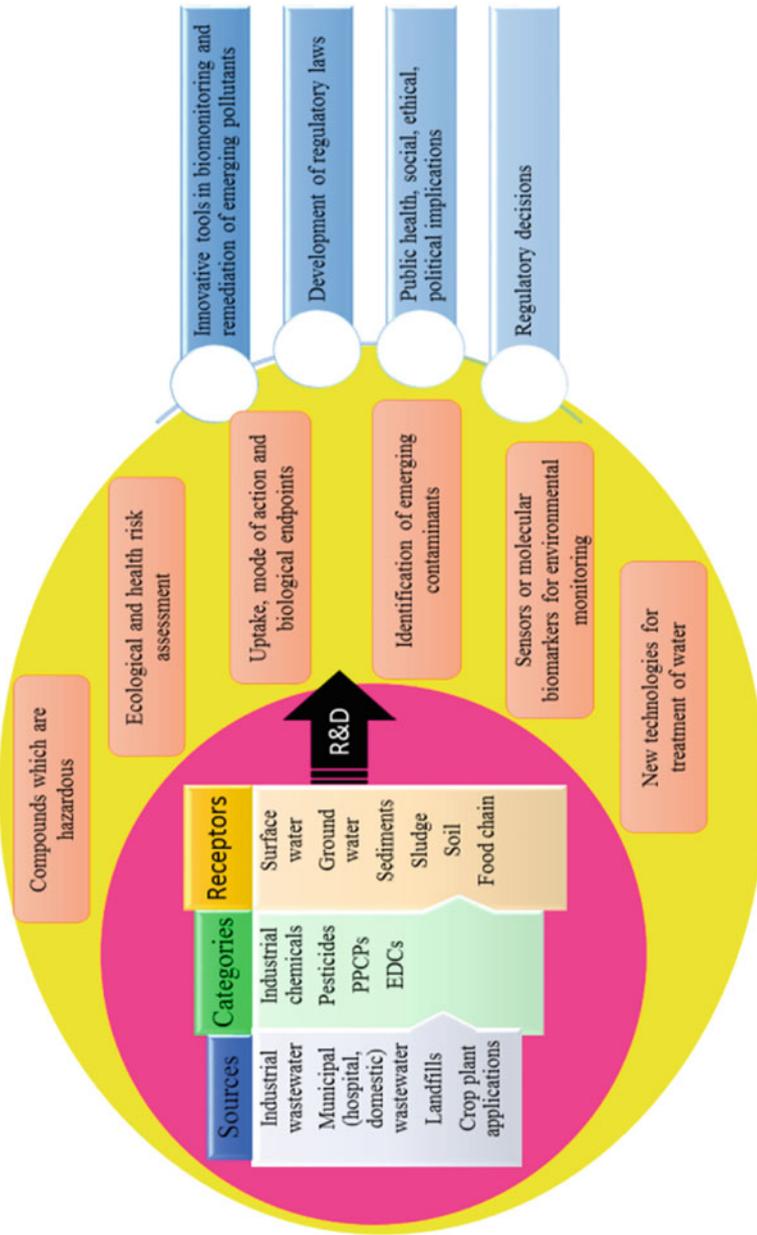


Fig. 11.2 R&D framework for assessing sources, monitoring, ecological risks, and remediation of micropollutants

11.6.4 Risk Characterization

The fundamental aim of risk characterization is not only the protection of ecological communities present in an aquatic environment but also the health of people living in contact (directly or indirectly) with water. Earlier, the ecological risk of pollutants was assessed on its concentration in the environment with predicted no-effect concentration (PNEC) (Lepper 2002). However, this approach has some limitations in dealing with diverse PNEC values reported for a particular species. Thus, risk assessment is generally based on the quality and robustness of database, as noxiousness and ecotoxicity of endpoints vary depending on the sources. Recently, for studying the chemical compounds Intelligent Testing Strategies (ITS) have been considered as sustainable tools thereby, minimizing the cost and animal testing. It includes series QSARs, chemical categorization, thresholds of concerned compounds, exposure characterization, methodologies for in vitro testing, as well as computational models. Moreover, the development of physiologically based pharmacokinetic (PBPK) models has increased. These models describe the intake, distribution, metabolism, and excretion of chemicals in humans and animals (Fàbrega et al. 2013).

11.7 Conclusion and Future Perspectives

During the past decade, enormous studies have been focused on the assessment of the occurrence of MPs in the environment. In particular, the occurrence of MPs in surface water was much higher which revealed an environmental concern and main source was WWTP effluent. The diverse nature and low concentrations of MPs ultimately affect their removal in current WWTPs. Hence, optimization of wastewater treatment, to build a complete barrier to MPs emission, remains a task of high importance. Biological treatment was found to enhance the removal efficiency of different classes of MPs but unable to remove persistent polar MPs. On the other hand, chemical treatment is the best process for the removal of various MPs but it leads to the generation of secondary pollutants. Recent studies suggested improvements regarding MPs degradation using hybrid processes. These processes containing biofilm carriers, suspended/attached growth system showed better removal of MPs, even on recalcitrant compounds. Since, advanced treatment technologies have been proven to be promising alternatives for MPs removal but the high operation costs, the formation of by-products, and concentrated residues are two major concerns linked with the applications of these treatments. Furthermore, to efficiently envisage the influence of MPs on the receiving environment, a comprehensive understanding and modeling of MPs fate are needed.

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Chapter 12

Microbial Degradation of Nonsteroidal Anti-inflammatory Drug Ibuprofen



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Abstract Pharmaceutical consumption is gradually increasing because of improved health care systems in India and worldwide. The occurrence of pharmaceuticals in the environment has been recognized as an emerging issue. These pharmaceuticals get excreted with urine and feces as parent compound or as their metabolites after the requisite action in the body. On the other hand, pharmaceutical compounds (PCs) are also directly disposed of through pharmaceutical manufacturing plants, hospitals, veterinary drug use. Pharmaceuticals found in the environment even at a very low concentration from ng/L to µg/L have toxic effects on the terrestrial and aquatic organisms. Studies have shown that pharmaceuticals enter the organisms through sewage water and animal carcasses. It magnifies through bioaccumulation in the food chain. The proper degradation process of pharmaceuticals has become the need of the hour to get rid of the harmful impacts of pharmaceuticals on the environment. Many studies have been focused on the degradation of pharmaceuticals. Most of them were based on physical and chemical treatment but they were not so much efficient. The degradation with the microbial strains was found very efficient and effective. In the present work, the degradation of ibuprofen is performed by selected bacterial strain. Various growth factors, micronutrients, and process parameters were provided during the degradation studies. These factors and parameters supply the natural source of food and energy for the bacterial growth for enhancing the degradation rate. In the present study, an experiment was done to observe the potential of selected bacterial strain for the degradation of pharmaceutical wastewater. Optimum conditions for this degradation were these: dextrose and peptone concentration 1.5% (w/v), with 2% (w/v) inoculums size at pH 7 incubated at 25 °C at 150 rpm. After providing these growth factors and process parameters the degradation rate was reached more than 78% in terms of chemical oxygen demand (COD) removal. Thus, this study illustrates the great potential to develop microbial degradation of pharmaceutical waste, which is effective, reliable and lowers the environmental risk.

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Keywords Biodegradation · COD removal · Environment · Growth factors · Pharmaceuticals · Process parameters

12.1 Introduction

Pharmaceutical industries are widespread all over the world and gradually increasing across the globe. The uses of pharmaceuticals are constantly increasing to cure the disease. The presence of pharmaceuticals in the environment has become an emerging issue of concern in the past few years due to their harmful effects on humans and the environment. Pharmaceuticals are called “pseudo-persistent” contaminants in the environment due to their constant consumption and their polar and nonvolatile properties (Daughton 2003). There are various groups of pharmaceutical compounds, for example, nonsteroidal anti-inflammatory drugs, antibiotics, blood-lipid regulators, antihistamines, blood-lipid regulators, β -blockers, steroids, endocrine disruptors, etc. These compounds mainly enter in environment through various pathways such as the effluents from wastewater treatment plants (Nikolou et al. 2007; Pereira et al. 2015), discharge from sewage sludge (Li et al. 2013), seepage from landfills (Topal and Topal 2015), septic systems and conjugation of human excreta in sewer lines (Zhang et al. 2008), runoff from livestock waste (Luo et al. 2011) and their use as manure and fertilizers (Glassmeyer et al. 2005) (Wu et al. 2009). Moreover, direct dumping of waste drugs and wastewater from the hospitals and pharmaceutical manufacturing units also responsible for the total amount of pharmaceuticals in the wastewater (Santos et al. 2013). However, various pharmaceuticals such as some antibiotics and steroids are resistant to biodegradation and transformation in a natural way, thus they do not degrade completely even in the conventional set up of municipal wastewater treatment plants (WWTPs) (Vidal-Dorsch et al. 2012) as they are released into reservoir, rivers, lake, groundwater, marine water, and drinking water (Jing et al. 2015) and thus persist into aquatic ecosystem for a long time (de Jongh et al. 2012) lakes (Kleywegt et al. 2011; Jelic et al. 2011). In the environmental matrices pharmaceutical compounds were detected in the concentration of ng/L to $\mu\text{g/L}$ (Kolpin et al. 2002). Pharmaceuticals may cause specific adverse impacts to the organisms even at very low concentrations and have the potential risks to the aquatic ecosystem and supposed to have a toxicological impact on certain aquatic organisms (Quinn et al. 2008). In recent years, many advanced analytical techniques have been developed to detect the trace amount of pharmaceutical residues; many studies have reported the occurrence of pharmaceuticals in the environment (Pugajeva et al. 2017; Nadim et al. 2015). Now the concern on this issue has been raised to inspect the source, behavior, fate, and degradation of pharmaceuticals present in the environment (Jiang et al. 2013; Pal et al. 2010). So the degradation of pharmaceutical compounds in the environment has become very essential due to its toxic effect on the ecosystem.

In the last few years, various advanced technologies have been employed for the treatment of pharmaceutical wastewater such as advanced oxidation process,

activated carbon sorption, membrane separation, and membrane bioreactor. These technologies are effective for the removal of wastewater (Klamerth et al. 2010; Alygizakis et al. 2016). Although, these advanced treatment processes are too costly to use for large-scale applications. Consequently, the less costly substitute of technologies has immense significance. The biodegradation of pharmaceutical compounds can be the most significant method. The biodegradation process using microorganisms has been found in an eco-friendly and cost-efficient way for the treatment of wastewater. Different kinds of microorganisms such as bacteria (Langenhoff et al. 2013), fungi (Marco-Urrea et al. 2009), yeast (Ibegbulam-njoku et al. 2013), and algae (Abdel-Raouf et al. 2012) have been expressed their effectiveness to degrade the pollutants in wastewater. Various researches have been carried out on bacterial degradation and biotransformation of pharmaceuticals in the last few years (Gauthier et al. 2010). This research aimed to assess the use and COD removal efficiency of the screened bacterial isolate in pharmaceutical wastewater and the use of various growth factors for bacterial growth to accelerate the rate of COD removal.

12.2 Methodology

12.2.1 Collection of the Sample and Chemicals

Soil samples were collected from nearby the pharmaceutical industry. The samples were collected in dry, clean, and sterile polybags. Ibuprofen (IBP) tablets were obtained from a chemist store, Kishangarh, India, manufactured by Abbott India ltd. Solvents and other chemicals used were of HPLC and analytical grade.

12.2.2 Isolation and Screening of COD Removal Bacteria

The bacteria employed in the present work isolated from the soil sample. One gram soil was used in 10 mL of distilled to prepare a stock solution. This solution was used for preparing the 100fold dilution by transferring the 1 mL of stock solution to 9 mL of distilled water and the serial dilution was conducted by repeating the steps to obtain dilution up to 10^{-5} . About 200–300 μL of the suspension was inoculated on Petri plates consisting of nutrient agar media. The plates were incubated for 24 h at 32 °C. The individual colonies were then streaked on individual nutrient agar (NA) plates for further use in the study. The bacteria were mass cultured in nutrient broth (NB) medium for 12 h at 32 °C and pH 7 under the aerobic condition at 120 rpm. Almost one or two loops full of the bacterial colonies were inoculated in 1000 mL of NB media. After the incubation period was over, the pre-cultivated culture was centrifuged at 3500 rpm for about 15 min to spin down most of the cell suspended in the media. The cells were then used for further experiments. Bacterial

isolates were screened for their efficiency to degrade the pharmaceutical wastewater based on their potency for COD removal. For this 10% wastewater and 1% of respective bacterial inoculum were transferred in 100 mL of distilled water in 6 different flasks. After that degradation setup was employed at 32 °C for 12 h at 120 rpm. After 12 h samples were centrifuged at 4000 rpm and the clear supernatant was used for COD removal assessment. The most efficient bacterial strain was used for further degradation process.

12.2.3 Screening for the Degrading Activity of Bacterial Isolates

Selected bacterial isolate was screened for its ability to reduce COD using growth media mineral salt medium (MSM) (g/L): 1.0 NaNO₃, 1.0 NaCl, 0.5 K₂ HPO₄, 0.5 KH₂PO₄, 0.2 MgSO₄.7H₂O, pH 7.0. For this assessment, ibuprofen was spiked for standardize the degradation. The medium was gradually acclimated to increasing concentration of ibuprofen (mg/l) 20, 30, 40, 50, 60, 70, 100, 200, respectively, incubated at 32 °C for 24 h at 120 rpm for finding best degradation. After incubation degradation was determined by percentage COD removal.

12.2.4 Optimization of Degradation Experiments Using Various Growth Factors

Various kinds of factors were optimized to attain the maximum rate of COD removal by the selected bacteria at different standard conditions such as substrates, their concentration, pH, temperature, rpm, etc., as described by Shah et al. (2013).

12.2.4.1 Selection of Carbon and Nitrogen Source

The composition of growth media plays a significant role in determining organisms' activity (Murdoch and Hay 2015). Hence, experiments were carried out to screen the most appropriate carbon and nitrogen sources. For these, various carbon (fructose, dextrose, sucrose, and acetic acid) and nitrogen sources (yeast, peptone, sodium nitrate (NaNO₃), and ammonium chloride (NH₄Cl)) were used at 0.1% (w/v) initial concentration. Minimal salt medium (MSM) containing IBP was used as a control. The batch experiments were performed in Erlenmeyer flasks holding 150 mL MSM, 0.1% IBP, and 1% (w/v) inoculum supplemented with identified nitrogen and carbon sources. Percent COD reduction was analyzed as preliminary analysis after different time intervals (6, 12, 24, 36, and 48 h).

12.2.4.2 Concentration of Selected Carbon and Nitrogen Source

Different concentrations of best carbon and nitrogen sources (% wv^{-1}) 0.05, 0.1, and 0.15 were used to find their best concentration for maximum %COD removal. One percent of inoculum was added to MSM enriched with 0.1 g/l IBP. The degradation process was set up at 32 °C at a different time interval of 6, 12, and 24 h at 120 rpm. Best concentrations of carbon and nitrogen sources were used for further experiments.

12.2.4.3 pH

The effect of pH ranging from 6 to 9 was examined on the COD removal efficiency of the bacterial strain. MSM was enriched with 0.1 g/L IBP and 1% inoculum. The best degrading concentration of C and N sources was also added in this media. The incubation temperature was maintained at 32 °C at 120 rpm. The final pH was adjusted by using 0.01 M HCl or 0.01 M NaOH solution.

12.2.4.4 Inoculum Size

Inoculum size is a very important factor in the biodegradation process. Different concentrations of inoculum size ranging from 1 to 4% provided in MSM enriched with 0.1 g/l IBP, C and N sources at best-selected concentration with selected pH. Degradation setup was maintained at 32 °C and 120 rpm.

12.2.4.5 Temperature

The effect of temperature on bacterial growth was studied at 20 °C, 25 °C, 30 °C, 35 °C in MSM with 0.1 g/L ibuprofen with most favorable C and N sources, inoculum size, and optimum pH and incubated in an orbital shaker at 120 rpm. The temperature that endorses the maximum biomass yield for degradation was used for the following steps of the investigation.

12.2.4.6 Speed of Agitation

The effect of agitation during incubation on growth was executed in MSM with 0.1 g/L ibuprofen along with most favorable C and N sources, inoculum size, and determined pH and temperature incubated in an orbital shaker at orbital at 50, 100, 150, and 200 rpm. The agitation speed promoted the aeration for bacterial growth which enhances the rate of biodegradation.

The results of these screening experiments and the obtained favorable conditions (C, N, their concentrations, pH, inoculum size, temperature, duration, speed of agitation) after the screening experiments were also applied for the optimization of PIWW degradation.

12.3 Results and Discussion

12.3.1 Selection of COD Removing Bacteria

Six Bacterial strains (KGP01, KGP02, KGP03, KGP04, KGP05, KGP06) were isolated from contaminated soil. All strains were shown the potential for degradation for pharmaceutical wastewater. But KGP4 was the most efficient bacterial strain that had great potential to remove COD from wastewater than other bacterial strains as shown in Table 12.1.

12.3.2 Effect of Various Optimization Factors in COD Removal

12.3.2.1 Effect of C Source in COD Removal

The degradation studies showed that the efficiency of KGP04 in presence of dextrose and fructose was found higher as compared to sucrose and lactose. The effective degradation in terms of COD removal found to be 65% due to presence of dextrose and 62.5% in the presence of fructose, while in case of sucrose and acetic acid the degradation was 58.3% and 60%, respectively, after 6 h as shown in Fig. 12.1. Hence, dextrose was selected as most effective C source for biodegradation. Similarly, *Bradyrhizobium sp.* could be able to eliminate 70% of ciprofloxacin when glucose and sodium acetate were used as external carbon source (Nguyen et al. 2018).

Table 12.1 Screening of biodegradation potential of isolated bacterial strains

Isolated strains	% COD reduction
KGP01	39
KGP02	29.33
KGP03	35.56
KGP04	41.57
KGP05	30.57
KGP06	25.26

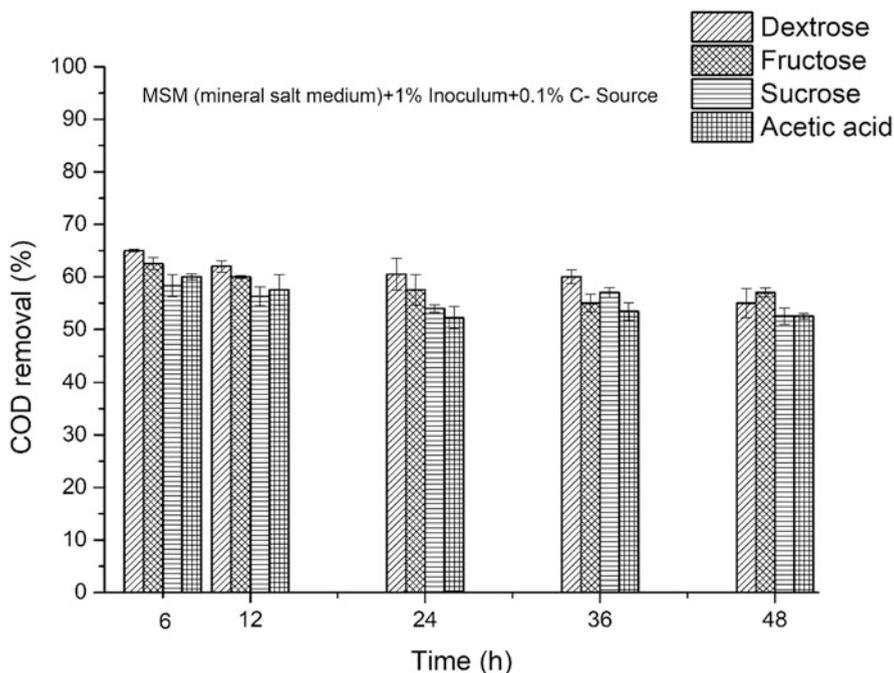


Fig. 12.1 Effect of various C source on COD removal (%)

12.3.2.2 Effect of N Source in COD Removal

The experimentation was carried out at 0.1 gL^{-1} IBP, 0.1% (wv^{-1}) dextrose, temperature and pH. Four nitrogen sources (two organic and two inorganic) namely peptone, yeast, sodium nitrate, and ammonium chloride were used. The effect of nitrogen sources on wastewater degradation was shown in Fig. 12.2. It is noticeable that peptone among all nitrogen sources was most suitable growth factor for degradation with 70.83% COD removal after 6 h followed by yeast with 66.57% COD removal. Both inorganic nitrogen even showed lesser degradation 56% and 51.84% after 12 h respectively. However, in case of degradation of cefdinir by yeast isolates did not shown any improvement after adding external nitrogen source (Selvi and Das 2014).

12.3.2.3 Effect of Concentration of C and N Sources

The data regarding the effect of the concentration of dextrose and peptone on the degradation are presented in Figs. 12.3 and 12.4. The maximum COD removal found at 0.15% concentration of both dextrose and peptone after 6 h. The maximum degradation in the presence of dextrose and peptone was 67.35% and 70.5%, respectively. Among all various growth parameters, carbon and nitrogen sources are considered as chief factors for bacterial metabolic activities.

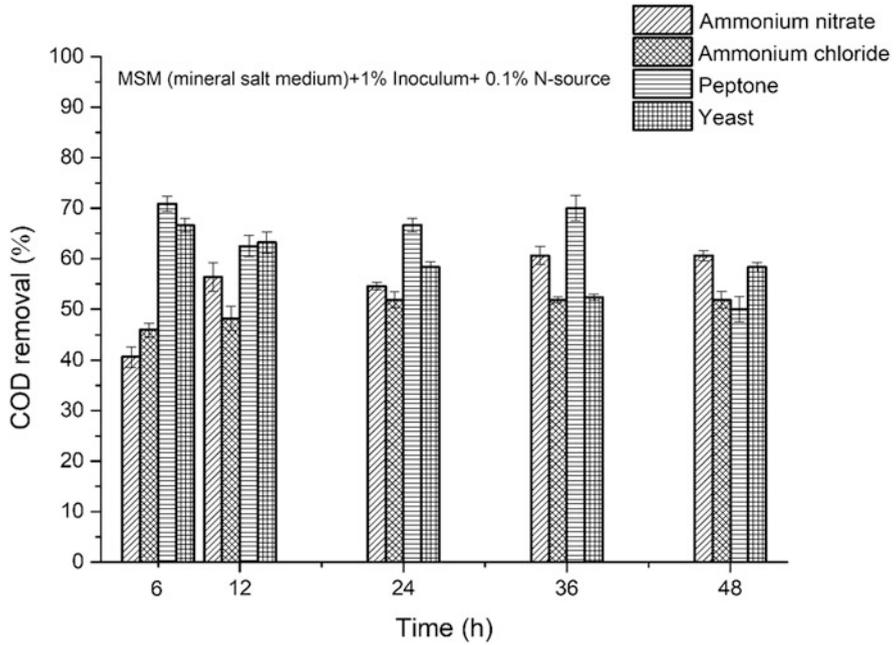


Fig. 12.2 Effect of various N source on COD removal (%)

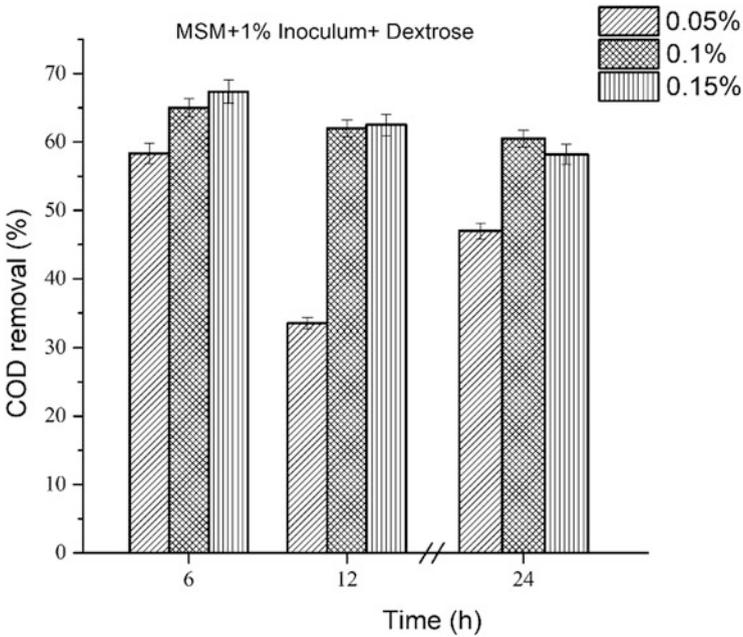


Fig. 12.3 COD removal (%) at various concentration of Dextrose

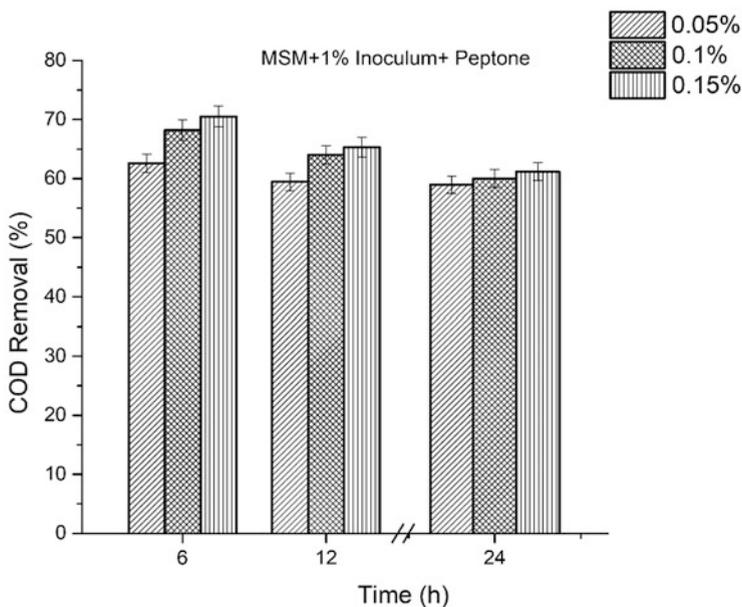


Fig. 12.4 COD removal (%) at various concentration of Peptone

12.3.2.4 Effect of pH

Effect of pH for degradation of IBP was evaluated. Bacterial strain KGP04 was capable to remove COD over a wide range of pH. Though, maximum removal was found at pH 7 as shown in Figure 12.5. COD removal for this range was 70.5% and at pH 8 COD removal was 68% which is approximately similar to pH 7. At pH 9% COD removal was 62.5%, but at pH 6 the %COD removal was least among all with 40% efficiency. It shows that KGP04 served best at pH 7. The degradation efficiency showed declining trend below and above this pH. Similarly, in a previous study the optimum degradation of phenol was found at pH 6.5 *Pseudomonas* sp. SA01 (Shourian et al. 2009). Thus, it illustrates that neutral pH is optimum for biodegradation process by bacteria.

12.3.2.5 Effect of Inoculums Size

The effect of inoculum sizes on biodegradation was analyzed by using different ranges of % inoculum size (wv^{-1}). The range was selected from 1–4% (wv^{-1}) of KGP04 inoculum. The maximum COD removal (73.82%) was attained when 2% (wv^{-1}) of inoculum was augmented with in the MSM at pH 7 as shown in Fig. 12.6. However, there was no significant difference observed while augmented with 1% 3% and 4% (wv^{-1}) of inoculum size. Two percent with numerically higher value

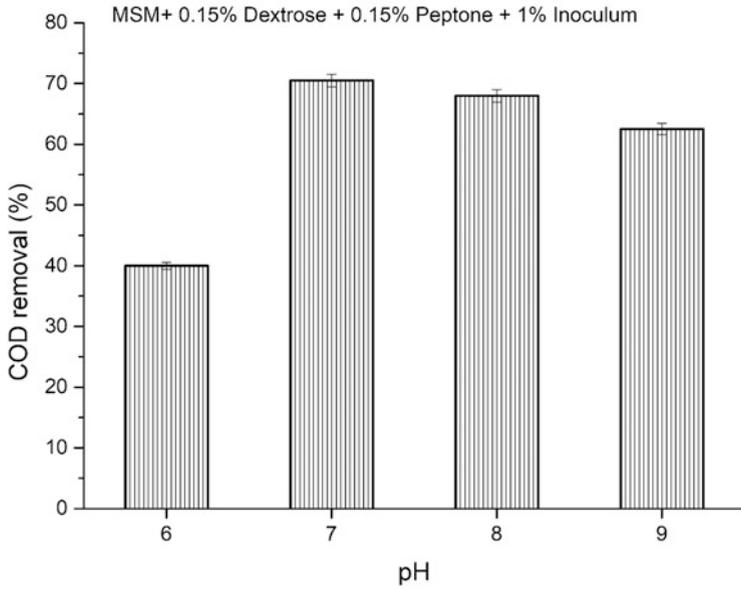


Fig. 12.5 COD removal (%) at various pH ranges

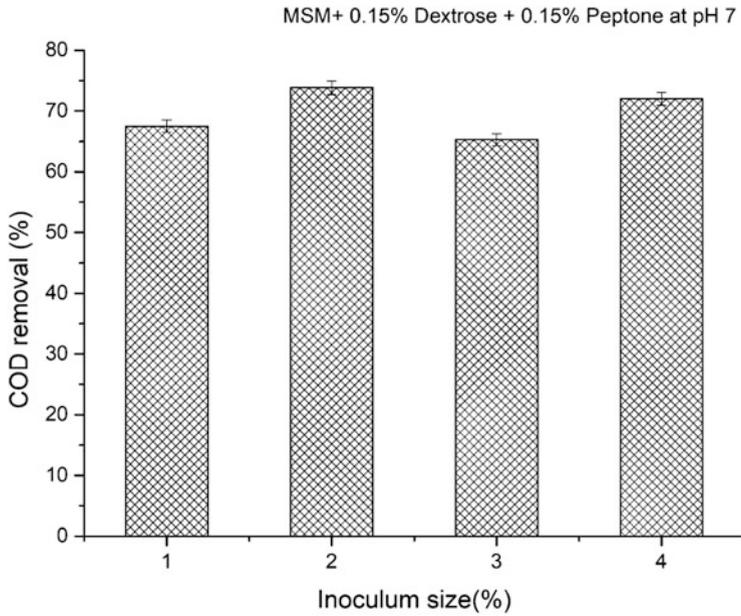


Fig. 12.6 COD removal (%) at various inoculums size

was selected for further experiments. Though, the increased amount of inoculum increased the microbial activity to degrade the pollutants (Ungureanu et al. 2015).

12.3.2.6 Temperature

Temperature plays an important role in microbial growth and enzyme activity and is one of the most important parameters taken into consideration in the development of biodegradation processes. Bacterial isolates were able to degrade the drug over a wide range of incubation temperature. Incubation temperature from 20 to 35 °C was selected to identify the optimum level for the biodegradation of IBP by the selected bacterial strain KGP04. The highest degradation was 76.83% at 25 °C as shown in Fig. 12.7. There was also a marginal decrease observed in degradability with increase in temperature at 30–35 °C. Another report stated that complete degradation of tylosin was achieved at 30 °C by bacteria *Citrobacter amalonaticus* (Ma et al. 2015).

12.3.2.7 Speed of Agitation

Aeration is again an important factor for the growth of aerobic bacterial strain and it largely affects the rate of biodegradation. The highest rate of COD removal was found at 150 rpm after 6 h. It presents that bacteria KGP04 was able to remove 78.88% COD at this rpm while at 200 rpm the removal was comparatively lesser,

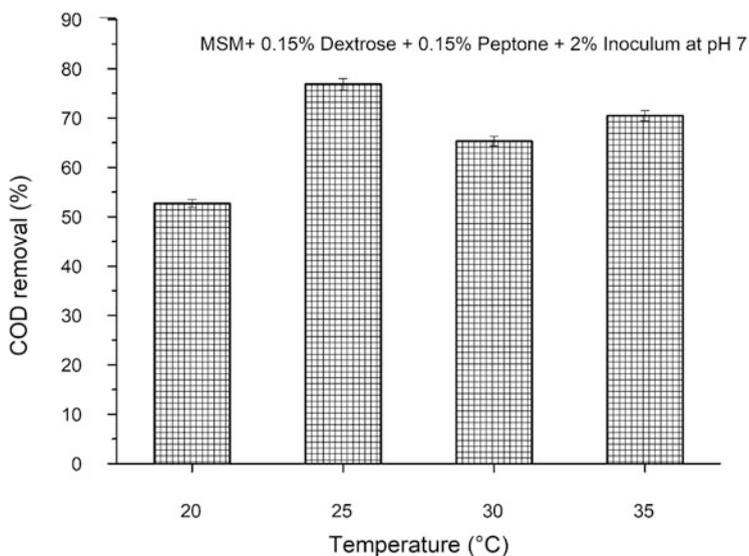


Fig. 12.7 COD removal at a various range of temperature

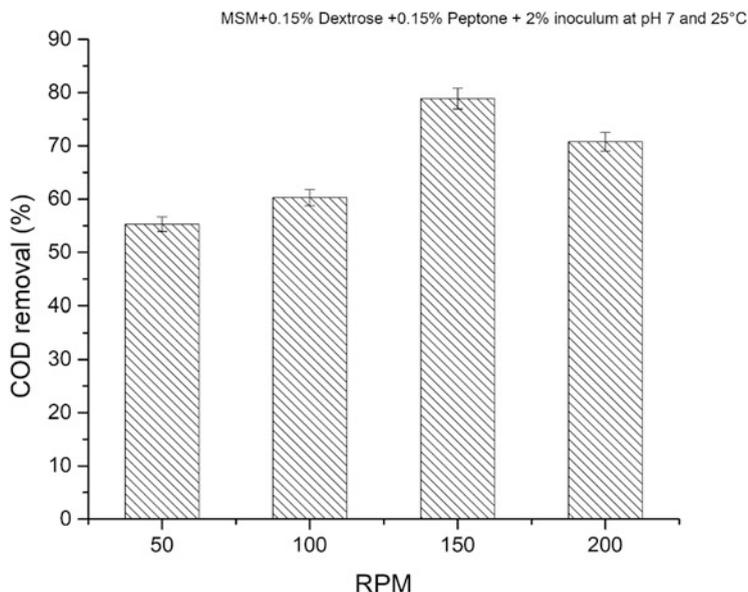


Fig. 12.8 COD removal (%) at various ranges of RPM

i.e. 70.80%. The removal efficiency was even low at 50 and 100 rpm, i.e. 55.3% and 60.3%, respectively, as shown in Fig. 12.8. Hence, a speed of 150 rpm was found to be the most efficient rate among the tested ones. Similar results were also reported by Ungureanu et al. (2015) that best degradation of carbamazepine by *Streptomyces* MIUG 4.89 was found at 150 rpm on incubation at 25 °C (Ungureanu et al. 2015). Thus, aeration can be proved as good promoting factor for the growth and activity of microbial cells with respect to rate of degradation.

12.4 Conclusion

The occurrence of the pharmaceutical compound in the environment can be very dangerous. So the concern has been raised to mitigate this problem. For this degradation of pharmaceuticals is very essential. There is a need to increase knowledge about the fate of pharmaceuticals during sewage treatment for the implementation of better removal techniques. The degradation of pharmaceutical compounds by microorganisms has been proved a very effective strategy. Though, there are few studies have been reported in India related to the degradation of pharmaceutical compounds by microorganisms. In the present study, one important aspect is to solve a load of pharmaceutical residues in wastewater by optimizing the degradation process. In the present study rapid degradation was observed in the presence of supplemented carbon source dextrose as compared to other sources like fructose,

sucrose, and acetic acid. This might be due to the enhancement of the growth rate of bacteria and their degradation efficiency on the addition of dextrose to the media. The same was the case when peptone was added. It showed a rapid degradation rate compared to other nitrogen sources like yeast extract, sodium nitrate, and ammonium chloride. It may be because organic nitrogen sources such as peptone are considered as essential sources for the growth of biomass. Hence rapid degradation of the pharmaceutical wastewater was observed in the presence of dextrose and peptone at 1.5% concentration in the media only. Thus a commonly available carbon and nitrogen sources are imperative to enhance the bioremediation activity of this bacterium, which has been the most suitable for the treatment of pharmaceutical rich wastewater. The isolated bacterial strain showed optimum COD removal rate at incubation temperature 25 °C at pH 7, agitation speed 150 rpm.

12.5 Future Recommendations

Based on the above results of the present study, this strategy can be promoted for the degradation of pharmaceuticals in wastewater. For more best results, process optimization of parameters will be applied in further studies. Present study concluded that some bacterial enzymes may play significant role in biodegradation. So, the future research can be focused on isolation and production of pharmaceutical degrading enzymes from bacteria and enzymatic degradation of pharmaceutical and other industrial wastewaters.

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Chapter 13

VOCs and GHGs Intrusion and Its Impacts on Subsurface Microbial Community



Pankaj Kumar Gupta and Basant Yadav

Abstract Volatile organic compounds (VOCs) and GHGs (CO₂) movement in subsurface is topic of interest due to growing extraction and transportation of petroleum hydrocarbon products and CCS sites, respectively. The transport of raw and processed petroleum hydrocarbons through pipelines crossing urban setting and underground storage tanks cause these landscapes to be vulnerable to petroleum hydrocarbon spills. Fate and transport of these gases were studied in past too; however, very little attention was paid to the effects of hydrological variables on its movement of these contaminants in subsurface. Hydrological variables (e.g. soil moisture, infiltration, thickness of capillarity zone) controlled by direct (draining) and indirect (climate change) significantly affect the movement of VOCs in unsaturated zone. Increasing soil moisture content reduced the air-filled porosity of unsaturated zone, which directly decreases the gas diffusion, increases the gas-liquid partition and causes reduced risk of VOCs intrusion. Thus, a better understanding of influences of hydrological variables on VOCs movement will help environmental scientist and geochemist to accurately predict the vapour intrusion and its risk. This review manuscript is intended to narrow the gaps of understanding of role of hydrological variables on VOCs intrusion and its risk. A brief description is presented first to highlight the current knowledge on fate and transport of VOCs followed by the role of matrix setting on its movement in subsurface. Thereafter, a section is presented to elaborate the impact of VOCs and GHGs intrusion on the subsurface microbes.

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13.1 Introduction

Vapour (gas phase) intrusion is a common governing process of volatile organic compounds (VOCs) movement in subsurface, where gas-phase VOCs flow from saturated zone to above laying unsaturated zone and subsequently enter into atmosphere (Jury et al. 1990; Mercer and Cohen 1990). Such intrusion of VOCs may cause most relevant pathway for human health risk at polluted sites, especially in urban building and indoor conditions. For this reason, environmental scientist and geochemist should able to predict the behaviours of VOCs and temporal evolution of its plume under varying subsurface conditions. The accurate forecasting and field assessment of VOCs intrusion and its risk analysis is complicated due to (1) transport mechanisms of unsaturated zone and (2) biodegradation and volatilization in unsaturated zone that are controlled by (a) hydro-meteorological responses, (b) groundwater table fluctuations and (c) background geochemical makeup of subsurface (Rivett et al. 2011; Shen et al. 2012). Generally, the soil gas and indoor VOCs concentrations predicted by existing techniques are reported to be either overestimated or underestimated by several orders of magnitudes (Picone 2012). This is due to hydrological influences, especially fluctuation of groundwater table, moisture variation and diffusion of liquids along with biogeochemical response of pollutants that are not adequately addressed for.

There is growing interest in understanding and predicting how hydrological processes in unsaturated zone of various aquifer media respond to VOCs intrusions. The focus of this study is to present the current knowledge and state of art of literature on VOCs intrusion and its risk analysis, with special emphasis on the role of variations in physical/matrix setting, hydrological variabilities, and background geochemical makeup of subsurface. A detailed description of fate and transport of two-phase and multi-phase flow is provided first. Then, the variations in VOCs intrusion and its pathway are presented to highlight the impact of physical setting and geochemical makeup of aquifer media. Finally, the knowledge on responses of hydrological factors is elaborated to improve the current understanding on VOCs intrusion. Our review manuscript, we hope, will provide the environmentalist and geochemical communities with current development to the research on the processes and factors relevant to VOCs intrusion and its risk analysis.

13.2 VOCs: Sources and Impacts

Widespread transportation corridors and pipelines crossing the large landscape make them vulnerable to hydrocarbon spill and accidental release. Other main causes of VOCs pollutions are due to industrial followed by municipal waste disposal (Picone 2012). Generally, petroleum and chlorinated hydrocarbons are referred as volatile organic compounds (VOCs) due to their high tendency to easily evaporate under normal/atmospheric pressure and temperature conditions. VOCs have a vapour pressure greater than 0.01 KPa at 20 °C. Petroleum hydrocarbons, including benzene, toluene, ethylbenzene and xylene (orto-meta-para), known as BTEX, are the most commonly reported VOCs sources in subsurface environment. These are aromatic hydrocarbons having alkane rings containing double bond in chain. Similarly, the other class of VOCs is chlorinated hydrocarbons in which one up to four carbon atoms may be displaced by chlorine. They include tetrachloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE) and vinyl chloride (VC), in order of decreasing chlorine atoms. These chemicals were intensively used as intermediate for plastic production, degreasers in metal industry and solvents in dry cleaning facilities.

Pollution from VOCs significantly affects the ecosystem and human health (Mustapha et al. 2018; Gupta and Sharma 2019; Gupta et al. 2019; Gupta 2020a, b; Gupta and Yadav 2020a, b). VOCs in subsurface negatively affect the invertebrates, earthworms and microbial communities due to its toxicity (Vaajasaari et al. 2002). Intake or inhaling of benzene compounds may cause leukaemia (referred to as human carcinogen) and other blood-related types of cancer. Other BTEX like toluene, ethylbenzene and xylenes have lower toxicity but may still cause negative health effects. Persistent exposure to toluene can harm the central nervous system. Similarly, TCE and PCE may cause cancer of kidney, liver, cervix, and lymphatic system. Common source of these contaminations in indoor environment (buildings) is leakage from basement/subsurface. These compounds are generally well soluble in water and thus easily migrate in groundwater, to form large plumes of contaminated groundwater and contaminated soil vapour phase in the unsaturated zone above. Thus, dissolved concentration of these compounds in groundwater is another most possible pathway to enter in human body. Therefore, it is important to remediate or mitigate such VOCs intrusion from subsurface to buildings and/or atmosphere.

13.3 Fate and Transport of VOCs from the Subsurface to Buildings/Atmosphere

Once the pure/free phase of non-aqueous phase liquids (NAPLs), immiscible with water, released from the sources form a two (Water-NAPL) or multi-phase (Water-Air-NAPL) system in porous media (Essaid et al. 2015). Figure 13.1 shows a

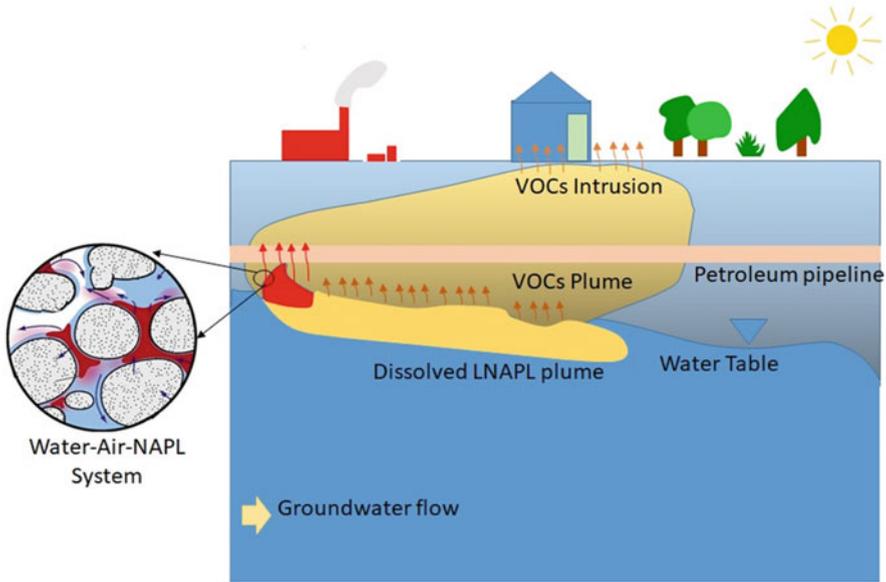


Fig. 13.1 Schematic diagram of petroleum leakage from underground pipeline and origin of water-air-NAPL system, which further creates a dissolved and vapour phase contamination plume in saturated and unsaturated zone, respectively (adapted from Niessner and Helmig 2007 and Essaid et al. 2015)

schematic diagram of the subsurface environment contaminated from the NAPL released from a pipeline. As can be seen, the top part of this subsurface system corresponds to the partially saturated zone, where air and water fill the void space between the soil particles. Moving further down, the groundwater table is located, and below, all the pores are filled with water. It can be seen that mechanisms of diverse complexity occur in various parts of the subsurface zone, involving a different number of pollutant phases (p) and its components (c). In unsaturated zone, contaminants form a 3p3c system (water-air-NAPL); while moving to capillary zone, it creates a 2p2c/3c system (water-NAPL) (Niessner and Helmig 2007). Further moving downwards, in saturated zone, it forms 1p2c system (either water or NAPL). Mass transfer processes governed in and around the contaminated zone, for example the volatilization of NAPL and evaporation of water and/or the dissolution of NAPL and gas/air in water, which may form a plume of contaminations (Picone et al. 2013). At pore scale and under assumption of equilibrium, Henry's law defines the partitioning between dissolved (C_{Liq}) and vapour concentration (C_{Gas}).

$$C_{Gas} = H' \left(\frac{C_{Liq}}{RT} \right) \quad (13.1)$$

where H' is expressed in Pa L Mol^{-1} , R is universal rate constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is absolute temperature (K). Henry's low constant can be present as dimensionless by

$$H = \frac{H'}{RT} \quad (13.2)$$

The vapour pressure and solubility are temperature dependent; thus, Henry's constant is also temperature dependent. Volatilization from pure/free phase of NAPL is governed by Raoult's law, which states that the vapour pressure of a gas phase NAPL is equal to the vapour pressure of pure phase NAPL times the mole fraction of NAPL in gas phase.

$$P_g = x_g \cdot P_{\text{vap}} \quad (13.3)$$

Once the VOCs partition occurs, the gas phase moves towards upward direction due to lighter density and concentration gradient. Diffusion fluxes may take place from sources zone and/or groundwater zone to surface or basement of building, where the initial VOCs concentration is zero (Akbariyeh et al. 2016). A positive pressure gradient between the surface and the soil gas pressure and barometric pressure fluctuations along with the effects of wind and heating can develop the pressure differentials. Such pressure differentials may cause the advective gas flux through air-filled pores of the subsurface. Wind pressure at the surface may also create the pressure differential in subsurface as it is entering from one side and leaving from another side (McAlary et al. 2011). Similarly, the barometric pressure difference may cause air to flow in and out from soil, which may accelerate the advective flow of gas in subsurface. Beside these mechanisms, preferential pathways through which vapour may migrate faster is the most important vapour transport mechanism. Preferential pathways in subsurface are generally found with utility drain filled with coarser media and so on. In regards of buildings, the foundations play a significant role in vapour intrusion (Picone et al. 2013).

13.4 Matrix Physical Setting and VOCs Intrusion

Air-filled porosities may enhance the diffusive flux of VOCs from high concentration (near source) to low concentration (at surface) zone (Yao et al. 2013). An increase in air-filled porosities may significantly accelerate the movement of VOCs and thus increases its risk. Furthermore, bulk density is another influencing parameter that, generally, increases with depth in subsurface. Thus, one can predict the fast movement of VOCs in shallow/thin unsaturated zone than larger unsaturated zone. Permeability (horizontal and vertical) of media plays a significant role in VOCs transport in layered subsurface (Yao et al. 2013). Pennell et al. (2009) investigated the effects of soil permeability at different soil gas flow rate. They

found that the soil gas flow rate increases from $7.9 \times 10^{-4} \text{ m}^3/\text{s}$ to $7.9 \times 10^{-8} \text{ m}^3/\text{s}$, which fortifies that the soil permeability has significant impact of the VOCs movement in subsurface. Yao et al. 2017 highlighted the preferential pathway for vapour intrusion can be a significant contributor and higher risk for receiving environments. Preferential pathway may occur as land drain, dry wells or cisterns and or due to fractures in subsurface. Sewers or utility tunnels are of greatest concern when they pass directly through contaminated groundwater or vadose zone of non-aqueous phase liquid (NAPL) sources. Modelling results of Yao et al. (2017) show that preferential pathway as land drain contributes significant amount on indoor VOCs concentrations.

13.5 Hydrological Responses on VOCs Intrusion

VOCs intrusion will significantly depend on the hydrological conditions of subsurface that include soil moisture flow controlled by recharge and groundwater table fluctuations (Shen et al. 2013a). Tillman Jr and Weaver (2007) modelled vapour intrusion under varying soil moisture contents by rainfall and found that high soil moisture content may reduce the vapour intrusion and its risk. Shen et al. (2013b) highlighted that the capillary fringe (high moisture level zone) acts as a large resistance to vapour diffusion to unsaturated zone from VOCs mixed with groundwater, because the diffusivity of VOCs in this zone is much lower than its diffusivity in unsaturated soil porosity. One can expect two hydro-chemical changes due to soil moisture contents in case of vapour intrusion. First, the VOCs diffusion will change by increasing and decreasing the moisture contents. Shen et al. (2013a, 2013b) indicated that high soil moisture contents will reduce the VOCs movement towards the surface. In contrast, low soil moisture contents will increase the air-filled porosity, which directly enhanced the VOCs transport in subsurface. Generally, the rate of gaseous diffusion is dependent on the air-filled porosity of the soil, which in turn is controlled by the amount of soil moisture. Second effect will be on the gas-liquid partition in different soil moisture zone. An increase in soil moisture will decrease the effective air diffusivity and result in additional partitioning to the liquid phase, thereby decreasing soil-gas concentrations.

The soil moisture level in subsurface is controlled by water infiltration into the soil and groundwater table fluctuations. Both hydrological responses may play significant role in vapour movement. As water infiltrates into soil, the existing VOCs are displaced. The displaced VOCs are either emitted from the ground or pushed downwards, thereby compressing the underlying soil gas. If the water infiltration rate is slow, all of the VOCs will be released. Subsequent VOCs emissions will decrease due to the lower air-filled porosity (and due to mass transfer to the new water). So, the effect of water infiltration is to have a short-term spike in air emissions due to displacement followed by a period of lower than average VOCs emissions (Eklund 1992). High rates of infiltrating water can result in a fresh water

lens above the groundwater, which acts as a barrier to volatilization by increasing the length of capillary fringes.

Groundwater table fluctuation is controlled by the climatic variability and draining conditions. A rise in groundwater table will reduce the travel pathway of VOCs from sources zone, which will directly increase the risk of VOCs movement towards surface/buildings. At the same time, however, the vadose zone will tend to have lower amounts of air-filled porosity, which will tend to decrease the rate of diffusive gas transport. In contrast, with a lowering of water table, water from partially saturated zone will drain, which significantly enhances the plume/sources of hydrocarbon liquids, thereby enhancing transfer of VOCs from groundwater zone (McHugh and McAlary 2009). Falling groundwater levels can result in additional oxygen transport into the vadose zone, and this may have implications for aerobic biodegradation of petroleum hydrocarbons. Gupta et al. (2019) investigated the role of dynamically fluctuating groundwater table conditions on fate and transport of LNAPL, including the vapour movement towards the surface using 2-D sand tank experiments. Two-dimensional sand tank setup used in the study was specially designed using 2.5-mm thick stainless steel box with inner dimensions of 150 cm long \times 120 cm high \times 10 cm deep. Indian standard clean sand (650 grade-II) of particle size 0.5–1 mm free from organic matter was packed in the central chamber between both the wells up to a height of 90 cm. The top 30-cm thick sand pack was kept as head space to maintain aerobic condition. An auxiliary column containing the collected groundwater was connected to the inlet port of upstream well with Viton tubes of a peristaltic pump. This peristaltic pump referred to as “upstream pump” was used to supply the groundwater to the sand tank through the upstream well. The objective of this auxiliary column was to provide sufficient groundwater storage required to maintain the dynamic groundwater table conditions. Similarly, the outlet of the downstream well was connected to another peristaltic pump (referred herein as downstream pump) to extract the groundwater and recirculate to the auxiliary column. The flow rate of the pumps was adjustable so that the desired pressure difference in the two reservoirs can be maintained, thereby controlling the groundwater flow within the tank setup.

A constant groundwater flux was applied as inflow (using the upstream pump) and the same was extracted as outflow (using the downstream pump) to maintain a constant flow velocity in the horizontal direction and, hence, keeping the water table location at a constant height for steady-state condition. However, in rapid, general and slow groundwater level fluctuation experiments the inflow/outflow flux was controlled by peristaltic pump to maintain a raising of the water table by 5 cm in 1, 2, and 4 h, respectively. The groundwater table was then lowered in the same manner; a drop of 5 cm was achieved in subsequent 1, 2 and 4 h for rapid, general and slow fluctuation conditions, respectively. It may be noted herein that “one fluctuation cycle” refers to a complete high-low-high cycle of groundwater table levels. Soil gas samples were collected periodically using needles attached with syringes (Hamilton gold) from the sampling ports embedded in the sampling layers in unsaturated zone and head space.

The observed break through curves (BTCs) show a high LNAPL concentration in case of rapid fluctuating groundwater table followed by general, slow and stable groundwater table case. The vapour equilibrium concentration was observed as 210–230 ppm in fluctuating condition, whereas 180–185 ppm was observed in stable groundwater case. This means a raising groundwater table carries pure phase LNAPL mass upwards and a falling groundwater allows LNAPL to move downwards. During dynamics of groundwater level, the trapped LNAPL remain behind in smear zone, which creates a large interphase area of air-LNAPL/water (Powers et al. 1992). Therefore, more vapour phase concentration was observed from the residual LNAPL. These results are in line with the findings of study conducted by Oostrom et al. (2006) with 2D experiments under water table dynamic conditions. The study found a considerable residual LNAPL saturation in smear zone. The high vapour concentration can also be attributed to the partition of LNAPL from large dissolved phase plume having high concentration. Further, lowering of groundwater table increases air-filled porosity in smear zone, which eventually affects vapour phase LNAPL partition.

Box 1: Variables Affecting the VOCs Transport in Subsurface

Soil Moisture:

High levels of soil moisture will reduce rates of diffusion via reduction in effective diffusivity and reduction in soil-gas concentration.

Water Infiltration:

Water infiltration into soil can reduce rates of gas transport by displacing the pore air and reducing its volume.

Dynamically Fluctuating Groundwater Table:

Falling groundwater levels result in worst-case conditions for vapour intrusion.

Capillary Zone:

Thickness of capillary zone will change the VOCs intrusion risk. Large capillary zone acts as a large resistance to vapour diffusion to unsaturated zone from VOCs mixed with groundwater.

13.6 VOCs Intrusion Risk Reduction Strategies

VOCs via vapour intrusion is a major health concern, which needs to be addressed by applying the effective risk reduction strategies. There is a growing body of literature to address such challenges in daily life. In this section, we reviewed the literature on monitoring, remediation and management of VOCs intrusion in subsurface.

13.6.1 Monitoring/Indicators of VOCs Intrusion

Advances in the analytical chemistry and sensor-based investigations provide a wide variety of methods such as GC-MS detection of VOCs in groundwater, soil gas, indoor air and plant tissue. Passive sorbent samplers are very common in the USA (USEPA 2014), Canada, Europe, Denmark, Australia, and New Zealand (McHugh et al. 2017a, b). Real-time on-site analysis integrates the sample collection and analysis, thus greatly improving the detection of source zone. In these directions, some mobile-based applications such as portable and micro GC (μ GC), ion mobility spectrometers (IMS), SGX Sensortech and PID are very useful for VOCs detection (Spinelle et al. 2017; Agbroko and Covington 2018). One can find the details of commercial sensors and their detection limits in review manuscript by Spinelle et al. (2017). Isotopic analysis of carbon atoms from indoor samples and subsurface gas samples will help to locate the source zone of VOCs intrusion and its pathways (Beckley et al. 2016). As isotopic analysis is costly and not available to local managing authorities. In some case, phytoforensic analysis of plant core helps to detect and forecast the VOCs intrusion from sources zone (Wilson et al. 2018). Wilson et al. (2018) collected tree-core samples at the PCE southeast contamination site in York, Nebraska, and analysed and found positive correlation with soil gas/groundwater analysis. For a better understanding of the VOCs intrusion risk reduction, monitoring will be the first practice for field scientists and engineers.

13.6.2 Source Removal Approaches

After the detection or identification of source, one can focus on the source removal using suitable cost-effective techniques. In situ source removal may be based on physical techniques (soil flushing, air sparging, ozone injection), chemical (solvent injection), and/or biological (bio/phyto-remediation) (Garg et al. 2017). In soil flushing, polluted soil can be treated with water or reagents, whereas in soil washing, water is used with other physical separation/scrubbing tools. Concentrated soil fraction containing the LNAPL can be treated effectively by this method. Likewise, air stripping is a technique in which (hot) air is injected in polluted saturated zone. Air sparging or commonly known as SVE is an in situ remediation technique, mainly for LNAPL polluted sites. It basically involves the injection of air into the saturated zone and allowing venting through the unsaturated zone to remove LNAPL contaminants (Frutos et al. 2010).

In chemical treatment methods, oxygen-releasing compounds (calcium peroxide, urea peroxide, and magnesium peroxide) are injected for treatment of LNAPL polluted zones. Chemical oxidation using permanganate is another potential technique for treating LNAPL polluted sites. Certain chemicals (oxidants or other amendments) are injected directly into the contaminated zone (Franzetti et al. 2008; Tobiszewski et al. 2012). These chemicals destroy LNAPL constituents in

place and form by products such as carbon dioxide, water and chlorides. Commonly used chemical oxidants for LNAPL treatment are potassium permanganate, hydrogen peroxide, sodium permanganate and ozone. However, these techniques are expensive and sometimes disturb the indigenous biota.

Some of the conventional remediation techniques like air sparging, booming and skimming used for the removal of these VOCs pollutants are usually expensive and destroy the indigenous biota capable of natural bioremediation (Basu et al. 2015). Moreover, these techniques might result in incomplete mass removal or toxicity and are often not feasible in remote locations. The other promising technique is bioremediation in which microbes degrade contaminants into harmless daughter products. The natural bioremediation is safer and less disruptive than some of the other conventional technologies; however, it takes considerably long to restore the polluted site under prevailing environmental conditions. Therefore, engineered bioremediation techniques such as biostimulation and bioaugmentation are gaining popularity due to their faster remediation rates.

13.6.3 Barriers and Pathway Sealing

Physical barriers to VOCs intrusion pathway is one of the most approachable methods to prevent such contaminants exposures. Reactive material-based barriers like permeable reactive barriers (PRBs) are also effective approach to reduce the risk of VOCs intrusion. Mahmoodlu et al. (2014) performed column experiment to investigate the horizontal permeable reactive barrier for oxidizing VOC vapours prepared using potassium permanganate. They found high removal of trichloroethylene, toluene and ethanol vapours at high water saturation and high reactivity of selected PRB material. Similarly, Verginelli et al. (2017) investigated trichloroethylene (TCE) removal using a horizontal PRB containing a mixture of potassium permanganate, water and sand.

13.6.4 Sustainable Building Solution

Sustainable building solution means the improvement of building design by incorporating (1) passive barrier, (2) passive active venting system, (3) subslab or sub-membrane depressurization systems and (4) positive building pressurization (Moyer et al. 2009). Installing passive barriers will help to maintain moisture intrusion from groundwater to subslab vapour barriers for long term. Likewise, the active or passive venting system below the subslab/foundation may help to collect the VOCs through installed pipe. Pressure difference between the subsurface and subslab using depressurization system can help to mitigate the VOCs intrusion. Thus, one can install a depressurization system below a membrane laid on top of

the ground surface in the crawl space. Sealing the building envelope is another option to mitigate the VOCs intrusion and to maintain the quality of indoor air.

13.7 CO₂ Intrusion at CCS Sites

CO₂ capture and storage (CCS) is emerging as an important tool for the mitigation of the greenhouse gas (GHG) emissions by deep cutting of the global atmospheric CO₂ concentration (Figueroa et al. 2008). Further, CCS projects were getting high interest globally not only to cut GHG emissions but also to enhance recovery of oil/gas (Michael et al. 2010). In early stage, the major attention was paid to develop economically acceptable techniques to capture CO₂ (Figueroa et al. 2008) and on estimations of potential geological sinks (Herzog 2001). Herzog (2001) reported about the storage capacity of different geological units, including ocean, saline formations and coal seams for future CCS activities. In 1990s, Alberta basin (Acid Gas) in Canada was the first geological sequestration project in which CO₂ was injected with H₂S for storage in deep zone. In early 2000s, the saline aquifer CO₂ storage (SACS) project, Sleipner in middle of the North Sea was a first commercial CCS project. This project established as an example for the global community gaining international acceptance and provided an option for CO₂ mitigation (Herzog 2001; Torp and Gale 2004). Since initial days, the tendency of CO₂ to escape from the storage zone to atmosphere via cap rock leakages was highlighted as a major concern for CCS project's success (Zhou and Birkholzer 2011; Lewicki et al. 2007).

Introduction of CO₂-brine in fresh groundwater zone may also cause three major geochemical changes: (1) drop in pH, (2) enrichment of organic compounds and (3) mobilization of metalloids. These changes were commonly found in previous studies as an impact of CO₂/CO₂ enrich brine in fresh aquifer zones (Kharaka et al. 2010; Kharaka et al. 2017; Zheng and Spycher 2018). Acidification of soil-water systems may significantly enhance the sorption of exiting pollutants, especially arsenic (As), lead (Pb), iron (Fe) and manganese (Mn) (Smyth et al. 2009; Lu et al. 2010; Humez et al. 2013). Geochemical alteration due to the leakage of CO₂/CO₂ enrich brine may also affect the soil microbe, vegetation and ultimately human health. However, very little attention has been paid in the past to understand potential impacts of CO₂-brine leakage on subsurface microbiological resources and on plants at CCS sites.

13.8 Impacts on Subsurface Microbial Communities

Intrusion of CO₂ into the biosphere may alter microbial community composition, thus understanding their response to short- and long-term changes is crucial for ecological balance. Extremely low bacterial cell counts were observed in area of vent core (>90% CO₂) having high CO₂ flux and low plant cover. Bacteria cell counts

increase as moved away from the vent core. Frerichs et al. (2013) observe that the bacterial sequences were affiliated to the *Betaproteobacteria*, *Acidobacteria* and *Bacilli*, whereas archaea to the *Thaumarchaeota*. They also report that the *Geobacteraceae* showed a significant decrease under high CO₂ concentrations. Likewise, 16S rRNA gene sequencing studies have also been carried out by de Miera et al. (2014) at the Campo de Calatrava natural CO₂ site in Spain. It was observed that the relative abundance of *Chloroflexi* increases, whereas the relative abundance of *Acidobacteria*, *Verrucomicrobia* and *Gemmatimonadetes* phyla decreases as CO₂ flux increases. Within the *Chloroflexi* phylum, the genera *Thermogemmatispora*, *Ktedonobacter* and *Thermomicrobium* dominated bacterial communities sampled in sites with the highest CO₂ flux.

An artificial CO₂ release experiment was conducted on a farmland at the campus of China University of Mining and Technology, Xuzhou, China, by Chen et al. (2017) to investigate the potential impacts on soil microbes. Fluxes of CO₂ were applied at different intensities (400–2000 g m⁻² d⁻¹) and 16S rRNA gene sequencing was performed. It was observed that the relative abundance of *Bacteroidetes* phylum decreases, whereas the relative abundance of *Firmicutes*, *Acidobacteria* and *Chloroflexi* phyla increases as CO₂ flux increases. The abundances of *Acidobacteria* increased with increasing CO₂ leakage, which indicated that they might be potentially important indicators for the detection and resolution of gas leakage (in line with results of Oppermann et al. 2010). However, Ma et al. (2017) found that the abundance of *Acidobacteria* and *Chloroflexi* phylum decreased with increased CO₂ flux, which may be due to high abundance of *Proteobacteria* or other environmental conditions. Microbial shifting is not straightforward, but these studies indicate that high molecular gene and microbiome sequencing can be an indicator to CO₂ leakage and risk evaluation. However, very little research has been focused towards the risk analysis of CO₂ seep at industrial CCS sites on soil archaea and bacteria from these environments.

13.9 Concluding Remarks

The loss of quality of groundwater supplies and human health from point-source leaks and spills of VOCs as well as GHGs (CO₂) was well documented, which may enter the subsurface as slightly soluble and volatile non-aqueous phase liquids (NAPLs), as a result of pipeline breaks and poor storage. Considerable progress has been made to understand the VOCs and CO₂ intrusion and its closure at many contaminated sites. Increasingly detailed knowledge on the VOCs intrusion and its risk analysis is becoming available. However, additional studies are required to understand the complexity of polluted sites, including the role of hydro-geological and background geo-chemical makeup. In particular, our understanding of how the spatial and temporal variation of hydrological conditions have impact on solute transport and biogeochemical activity at the landscape scale remains fairly limited. There is need of a better understanding that integrates the acquisition of physical,

hydraulic, chemical and microbial data on hydrology, pore water geochemistry, microbial diversity and functions, and biogeochemical rates and fluxes.

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Chapter 14

Biological Treatment of Pharmaceuticals and Personal Care Products (PPCPs) Before Discharging to Environment



Monica Simon, Ajay Kumar, Alok Garg, and Manisha

Abstract Nowadays, pharmaceuticals and personal care products (PPCPs) in the environment have gained considerable attention among the research groups from the past two decades. Their occurrence and fate in the ecosystem from including pharmaceutical industry wastewater are of concern worldwide. Several studies were investigated to understand the different aspects of these compounds around the world. In literature, a number of techniques such as bioremediation, phytoremediation, conventional treatment process, constructed wetlands, activated sludge processes, membrane bioreactors and sequencing batch reactor have been reported for the removal of these PPCPs. The continuous efforts are being made in developing the appropriate techniques for their removal. The remediation through traditional methods, such as activated sludge, has not been found effective for the removal PPCPs from wastewater. This study focuses on demonstrating the understanding related to the removal techniques based on the remediation methodologies available in the literature. Moreover, this study leads to evaluate and compare the available options for the PPCPs removal under variable environmental conditions.

Keywords PPCPs · Wastewater · Aerobic and anaerobic technologies · Remediation

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14.1 Introduction

Pharmaceuticals and personal care products (PPCPs) include several classes of chemical compounds. These are a group of “emerging contaminants” that are primarily utilized to prevent/for treatment of diseases and improve the quality of daily life of human beings and animals (Liu and Wong 2013). Nowadays, their presence in environment has raised widespread concern due to their severe consequences on environment. Both pharmaceuticals and personal care products can be categorized into different categories depending on their nature and utility. Pharmaceuticals can be classified based on their therapeutic use or the physico-chemical property of the active ingredients present in them. Therapeutically, they are classified into a number of classes such as antibiotics, analgesics, antidepressants, steroid hormones, retroviral, bronchodilators and cardiovascular drugs, including antianginal, antiarrhythmic, antithrombotic, antihypertensive, anti-haemorrhagic and lipid regulating drugs, stimulants, antiepileptic, antidiabetic, antiallergenic drugs, anxiolytic, antiparasitic, antipsychotic, antineoplastic, antifungal, immunosuppressant, lipoprotein, proton pump inhibitor, antispasmodic keratolytic agent etc. Personal care products based on their use can be classified into fragrances, UV blockers, antimicrobials, preservatives, disinfectants, etc. These are known as biologically active compounds that have the ability to interact through specific pathways and processes in the targeted humans and animals.

Pharmaceutical industries all over the world are perpetually engaged in designing more active pharmaceutical ingredients (APIs) with higher potency and bioavailability; as a result, pharmacologically significant properties such as degradation resistance and enhanced bio availabilities threaten non-target organisms (Jones et al. 2001). Personal care products, however, with ever-growing standards of beauty and lifestyle, are increasing in the market. They are deliberated for external use unlike pharmaceuticals and thus do not encounter metabolic alterations and hence enter the environment unaltered (Brausch and Rand 2011).

Several authors have demonstrated the existence of PPCPs in natural environment (Kolpin et al. 2002; Ramirez et al. 2009). These have been reported to be detected in a variety of climatic zones, primarily in lower concentrations. These also have capabilities to persist in ecosystem from months to several years (Monteiro and Boxall 2009). To combat the consequences related to these compounds, the scientific community has raised a concern to examining the occurrence, fate, effects and risks of PPCPs in the environment. Moreover, regulations have also been developed regarding the assessment of risks as well as environmental exposure to PPCPs.

14.2 Sources and Types of PPCPs

These contaminants (PPCPs) mainly affect three main environmental compartments: groundwater, surface water and soil. It is important to understand how PPCPs enter into the aquatic ecosystem. These micro-pollutants and their derivatives are released into the water cycle by several sources. One of the major sources is through human metabolism; upon drug ingestion, partial metabolism of APIs occurs in the human body, after which they invade the water cycle either as metabolites or unaltered as parent compounds that are released mainly by urine and partly by faecal matter (Al Aukidy et al. 2012).

Wastewater treatment plants (WWTPs) are reportedly the biggest sources of PPCPs in the environment. The ineffectiveness of traditional wastewater treatment plants in treating the PPCPs is one of the main causes of PPCP pollution in surface water and inadvertent flora and fauna in various environmental counterparts (McArdell et al. 2003; Petrović et al. 2003). This leads to recurrent occurrence of pharmaceuticals and their derivatives in wastewater effluent (Wu et al. 2008; Waiser et al. 2011). This is because of the fact that these compounds cannot be effectively handled by traditional wastewater treatment plants. PPCPs discarded in sinks and toilets eventually meet the same fate, as they are excreted from WWTPs, wrong disposal, pharmaceutical manufacturers and other anthropogenic means. The other release points are factories and hospitals that dispose of pharmaceuticals from landfills to soil and then groundwater. In this way, PPCPs continue to shift, thus polluting the environment.

Severe problems are created by reckless dumping of pharmaceuticals and personal care products. Residue analysis of human and veterinary pharmaceuticals confirms their existence in various environmental compartments, including sewage (Ternes 1998), surface water (Kasprzyk-Hordern et al. 2008; Kim et al. 2009) and sea water (Weigel et al. 2004). Polar PPCPs present in surface and wastewater may also affect groundwater if it is used for groundwater recharge. Though many PPCPs get degraded while percolating the subsurface, compounds such as carbamazepine remain during groundwater recharge even in anoxic saturated as well as aerobic unsaturated conditions during travel times up to 8 years (Drewes et al. 2003; Chen et al. 2016). Figure 14.1 shows the possible pathways for PPCPs entry into the environment.

14.3 Impacts of PPCPs on Aquatic Environment and Public Health

Pharmaceuticals and personal care products (PPCPs) have been found in water bodies around the world, yet their environmental impacts are not completely known. Current toxicity studies indicate that low-concentration PPCP mixtures may be toxic to exposed species, emphasizing the need to eliminate PPCPs from

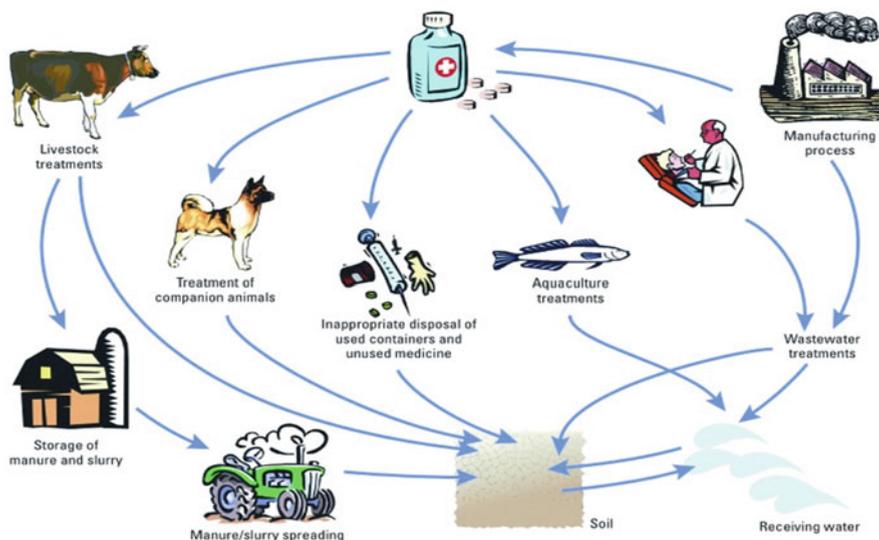


Fig. 14.1 Major pathways for PPCPs release into the environment (Boxall et al. 2012)

wastewater treatment plant effluent before it is released into the environment (Onesios and Bouwer 2012). The possible toxicological effects of pharmaceuticals released into the environment on aquatic organisms have already been documented by several researchers, although the effects of these contaminants on human health and safety are not well comprehended (Schulman et al. 2002; Kumar et al. 2010; Escher et al. 2011).

Most of the PPCPs are not persistent and have short half-lives, but they are known to be pseudo-persistent because of their continuous input in the aquatic environment. There is a growing interest regarding presence and fate of these micro pollutants in the environment due to manifestation of potential adverse effects of PPCPs on non-target organisms even at trace concentrations. A range of adverse environmental impacts such as masculinization or feminization of fish by hormones or structurally similar xenoestrogens, antibiotic resistance in bacteria and synergistic toxicological effects are evident in the literature and has apprehended ecotoxicologists and environmentalists all over the world. Occurrence of bioaccumulation of antidepressants, antimicrobials and hormones is reported in a variety of aquatic organisms.

A review suggests that possible health effects of chronic exposure to pharmaceuticals via drinking water could result in antibiotic resistance, endocrine disruption, allergic reactions, carcinogenic effects, genotoxicity, effects on reproduction and foetal/child development (Daughton and Ternes 1999). However, toxicologists are working proactively in determining whether the relatively low environmental concentrations of PPCPs are potent of producing adverse effects on aquatic and terrestrial biota and to what extent; whether the complex cocktail of these micro pollutants exhibits any synergistic or antagonistic effects, but due to incomplete assessment

data, they still lack a complete knowledge of the environmental effects of most PPCPs (Ternes et al. 2004).

14.4 PPCPs Removal Involving Biodegradation Process

The removal of PPCPs organic pollutants involving biological degradation is known to be important. This process of remediation has several advantages in terms of characteristics involving mild operating conditions, easy operational process and cost-effectiveness. The mechanisms of removal occur by utilizing the organic pollutants as a metabolite during the growth of microorganisms, which finally leads to degradation and transformation of PPCPs. The different microorganisms are also known to be performed synergistically for the removal of these pollutants. The microbes require a primary substrate as a growth material in the removal process of PPCPs involving bacterial degradation (Vasiliadou et al. 2013). Besides this, some bacteria have the capability to utilize the PPCPs as a source of carbon and energy, which ultimately leads to the cost minimization of process.

In biological systems, the studies exploring the removal of PPCPs focus on the factors such as treatment effectiveness, sorption process and degradation potential. The potentiality of traditional biological removal systems is relying on the seasonal variations. The generation of secondary pollutants with sludge is also reported to occur after the biological degradation, which has also a great concern among scientific community (Banerjee et al. 1997). Thus, it is appropriate to develop the treatment systems that may overcome the problems relating to the generation/ degradation of secondary pollutants as well.

Generally, the traditional design of systems for pharmaceuticals wastewater management is based on biological treatments. This can be classified as aerobic and anaerobic processes. In aerobic treatment, the mode of its application is further divided into the techniques such as activated sludge process (ASP), membrane batch reactors (MBRs) and sequence batch reactors (SBRs). On contrary, the anaerobic treatment includes methods such as anaerobic sludge reactors (ASRs), anaerobic film reactors (AFRs) and anaerobic filters (AFs) (Deegan et al. 2011). Some of the studies evaluating the removal of PPCPs are compiled in the Table 14.1, and these technologies are discussed in detail individually further.

14.4.1 *Enhanced Aerobic Treatment*

14.4.1.1 **Activated Sludge Process (ASP)**

In the wastewater treatment processes (WWTPs), ASP is a most commonly explored method for the treatment of PPCPs. Its removal is based on the synergistic utilization of microbial consortium. However, insignificant removal capabilities of these PPCPs

Table 14.1 Overview of the methodologies explored for the removal of PPCPs

Targeted compound(s)	Source/Treatment process	Experimental conditions	Removal efficiency (%)	Outcomes/Remarks	Ref.
Pharmaceuticals	Wastewater/membrane bioreactor (MBR)	Temp.: Mesophilic HRT: 18 h SRT: 26 days	99	1. The authors suggested removal method to be superior as compared with those of conventional activated sludge process for most of pharmaceuticals or steroids 2. The compound carbamazepine was found to be highly persistent during the removal process	Lesjean et al. (2005)
Sulfamethoxazole	-do-	pH: 7.8 ± 0.1 Temp.: 22 ± 2 °C DO: $0.5-2.0$ mg L ⁻¹ MLSS: 10500 HRT: 24 h	99	3. This study provides a methodology for the removal of above-mentioned recalcitrant carbamazepine compound 4. Carbamazepine degradation has been reported to be very sensitive towards operating conditions, in comparison to sulfamethoxazole	Hai et al. (2011)
Caffeine, ibuprofen, paracetamol, methyl-dihydrojasmonate, oxybenzone, furosemide	Wastewater/waste stabilization pond	pH: 7-8 Temp.: 4-20 °C DO: 0.3-1.2 mg L ⁻¹ HRT: 20 days	> 99	5. Compared the treatment processes such as aeration system, rotating biological contractor (RBC), constructed wetland and waste stabilization pond (WSP) along with seasonal variation 6. The degradation rate was higher during cold season 7. WSP is considered efficient when surface area of treatment is large; however, RBS should be a logical choice for small area of treatment	Matamoros et al. (2007)

Cotinine, caffeine, atenolol, nadolol, metoprolol, sulfapyridine, acetaminophen, naproxen, ibuprofen	Wastewater/ constructed wetlands	HRT: 27 days	>99	8. Sotalol and carbamazepine were reported to be highly persistent to degradation 9. High removal rates of highlighted compounds were contributed to longer HRT values	Conkle et al. (2008)
Galaxolide and tonalide	Wastewater/waste stabilization pond	pH: 7-8 Temp.: 4-20 °C DO: 0.3- 1.2 mg L ⁻¹ HRT: 20 days	98 and 83	10. Higher removal was reported to be examined at low temperature conditions 11. Removal process was primarily found due to sorption	Matamoros et al. (2007)
Enrofloxacin and tetracycline	-do-	pH: 7.3 ± 0.4 Temp.: 16 ± 2- 28 ± 8 °C HRT: 7-84 days	98 and 94	12. For Enrofloxacin, adsorption onto the substrate was found to be predominant phenomena of removal; however, some signs of degradation in case of tetracycline was observed	Carvalho et al. (2013)
Triclosan	-do-	pH: 7-8 Temp.: 4-20 °C DO: 0.3- 1.2 mg L ⁻¹ HRT: 20days	97	13. Seasonal variation studies revealed that the degradation was higher during warmer period. The authors also claimed that compounds such as caffeine, ibuprofen, paracetamol, methyl-dihydrojasmonate, oxybenzone and furosemide have high degradation during colder period	Matamoros et al. (2007)
Triclosan and tetracycline	Wastewater/membrane bioreactor (MBR)	pH: 6-8 Temp.: >30 HRT: 6.6 SRT: 7.6 MLSS: 9648 1.2 mg L ⁻¹	84-97 and 87-94	14. The biodegradation and hydrophobic interactions have been found to be responsible for its removal	Tran et al. (2016)

(continued)

Table 14.1 (continued)

Targeted compound(s)	Source/Treatment process	Experimental conditions	Removal efficiency (%)	Outcomes/Remarks	Ref.
Berberine	Waste water/anaerobic treatment	Temp.: 37 ± 1 °C HRT: 1 day MLSS: 9560 mg L^{-1}	>95.2	15. The microorganisms such as <i>Firmicutes</i> , <i>Bacteroidetes</i> , <i>Clostridium</i> , <i>Eubacterium</i> and <i>Synergistes</i> were reported as significant species responsible for removal 16. Higher removal was reported to be examined at low temperature conditions	Qiu et al. (2013)
Caffeine, salicylic acid, methyl dihydrojasmonate, CA; ibuprofen, hydrocinamic acid, oxybenzone, ibuprofen, OH; ibuprofen	Wastewater/constructed wetlands	pH: 6.7–8.2 DO: 0.1– 9 mg L^{-1} HRT: 13 h	>95	17. Shorter value of HRT in vertical subsurface flow has been considered appropriate in the space limiting area for their removal 18. These types of constructed wetland have been suggested to be efficient for the removal of PPCPs from domestic wastewater from compact systems	Reyes-Contreras et al. (2011)
Diclofenac	-do-	Temp.: 9.5– 19.2 °C pH: 6.8–7.7 HRT: 3.5 days	> 95	19. Its removal has been reported to be maximum under higher redox conditions 20. The authors also suggested that these wetland systems might be improved using batch operation strategies	Ávila et al. (2013)
<i>N,N</i> -diethyl-meta-toluamide (DEET), paracetamol, caffeine and triclosan	Surface water/constructed wetlands	pH: 7.6–8 Temp.: 23 ± 2 °C HRT: 7 days	> 95	21. This wetland system has been explored along with stabilization tank and sandwich slow sand filtration units 22. The dominant phylum was found to be <i>Proteobacteria</i>	Li et al. (2019)
Triclosan	Wastewater/activated sludge process	Temp.: 30 °C HRT: 8.2 h SRT: 5.7 days MLSS: 1760	87.4–94.2	23. Removal by sorption onto solids and activated sludge was examined to be significant due to its high octanol-water distribution coefficients	Tran et al. (2016)

Ketoprofen and ibuprofen	Wastewater/ sequencing batch reactor (SBR's)	pH: 6.5–8.2 DO: 5.5– 7.6 mg L ⁻¹ HRT: 24 h ORP: 152– 191 mV	13–92 and 63–90	24. The microbes such as <i>Bacillus pseudomycoloides</i> , <i>Rhodococcus ruber</i> and <i>Vibrio mediterranei</i> were reported to have higher toxicity resistance, causing effective degradation of pharmaceutical compound	Abu Hasan et al. (2016)
Ciprofloxacin, ibuprofen, fluoxetine, and norfloxacin	Wastewater/activated sludge process	Temp.: 14.3 and 19.8 °C HRT: 20 h SRT: 8 days	> 90	25. Biodegradation or sorption to sludge was considered to be probable removal mechanism 26. Diclofenac and ofloxacin have shown insignificant removal	Zorita et al. (2009)
Ibuprofen and ketoprofen	Wastewater/membrane bioreactor (MBR)	HRT: 24 h MLSS: 2700– 3500 mg L ⁻¹	>90 and > 70	27. Low pH favours high degradation, which is due to enhancement of adsorption to sludge particles 28. This is further removed through biological degradation	Urabe et al. (2005)
β-lactams, sulphonamides, reductase inhibitor, macrolides, fluoroquinolones, tetracyclines, lincosamides	Wastewater/activated sludge process (ASP)	pH: 6–8 HRT: 20 h	7–99.7, 52.2–96, 8–42.2, 4–80.9, 6–92.4, 4–93.9, 8.1–85.7	29. The study suggested that the membrane bioreactor removal of these pharmaceuticals is beneficial, compared with ASP 30. Perturbations in operational parameters lead to lower impact on the degradation/hydrolysis process	Zorita et al. (2009)
Estriol (95%), benzhabite (88%), caffeine (88%) and atenolol (87%)	Wastewater/membrane bioreactor (MBR)	pH: 7.8 Temp.: 16.7 ± 0.5 °C HRT: 3.2 h SRT: 40 days	> 87	31. Integration with the reverse osmosis and nanofiltration techniques proved significant potential in the PPCPs removal effectively 32. Estriol has shown high removal percentage, which is due to formation of hydrogen bond with the carbonyl group of MLSS	Wang et al. (2018)

(continued)

Table 14.1 (continued)

Targeted compound(s)	Source/Treatment process	Experimental conditions	Removal efficiency (%)	Outcomes/Remarks	Ref.
Tetracycline	Wastewater/ sequencing batch reactor (SBR)	pH: 7.1, 7, 7.38 DO: > 2 mg L ⁻¹ HRT: 24, 7.4 and 7.4 h SRT: 10, 10 and 3 days MLSS: 509–1246	86.4	33. Lab scale studies interpret that the biomass is a major component that acts as sink for tetracycline antibiotics 34. Sorption has been found to be principal removal mechanism. This also creates an issue for the land applications of bio-solids containing tetracycline	Kim et al. (2005)
Naproxen, sulfamethoxazole, roxithromycin and oestrogens	Activated sludge/ anaerobic treatment	pH: 7.7–8.6 ± 0.2 Temp.: 37–55.5 ± 5 °C SRT: 10–30 days	>85	35. An insignificant effect of SRT and temperature has been examined on the removal these PPCPs	Carballa et al. (2007)
Salicylic acid, caffeine methyl dihydrojasmonate, caffeine (CAF), ketoprofen and triclosan	Waste water/anaerobic treatment	pH: 5.8–7.2 Temp.: 18–23 HRT: 9.4–55 h	70–85	36. In summer, the high operational temperature leads to higher removal efficiency for most of PPCPs 37. This enhancement of removal efficiency demonstrated to be occurred due to the increased volatilization, biological degradation as well as plant uptake processes 38. The degradation of PPCPs such as phthalate esters and fragrances has not been reported to exhibit the seasonal variations	Hijosa-Valsero et al. (2010)

Ibuprofen, naproxen	Activated sludge/ anaerobic treatment	Temp.: 37 °C SRT: 17 days	>80	39. An efficient removal has been reported as compared with the studies based on laboratory-scale mesophilic anaerobic digesters 40. Mechanisms involving the biodegradation and biotransformation found to be responsible for the removal of these PPCPs 41. Removal of trimethoprim and sulfamethoxazole was lesser in anaerobic conditions, as compared with those of naproxen 42. The methanogenic rate was found to be correlated with the degradation of PPCPs 43. Sorption was examined to be increased with an increase in the time of treatment, which is due to existence of intra-molecular diffusion onto granular mass structures	Samaras et al. (2013)
Naproxen, trimethoprim and sulfamethoxazole	Waste water/anaerobic treatment	pH: 6.5–7.2 Temp.: 20–22 °C HRT: 0.5–1 day SRT: >100 days	>80	44. Ibuprofen removal occurred predominantly by aerobic and microbiological pathway of degradation 45. Involvement of various microenvironments along with different physicochemical conditions favours the formation of several metabolic paths of degradation of PPCPs	Alvarino et al. (2014)
Caffeine, naproxen, methyl dihydrojasmonate, salicylic acid and ibuprofen	Wastewater/ constructed wetlands	DO: > 1 mg L ⁻¹ HRT: 1.2–5.7 days	>70	46. The authors suggested the hybrid constructed wetlands for these PPCPs removal 47. During winter, the lower global	Hijosa-Valsero et al. (2010)
Diclofenac, 3-hydroxycarbamazepine, venlafaxine, acyclovir, odesmethylvenlafaxine, tramadol, trimethoprim	-do-	pH: 6.8–7.0 Temp.: 7–23 °C HRT: 4–11 days	>		Rühmland et al. (2015)

(continued)

Table 14.1 (continued)

Targeted compound(s)	Source/Treatment process	Experimental conditions	Removal efficiency (%)	Outcomes/Remarks	Ref.
Erythromycin, atenolol clarithromycin, codeine, metoprolol, bezafibrate		ORP: 150–340 mV		radiation and microbial activity cause a decrease in the removal of these PPCPs 48. Dominant removal mechanism includes aerobic biodegradation, anaerobic biodegradation and photo-degradation	
Trimethoprim and 4-nonylphenol	Wastewater/membrane bioreactor (MBR)	Temp.: 25 °C DO: 0.5–6.0 mg L ⁻¹ HRT: 5 h SRT: 20 days MLSS: 9400 mg L ⁻¹	65	49. The PPCPs such as carbamazepine, diclofenac and sulpiride have shown an insignificant removal efficiency using this process 50. The slow biodegradation has been considered as rate determining step of degradation that was found to be directly correlated with the level of dissolved oxygen	Xue et al. (2010)
Sulfamethoxazole and 17 β -estradiol	Wastewater/activated sludge process	pH: 2 Temp.: Mesophilic HRT: 24 h	>60	51. Lipophilic properties of 17 β -estradiol facilitate its removal during primary treatment 52. The mechanisms involved in the removal include degradation and sorption onto primary and secondary sludge 53. The authors suggested that variations in the operational conditions such as SRT and different combination of aerobic/anaerobic processes might enhance the removal efficiency of these PPCPs	Carballa et al. (2004)

Nonylphenol ethoxylates	Activated sludge/ anaerobic treatment	pH: 7.1– 7.6 ± 0.1 Temp.: 35– 55 ± 0.2 °C SRT: 15– 30 days ORP: –419.8 ± 36.9	92 and 58	54. Its removal in mixed sludge digestion has been reported to be higher as compared with primary sludge digestion process 55. Removal under thermophilic conditions was found to be higher compared with mesophilic temperature conditions	Paterakis et al. (2012)
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have been examined in some conditions. Therefore, several studies have been reported to focus on enhancing the biodegradation potential by using mixed microbial culture in activated sludge (Zhou et al. 2014). These steps were also found to lead the high biodegradation not only to particular PPCP but also to several other PPCPs (Vasiliadou et al. 2013). It might occur due to the fact that some PPCPs are involved in the growth process of microbial culture along with facilitating the degradation of PPCPs. Thus, some authors have interpreted that the blending of microbes is a potential option for PPCPs removal effectively (He et al. 2018).

Plósz et al. (2012) have developed a modelling framework for xenobiotic trace chemicals, which is further explored for assessing the factors influencing the removal capabilities of carbamazepine and diclofenac. In another study, the compounds such as trimethoprim, sulfamethoxazole, carbamazepine and diazepam were examined to demonstrate the high resistance to biological transformation (Suarez et al. 2010). The evaluation of degradation studies indicated that the compounds such as musk fragrances (HHCB, AHTN and ADBI), fluoxetine and natural estrogens (E1 þ E2) have been reported with the biodegradation (%) of >65 and >75 under anoxic and oxic conditions, respectively. However, naproxen, erythromycin, roxithromycin and ethinylestradiol have shown the significant biological degradation (>80%) in aerobic reactor. Further, the involving anti-depressant compound citalopram was examined with the percent transformation of 60 and 40 under oxic and anoxic environment, respectively.

The removal of 29 antibiotics was explored using conventional activated sludge (CAS) process by Verlicchi et al. (Verlicchi and Zambello 2014), where biological transformation of most of the compounds including norfloxacin, erythromycin, sulfamethoxazole, ciprofloxacin and roxithromycin has been reported. Spiramycin was found to show insignificant removal, whereas cefaclor has shown the removal rate of up to 98%. The authors also examined the removal of these compounds by comparing with membrane bioreactors (MBRs) process. Only the compound azithromycin has shown the higher removal capability during CAS as compared with MBRs treatment process.

In a pilot scale investigation (in France), the utilization of micro-grain-sized activated carbon in tertiary treatment process has shown the reduction of BOD, COD, DOC, PPHs and PCPs (including artificial sweeteners, pesticides, etc.) up to the percent (%) levels of 38–45, 21–48, 13–44, 60–80 and 50–90, respectively (Mailler et al. 2016). This removal is significantly higher as compared with those of powdered activated carbon.

14.4.1.2 Membrane Bioreactor (MBR)

From the past two decades, the MBR process has been considered as an alternative treatment process compared with CAS in terms of PPCPs removal. It also has significant potential towards the removal of conventional pollutants during the wastewater treatment process such as organic matter and nutrients. This technology includes a synergistic approach of membrane and activated sludge treatment

processes. In achieving a sludge solid-liquid separation, this technique leads to the utilization of an ultrafiltration membrane instead of secondary sedimentation tank (Yang et al. 2019). Moreover, several authors have also suggested MBRs process as superior compared with CAS process (Tran et al. 2009; Sahar et al. 2011; Kimura et al. 2007; Sipma et al. 2010).

Sahar et al. (2011) have compared the CAS and MBR techniques to investigate the fate and removal of antibiotics such as macrolide and sulfonamide during a wastewater treatment process. The study revealed the 15–42% high removal of antibiotics during MBR process compared with CAS process. In a similar study, the MBR and CAS have shown the removal percentage for lincomycin, azithromycin, sulfamethazine, tetracycline, oxytetracycline, trimethoprim and triclocarban as 62, 91, 88, 92, 93, 69 and 80 and 42, 78, 80, 67, 80, 33 and 70, respectively (Tran et al. 2009). An insignificant difference has been observed in removal of PPCPs such as sulfamethoxazole, trimethoprim and erythromycin between the CAS and MBR processes (Radjenović et al. 2009). Out of 26 PPCPs, this study demonstrated that the adopted process is able to remove 23 PPCPs up to 90%. It is revealed that the compounds such as cotinine, caffeine, paraxanthine, enalapril, atorvastatin, metformin, 2-hydroxyibuprofen, naproxen, acetaminophen and ibuprofen have exhibited the maximum degradation/transformation potential. However, the PPCPs including the doxycycline, triclosan, miconazole, tetracycline, norfloxacin, triclocarban, ciprofloxacin, 4-epitetracycline, paroxetine and ofloxacin have shown the removal through sorption onto solids. Moreover, this MBR process has not been found to be significant in the removal of compounds such as carbamazepine, meprobamate, clarithromycin, trimethoprim, thiabendazole, erythromycin-H₂O, hydrochlorothiazide, oxycodone and propranolol. Therefore, few authors have suggested to explore the MBR performance for longer HRTs and SRTs in PPCPs removal showing insignificant biological degradation and sorption (Kim et al. 2014). Moreover, MBR has been found to be an extensively explored process for the removal of PPCPs.

14.4.1.3 Sequencing Batch Reactor (SBR)

In SBR process, the selection of appropriate organisms that have the ability to remove the PPCPs effectively is of concern among the scientific group. The compounds such as butyl-benzyl phthalate, diltiazem, acetaminophen, carbamazepine, estrone and progesterone are considered to primarily occur in wastewater. Muz et al. (2014) have investigated the removal of endocrine disrupting compounds using lab-scale SBR units under both oxic and anoxic conditions. At SRT of 5 days, the removal of targeted compounds was achieved up to 80% without any usage of nitrifying microorganisms. The study also revealed that the removal mechanism of carbamazepine includes accumulation onto sludge, whereas remaining compounds have been reported the removal through biodegradation.

14.4.2 Natural Aerobic Treatment

14.4.2.1 Waste Stabilization Ponds (WSPs)

This technique is also having significant potential for the removal of pharmaceuticals and personal care products. Li et al. (2013) have demonstrated the removal capabilities of WSPs up to 88–100% for PPCPs at HRT of 20–30 days. The average removal rate and overall weight reduction were examined to be 82% and 96%, respectively. This high effectiveness of WSP might be contributed to involvement of different removal mechanisms such as biodegradation, photo-degradation and sorption onto solids.

14.4.2.2 Constructed Wetlands

Nowadays, the constructed wetlands have gained a considerable attention for the removal of pharmaceutical contaminants from the wastewater (Li et al. 2014). However, their removal efficiency is largely influenced by designs of parameters. Sharif et al. (2014) have explored the impact of carbon load (CL) and hydraulic rate (HR) on the removal of emerging contaminants. The results revealed that the CL significantly influences the contaminated removal rate operated at 5 cm d⁻¹. At high CL, an increase in the removal of carbamazepine and estradiol has been observed, whereas a decreasing trend was reported in case of atrazine and testosterone. In another study, the removal of 11 micro-pollutants was investigated in the municipal wastewater (1–100 µg L⁻¹) in a CW (planted and unplanted) representing pilot scale horizontal sub-surface flow (Carranza-Diaz et al. 2014). The high organic load and *Phragmites australis* species were used during the study. The removal percent of caffeine and other micro-pollutants in the planted CW was found to be 66 and ~30, respectively. It not only leads to the removal of ibuprofen, carbamazepine, ketoprofen, diclofenac and naproxen but also combats the fragrances of galaxolide and tonalide. Moreover, an insignificant removal was observed for endocrine disruptors (bis-phenol A and nonylphenol) and antibacterial compound (triclosan).

Few authors have explored the removal of antibiotics and antibiotic resistance genes from rural domestic wastewater using integrated constructed wetlands (Chen et al. 2015). The removal efficiency of these compounds was found to be 78–100% and >99, respectively. Among those, the removal efficiency of cotinine, nadolol, ciprofloxacin HCl, oxytetracycline HCl and enrofloxacin has been observed to be >70%, whereas the compounds such as salinomycin, monensin and narasin have shown the removal percentage rate of 20–50%.

From these examinations, it is revealed that the constructed wetlands are having high potential towards the removal of pharmaceuticals, compared with those of traditional WWTPs. Thus, the utilization of CWs is a viable option for PPCPs removal during the secondary wastewater treatment process.

14.4.2.3 Microbial Cultures

Several authors have demonstrated the isolation of pure microbial cultures from the sediments, wastewater and activated sludge. These were further identified as significant in the removal of PPCPs such as sulfamethoxazole (Reis et al. 2014; Jiang et al. 2013), iopromide (Liu et al. 2013), ibuprofen (Almeida et al. 2013), paracetamol (De Gussemé et al. 2011), diclofenac (Hata et al. 2010), triclosan (Zhou et al. 2014) and carbamazepine (Santos et al. 2012). The pure culture of *Achromobacter denitrificans* isolated from activated sludge has exhibited the significant removal of PPCPs such as sulfamethoxazole and other sulfonamides (Reis et al. 2014). The microorganisms *Delftia tsuruhatensis*, *Pseudomonas aeruginosa* and *Stenotrophomonas* were reported to remove the paracetamol significantly. Additionally, these cultures not only degrade the PPCPs but also are able to utilize these as carbon source for growth, which further involves different degradation mechanisms (Almeida et al. 2013; De Gussemé et al. 2011).

The carbamazepine removal was explored using *Pseudomonas* sp. (16S rRNA) that was isolated from the activated sludge (Li et al. 2013). This microorganism has the ability to use PPCPs as source of carbon and energy. In another study, the degradation of different polycyclic aromatic compounds such as pyrene, phenanthrene and fluoranthene has been investigated using *Sphingomonas* strains, isolated from the mangrove sediments (Guo et al. 2010). Their percent degradation has been observed to be <30%, 50% and 30–60% after the 7 days of batch experiments, respectively. Moreover, the incorporation of co-cultures with *Sphingomonas* and *Mycobacterium* strains leads to the enhancement of PAH degradation and has shown the complete removal after 7 days.

The utilization of white rot fungi cultures, an alternative to the biological degradation in activated sludge, has also been reported in the literature (Wong 2009). These cultures have the ability to degrade several number of xenobiotics, which is due to the actions of fungal oxidative enzymes. The enzymes included in this process were found to be lignin peroxidase, versatile peroxidase, manganese peroxidase and laccase. In mixed culture, the usage of heterotrophic bacteria and ammonia oxidizing bacteria has shown to degrade the 17 α -ethinylestradiol effectively (Khunjar et al. 2011).

Further, an enhanced removal of PPCPs using mixed microbial culture into the activated sludge has been reported (Zhou et al. 2014), which was also demonstrated to have the efficient removal capabilities in the presence of several number of PPCPs as compared with that of individual PPCP (Vasiliadou et al. 2013). It is might be due to the fact that some of the PPCPs have been utilized as a source of carbon and energy during the usage of mixed cultures (Vasiliadou et al. 2013). These examinations are revealing that the mixed cultures of these organisms have the potential towards the enhancement of removal of PPCPs. The mixed cultures of microorganisms have been demonstrated to be extensively explored methods for the removal of PPCPs in activated sludge during WWTPs (Khunjar et al. 2011). However, in some studies it has been found ineffective for PPCPs removal. Therefore, steps are needed

to take care to upgrade the removal process by activated sludge efficiently. In some cases, activated sludge exhibits low removal capacity to the PPCPs. Hence, steps have been taken to improve the removal of PPCPs by the activated sludge.

14.4.3 Anaerobic Removal Technologies

14.4.3.1 Bench Scale Up-Flow Anaerobic Sludge Blanket (USAB)

The UASB reactor explored along with continuous stirred tank reactor (CSTR) has been investigated for the removal of sulfonamide sulfamerazine (Sponza and Demirden 2007). The study has examined the removal efficiency of up to the value of 97%. The utilization of high concentration (90 mg L^{-1}) of PPCPs is not relating with the real scenario to understand the actual removal mechanism. Carballa et al. (2006) have examined the removal of ibuprofen and naproxen through bench scale studies under mesophilic anaerobic conditions. The biodegradation/transformation of these compounds was reported to be 40% and 87%, respectively. For similar compounds, their removal capability of more the 90% has also been reported for the sludge (Samaras et al. 2013).

This process is advantageous as compared with aerobic processes in terms of factors such as ability to treat more wastewater, low energy inputs, improved biogas recovery, less space requirement and cost-effectiveness. However, this process has also been considered as an insignificant technique for the removal of several PPCPs (Deegan et al. 2011). This is due to the diversification of PPCPs in natural and xenobiotic organic compounds that are considered to be recalcitrant and non-biodegradable.

14.4.3.2 Up-Flow Anaerobic Stage Reactors (UASRs)

Generally, the removal of pharmaceuticals using UASRs as a primary treatment process to activated sludge has been considered to be effective even at high concentration of contaminants in industrial effluent (Chelliapan et al. 2006). The incorporation of methanogenic archaea in different treatment units such as bio-membrane reactors, fluidized bed reactors and stirred tank reactors has known to be effective in the removal of PPCPs as compared with non-adapted methanogens (Gangani Rao et al. 2004; Fountoulakis et al. 2008).

The maximum removal of COD has been observed from real pharmaceutical wastewater that contains avilamycina and tylosin (Chelliapan et al. 2006). During an organic load of 1.86 kg of COD, a percent reduction of 70–75% and 95% was examined for COD and tylosin, respectively, at the HRT of 4 days. In this study, a decrease in COD removal has also been demonstrated with an increase in concentration of tylosin. In another study, a synergistic approach using UASR and anaerobic filter technology has showed the significant removal of COD even at high

organic load (Oktem et al. 2008). In thermophilic conditions, this process has been reported to remove the COD and BOD up to 65–75% and 80–94%, respectively, at the organic load of 9 kg (Sreekanth et al. 2009). However, the compound carbamazepine was examined not to be degraded by using UASR.

Carballa et al. (2006) have explored the anaerobic digestion of sewage sludge and investigated the degradation of several PPCPs. A significant removal for the compounds such as sulfamethoxazole, naproxen, roxithromycin, galaxolide, tonalide, diclofenac and oestrogens diazepam and ibuprofen has been examined. An insignificant removal of iopromide was observed, whereas carbamazepine was found to be persistent. Moreover, the study also revealed that the SRT and temperature were not affecting the removal of these PPCPs.

14.4.3.3 ELAN

This reactor is based on removal techniques involving partial nitrification and anammox processes. Alvarino et al. (2015) have investigated the degradation of 19 PPCPs using ELAN reactor of 200 L. Under partial oxic conditions, the system was allowed to undergo the ammonium oxidation (anammox) processes and nitrification processes in a single-stage reactor. More than 80% removal has been observed for the organics such as compounds bis-phenol A, ibuprofen, 19 celestolide, hormones and naproxen, whereas carbamazepine and diazepam were found to degrade (~7%) insignificantly. The study also revealed that an increase in rate of nitrification lead to increase in the degradation of bis-phenol A, triclosan and ibuprofen. However, the removal of erythromycin was found to be strongly dependent on the anammox reaction rate.

14.5 Conclusions

Presently as such there are no legitimately controlled maximum permissible limits for the discharge of pharmaceuticals in the environment. Environmental impact of organic micro-pollutants on natural water sources and soil can be curtailed if would be able to treat the contaminants in an economical way. Moreover, controlled reuse of water can help restrict the use of fresh water, which is a widespread concern on rivers around the world. Because of the fairly new emergence or identification of these contaminants, there is a disparity in the knowledge of their fate, behaviour patterns and impact and treatment approaches for their effective removal. Various conventional methods including physical, biological and chemical processes have been in practice for the removal of PPCPs, but most of them are not eco-friendly and require huge capital, implementation and recurring cost. Among all these methods, the biological method stands out for its advantages such as high degradation ability, low energy consumption, no secondary pollution, simple operation and relatively lower implementation cost. In these ways, this study appraised the existing research

providing authentic and quantitative information on various biological treatment methods, their removal efficiencies, their respective operating conditions and key findings, as well as their impact on the environment.

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Chapter 15

Mechanistic Understanding of Heterogeneous Photocatalysis for the Dye Degradation in Wastewater



Sahil Thareja

Abstract Water is one of the fundamental needs for the life on earth. However, the wastewater released from the industries consists of dyes and other organic molecules, which become the serious issue for the water pollution. Among all water remediation techniques, heterogeneous photocatalysis has gained scientific attention for the water purification in terms of degradation of dyes and other organic pollutants. Heterogeneous photocatalysis is a very robust, low cost method and can provide complete mineralization of the pollutants. In this context, this chapter deals with the basic principle and mechanism of heterogeneous photocatalysis; and the parameters affecting the degradation kinetics. Furthermore, the different functional photocatalyst material, their limitation and the modification in the structure of semiconductor catalyst to absorb visible light are discussed in this chapter.

Keywords Dye degradation · Heterogeneous photocatalysis · Semiconductor · Visible light · Wastewater

15.1 Introduction

The rapid population growth and global warming are comprehensively affecting our ecosystem, which reducing its capability to provide with sufficient quantity of food, drinkable water and good environment to live a healthy life (Pimental 1991). Water is one of the essence requirements for the human kind to survive on earth. To feed large population, there is exponential increase in the industrialization, agricultural activities from which many hazardous chemicals as pollutants are flowing through the wastewater without any pre-treatment, which is adversely affecting the water resources. As per World Health Organization (WHO) report, more than five million

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peoples die annually due to diseases associated with unsafe drinking water and inadequate sanitation (Gleick 2015). The major sources of water adulteration are industrial and agricultural waste which deprive the quality of water sources by contaminating it with the hazardous wastes like textile dyes, paints, pesticides, herbicides, heavy metals (such as mercury (Hg), lead (Pb), etc.), benzene, and phenolic compounds (Singh et al. 2019). By keeping in mind about the steady decrease in the clean and safe ground water level, there is an urgent requirement for developing a low cost and high competent water treatment technology to manage the wastewater efficiently and to mitigate its harsh effects on the environment.

To save the clean water for drinkable and other important purposes, the recycling of wastewater effluent is one of the possible solutions by treating it to reuse in the agricultural and industrial consumption (Chong et al. 2010). As mentioned earlier, wastewater effluent contains hazardous chemicals like heavy metals and organic compounds; the efficient treatment of these is a challenging task. There are different wastewater treatment processes, which can be combined together in three types: primary, secondary and tertiary treatment process (Gupta et al. 2012). Primary treatment processes include filtration, centrifugation, sedimentation, coagulation and flotation method. Filtration and centrifugation are generally used to remove the suspended solid particles in wastewater physically; coagulation and flotation methods are used to remove the suspended solids, oil and grease by adding certain chemicals like activated silica (Gupta et al. 2012). However, these methods do not mineralize the pollutants completely. Furthermore, these methods have some working difficulties such as sludge generation and phase change of the pollutants (Saggiaro et al. 2016). Secondary water treatment process includes the removal of pollutants by using biological route in which certain microbes like bacteria are used to degrade the pollutants in simple molecules like water, carbon dioxide and ammonia gas (Gupta et al. 2012; Goswami et al. 2017; Kushwaha et al. 2017). However, most of the dyes effluent in wastewater are obstinate towards the biological degradation, which ultimately decrease the efficiency of degradation through this treatment method (Saggiaro et al. 2016). Tertiary wastewater treatment processes are mainly responsible to provide clean and safe water for consumption purposes by treating the wastewater upto 99% which include the processes like distillation, crystallization, oxidation, solvent extraction and electro-dialysis (Gupta et al. 2012). By considering the essential factors for adopting a technology like cost effectiveness, eco-friendliness, recyclability and overall efficiency of wastewater remediation, the complete oxidation of harmful compounds of wastewater effluent into non-hazardous products such as H_2O and CO_2 is attracting as a most reliable technology (Serpone et al. 2010; Oller et al. 2011).

Among all the available wastewater treatment techniques, the advanced oxidative processes (AOP) are the most attractive, which can be highly efficient for the degradation of dyes and other organic pollutants. These processes involve the in-situ generation of highly reactive and non-selective hydroxide radical (OH^\cdot) oxidant that promote the complete mineralization or endorse the production of biodegradable by-products like water (H_2O) and carbon dioxide (CO_2) (Yoon et al. 2001). Advanced oxidation processes (AOP) include a variety of methods

Table 15.1 Comparison of different chemical and biological methods with heterogeneous photocatalysis

Method	Comment
Physical/chemical methods—precipitation, adsorption, flocculation, coagulation, chemical oxidation, reverse osmosis, membrane filtration and electrochemical (Gupta et al. 2012)	These methods can purify wastewater but with the production of secondary sludge. The disposal of this secondary sludge is a costly process. Moreover, the transformation of hazardous materials from one form to another is not a long-term solution to save the environment from the toxic waste
Biological—Using bacteria for the removal of toxic material in the wastewater (Saggiaro et al. 2016)	Due to the high chemical stability of synthetic dyes, biological treatment using bacteria is not able to remove dyes efficiently
Heterogeneous photocatalysis (Serpone et al. 2012; Saravanan et al. 2017)	Heterogeneous photocatalysis has the advantage of complete mineralization of the pollutant especially dyes. Moreover, through this method, it is easy to separate the catalyst after degradation process as the phase of catalyst is generally solid which is dispersed in the liquid solution of wastewater

like Fenton process, ozonation, ozone with peroxide are chemical based methods to degrade the organic pollutants (Balciolu and Otker 2003; Khataee et al. 2009), whereas UV/fenton process, UV/ozone, UV/peroxide, homo and heterogeneous photocatalysis use photon to induce the degradation processes, thus called as photochemical processes. (Fujishima et al. 2000; Ghaly et al. 2001; Gernjak et al. 2003). Light induced methods increase the efficiency of the degradation process.

Among all light induced processes, the heterogeneous photocatalysis is the most attractive and efficient method for the degradation of wide range of hazardous organic pollutants into biodegradable compounds and ultimately complete mineralization by producing water (H₂O) and carbon dioxide (CO₂) gas. In the heterogeneous photocatalysis, light is incident on the surface of catalyst, which further induces the charge separation between the valence band and conduction band of the catalyst. This charge separation is the key of the photocatalysis for the organic/dyes pollutants mineralization without producing any secondary pollutants. This chapter presents the mechanistic understanding of photocatalytic degradation, operating parameters, photocatalytic materials and modification in the semiconductor photocatalyst to absorb visible light in detail (Table 15.1).

15.2 Mechanism of Heterogeneous Photocatalysis

Heterogeneous photocatalysis can be defined as the process in which light is used to increase the efficiency of the reaction in the presence of catalyst. In 1972, Fujishima and Honda were the first to describe the process of heterogeneous photocatalysis by

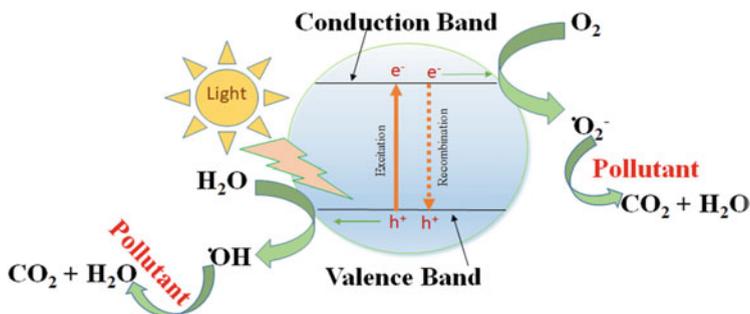


Fig. 15.1 Schematic representation of photocatalytic mechanism on semiconductor

demonstrating the photochemical splitting of water into hydrogen and oxygen under UV light by using TiO_2 as the catalyst (Fujishima and Honda 1972). By considering the importance of this viable process, many researchers have carried out extensive research for different application like water splitting into hydrogen and oxygen, degradation of organic and inorganic effluent in water and air, dehalogenation and many others related to energy and environment (Ollis 1985; Teoh et al. 2012; Serpone et al. 2012).

The fundamental processes involved in the heterogeneous photocatalysis are as follows (Saravanan et al. 2017; Ahmed et al. 2011):

- When the light (photon) incident on the surface of semiconductor having incident energy equal or greater than the bandgap energy of semiconductor, the electrons of the valence band adsorbs the energy and gets excited to the conduction band.
- This excitation process of electron into conduction band leaves a hole in the valence band. This charge separation is the fundamental of photocatalysis, which induces the degradation of harmful chemicals at the surface of semiconductor.
- The hole in the valence band can either oxidize the adsorbed harmful organic pollutants on the surface of semiconductor directly or react with the water (H_2O) to produce hydroxide radical. The reaction with water is the predominant process as generally the concentration of water molecules would be more abundant relative to pollutant(s). The generated hydroxide radical has high oxidizing character, which is mainly responsible for the degradation of the organic compounds.
- The electron in the conduction band further reacts with the adsorbed oxygen to reduce it into superoxide radical, which can further degrade the adsorbed pollutants.

This synergetic effect of charge separation into hole in valence band and electron in conduction band is responsible for the complete mineralization of harmful organic pollutants. A schematic representation of the photocatalytic mechanism of dye degradation on semiconductor photocatalyst is shown in Fig. 15.1. An important point for consideration is that the presence of oxygen or air is favourable to the

heterogeneous photocatalysis as it prevents the electron–hole recombination process by reacting with electron in conduction band.

15.3 Operation and Influence of Parameters on Heterogeneous Photocatalysis

The degradation of organic compounds by using heterogeneous photocatalysis process mainly depends upon the factors such as catalyst physical parameters (structure, size, shape and surface area), pH of solution, light intensity, impurity concentration in wastewater, catalyst concentration and oxidizing agent (Bahnemann et al. 2007; Cassano and Alfano 2000; Rajeshwar et al. 2008).

15.3.1 Effect of Catalyst Physical Parameters

The photocatalytic activity of the photocatalyst is dependent upon the catalyst physical properties such as its crystal size, composition, surface area, porosity, bandgap and hydroxyl functionalities on catalyst surface. Crystal size can be the most important parameter since its direct relation with the surface area of catalyst. In general, the catalyst particles with relatively high surface area shows better photocatalytic activity due to availability of large number of sites for the dye adsorption. Lu et al. (2007) use natural rutile (rutile ~90%) and P25 (80% anatase and 20% rutile) type of TiO₂ as catalytic surface to compare its efficiency for the photocatalytic degradation of methyl orange (MO). After 2 h illumination, the photocatalytic efficiency of the above two catalyst was found to be 82.3% and 94.8%, respectively. A possible reason was the particle size of P25 (~30 nm) which is significantly smaller compared with the natural rutile sample (70–80 μm). Another possible reason for the higher photocatalytic activity of P25 would be due to the slow electron–hole recombination process as compared to the case of natural rutile. As mentioned, P25 is composed of 80% anatase and 20% rutile phase in which nano-crystals of rutile are dispersed in the matrix of anatase. Due to lower bandgap of rutile (3.0 eV) compared to anatase (3.2 eV), rutile absorbs the energy of illuminated light, which separates the electron–hole pair. Then, the electron transfer from the conduction band of rutile to anatase inhibits the electron–hole recombination process, which can further move to the surface of the catalyst and increase the degradation process of dyes (Bahnemann et al. 2007). While in the case of natural rutile, the photocatalytic efficiency is low due to having more defects in its crystal structure, which serves as the electron–hole recombination centre (Lu et al. 2007). Besides these, other commercially available TiO₂ powders, namely Hombikat UV100 and PC500 have also been used for the photocatalytic degradation of organic dyes (Bahnemann et al. 2007; Saquib et al. 2008). Hombikat UV100 is composed of

100% anatase with a high specific BET surface area of $>250 \text{ m}^2/\text{g}$ and primary particle size of 5 nm. The photocatalyst PC 500 is also composed of 100% anatase having a specific BET surface area of $287 \text{ m}^2/\text{g}$ and primary particle size of 5–10 nm, while Degussa P25 have a specific BET-surface area of $50 \text{ m}^2/\text{g}$ and primary particle size of 20 nm. It has been found that the activity of these photocatalysts is not only depend upon their physical properties such as BET surface area, defects and density of surface hydroxyl groups but also depend on the type of the model pollutant for the degradation. Saquib et al. (2008) have reported that the Hombikat UV100 have high photocatalytic activity for the degradation of Fast Green FCF, whereas Degussa P25 have shown relatively higher activity for the Patent Blue VF. As discussed earlier, Degussa P25 shows the higher activity due to slow electron–hole recombination process, whereas Hombikat UV100 exhibit high photocatalytic activity due to fast interfacial electron transfer process (Martin et al. 1994; Saquib et al. 2008). Lindner et al. (1995) have reported that the UV100 have almost four times more photocatalytic activity as compared to P25 for the degradation of dichloroacetic acid. It is observed that Hombikat UV100 can be a better catalyst for the degradation of benzidine and 1,2-diphenylhydrazine (Muneer et al. 2002). Recently, Flores et al. (2014) have synthesized ZnO nanostructures with different morphology such as hexagonal disks, dumb bell shaped, rice and rod like structures for the photocatalytic degradation of methylene blue (MB) in aqueous solution. This study reported that the activity of these nanostructures is directly related with the surface area and defect content in the nanostructure. It has been suggested that the ZnO nanostructure might be a low cost alternative to the TiO_2 for the degradation of organic pollutants due to similar electronic bandgap (3.2 eV) and relatively higher photocatalytic activity especially for azo dyes (Flores et al. 2014). Akyol et al. (2004) have carried out photocatalytic decolourization of an azo dye Remazol red (RR), which shows that ZnO catalyst has much higher activity as compared to TiO_2 for the degradation process. Lee et al. (2009) have carried out the study using ZnO and TiO_2 for the photocatalytic degradation of total organic carbon (TOC) from aqueous solution of phenol which establishes that the ZnO nanopowder has 1.6 fold higher photocatalytic activity as compared to Degussa P-25 that is known as a standard photocatalyst.

15.3.2 Effect of pH of Solution

The photocatalytic degradation of organic dyes is strongly influenced by the pH of the solution as the charge on the surface of catalyst alters with the change in the pH of the solution. In addition, the physio-chemical properties of organic compound in the wastewater can also change with the change in the pH. As a result, the electrostatic interaction between the catalyst surface and organic dye is effected with the change in pH of the solution which will change the adsorption affinity of the organic pollutant on the surface of the catalyst thus would alter the degradation rate (Reza et al. 2017; Kazeminezhad and Sadollahkhani 2016). TiO_2 as a photocatalyst has an

amphoteric character, i.e. the surface of TiO_2 can be charged positive or negative in acidic and basic pH, respectively, which will affect the degradation kinetics of the dyes on the surface of TiO_2 (Poulios et al. 2000; Reza et al. 2017). Moreover, it has been found that the pH of the solution affects the formation of hydroxide radical by the reaction between light induced holes on the surface of catalyst and hydroxide ions. At low pH, the holes are considered as the major participant during the oxidation step in photocatalytic degradation, whereas at neutral and high pH, the hydroxide radicals are considered to be the predominant species for the degradation of organic dyes (Shifu and Gengyu 2005). As the presence of hydroxide ions are high on the surface of TiO_2 , which would increase the generation of hydroxide radical at high pH. Thus, the degradation efficiency would be high at higher pH in the case of TiO_2 , which have been indicated through the literature. Bubacz et al. (2010) have reported an increase in the rate of the photocatalytic degradation of methylene blue on the surface of TiO_2 with the increase in pH. Su et al. (2009) have reported the degradation of acid blue 80 dye at different pH (2–10) on the surface of TiO_2 and found the highest activity at pH 10, which can be attributed to the high adsorption of cationic acid blue 80 dye on the anionic TiO_2 surface at pH 10. Ling et al. (2004) have reported the degradation of methylene blue at the surface of TiO_2 at different pH and found highest activity at pH 12. Aly and Abd-Elhamid (2018) have reported the degradation of methylene blue on the surface of SiO_2 nanoparticles at different pH and found that discolouration increases at very low pH of 1 and high pH of 11. As stated above, these results can be attributed to the fact that the positive holes are predominant oxidation species at low pH. On the contrary, at high pH, OH^\cdot radical is more easily generated by oxidizing more hydroxide ions present on the surface of SiO_2 , which increase the efficiency of degradation (Goncalves et al. 1999). Chen et al. (2017) reported the degradation of azo dyes such as methyl orange (MO), direct black 38(DB38) and Congo red (CR) on the surface of ZnO at different pH condition. They found that the degradation of these dyes is more efficient at low pH (acidic) in contrast to high basic pH. This can be understood in terms of the charge on the surface of ZnO and the properties of dyes at different pH condition. The ZnO surface becomes positively at acidic pH and the above dyes are anionic in nature. Thus, at lower pH, the high degradation of these dyes was attained due to the high electrostatic attraction between anionic dyes and positively charged ZnO catalytic surface, which results in the increase in the adsorption of dyes. On the contrary, at higher pH, there would be electrostatic repulsion between the anionic dyes and negatively charged ZnO surface, which results in negligible adsorption.

15.3.3 *Effect of Light Intensity*

The wavelength and the intensity of the incident light affect the amount of light absorption by the semiconductor photocatalyst. The electron–hole separation in photochemical reaction is initiated by the incident light with a particular wavelength and intensity on the surface of photocatalyst, which eventually monitor the

degradation rate of the pollutant on the catalyst surface. It has been reported that the rate of photocatalytic degradation is better when the artificial UV-Vis light source is used as compared to solar irradiation (Viswanathan 2018). Ollis et al. (1992) have reported that the kinetics of the photocatalytic degradation is dependent on the intensity of incident light.

Accordingly,

1. At low intensity of light (0–20 mW/cm²), the kinetics of photodegradation would follow first order, i.e. the rate would increase linearly with increasing intensity of light;
2. At the intermediate light intensities, the kinetics follow half order, i.e. the rate of the photochemical reaction would depend on the square root of the intensity of incident light.
3. At high intensities of incident light, the kinetics follow zero order w.r.t light intensity, i.e. the rate of photochemical reaction is independent of the intensity of light.

With the increase in light intensity, there would be more photons per unit time and unit area. Which increase the electron–hole separation on semiconductor catalytic surface, which eventually enhance the photocatalytic activity. However, at high light intensity, the number of activation sites on catalytic surface remains the same beside the increase in photon concentration. Thereby, the photochemical reaction rate would become independent of the light intensity.

15.3.4 Effect of Pollutant Concentration

The pollutant type and its concentration in the solution also affect the photocatalytic degradation process. In the solution containing pollutant and the catalyst, the pollutant molecules get adsorb on the surface of the catalyst. When there is increase in the concentration of the pollutant substrate, there will be subsequently more demand of the catalyst surface to adsorb the large number of pollutant molecules, however with the same amount of catalyst, the pollutant molecules would cover all active sites. Therefore, the demand of reactive radicals (OH[·] and [·]O₂) for the degradation of pollutant would increase; however, the formation of these radicals on the catalyst surface would remain constant for a given catalyst amount, light intensity and irradiation time. Therefore, the available reactive radicals (OH[·] and [·]O₂) would not be sufficient for the degradation of pollutant at its higher concentration (Bahnemann et al. 2007). Consequently, degradation rate of pollutant decreases with the increase in its concentration. Qamar and Muneer (2009) have reported that with the increase in concentration of the vanillin from 0.35 mM to 0.5 mM, the degradation rate increases, but with further increase in concentration from 0.5 mM to 1 mM, the rate of degradation decreases.

15.3.5 *Effect of Catalyst Concentration*

The amount of the photocatalyst also influences the kinetics of photocatalytic degradation. In general, with the increase in the quantity of semiconductor catalyst in photochemical reactor, the number of active sites on the semiconductor photocatalyst increases, which in turn would produce more number of reactive radicals (OH^\cdot and $\cdot\text{O}_2$) (Ahmed et al. 2011). Hence, there will be increase in the degradation rate of pollutants. However, after an optimum concentration, the further increment in catalyst loading may adversely affect the kinetics of degradation. With the further increase in catalyst concentration, there will be decrease in the penetration depth of light into the solution, which would diminish the light scattering. In addition, the agglomeration of catalyst particles could increase with the increment in catalyst concentration, which decreases the overall surface area for light absorption. Due to these combined effect, the degradation rate decreases with the increase in catalyst concentration beyond optimum limit. However, optimum limit could be different with different type of catalyst and design of photochemical reactor. Sharma et al. (2008) reported the degradation of isoproturon on $\text{TiO}_2/\text{SBA-15}$ substrate with different loading of TiO_2 catalyst from 0.5 to 2 g/L. They found that there is increase in the degradation rate when catalyst concentration increases from 0.5 to 1 g/L and thereafter, the degradation rate decreases slightly.

15.3.6 *Effect of Oxidizing Agent*

In the photocatalysis process using conventional catalyst like TiO_2 , electron-hole recombination process is the major drawback, which decreases the efficiency of photochemical degradation of dyes. The presence of molecular oxygen traps the excited electron of conduction band, thus inhibit the electron-hole recombination process to some extent. However, the presence of oxidizing agent(s) such as ozone (O_3), hydrogen peroxide (H_2O_2), bromate (BrO_3^-) and peroxodisulphate ($\text{S}_2\text{O}_8^{2-}$) can further increase the kinetics of photochemical degradation of dyes (Wang et al. 2002; Saquib et al. 2008; Chen et al. 2018; Rehman et al. 2018; Feilizadeh et al. 2019). This is primarily due to their role in trapping more numbers of electrons from conduction band and thus further preventing the electron-hole recombination process, which may generate more oxidizing radicals (OH^\cdot) and thus leads to increase in the photochemical degradation of dyes. It has been found that the H_2O_2 influences the kinetics of photochemical degradation by producing more hydroxide radical (OH^\cdot) in two ways either by reduction of H_2O_2 by trapping electron at the conduction band or by self-decomposition of H_2O_2 into OH^\cdot when light falls on it, thereby increase the rate of dye degradation. Mahmoodi et al. (2006) have reported the effect of H_2O_2 on the photochemical degradation of the Reactive Blue 8 (RB 8) and Reactive Blue 220 (RB 220) and found increase in the degradation rate when

concentration of H_2O_2 increases from 0 to its optimal concentration (300 mg/L for RB8 and 450 mg/L for RB220).

The effect of various parameters on the photocatalytic degradation of pollutants shown in literature has been summarized in Table 15.2.

15.4 Photocatalyst Material(S)

In recent times, several semiconducting material such as metal oxide(s) like TiO_2 , ZnO , ZrO_2 , WO_3 , CeO_2 , Fe_2O_3 , Bi_2O_3 , V_2O_5 and metal sulphide(s) like CdS and ZnS are used as catalyst surface in heterogeneous photocatalysis (Saravanan et al. 2017; Viswanathan 2018). Among all these, TiO_2 has received the great attention in the photocatalysis industry due to its low cost and toxicity, chemical inertness, high photochemical activity, and non-specific oxidizing character (Akpan and Hameed 2009). TiO_2 comprises three phases: anatase (3.2 eV), rutile (3.0 eV) and brookite (3–3.6 eV). Among these, anatase is the most effective phase for the dye and other organic pollutant degradation due to its constituent favourable position to adsorb the pollutant. The oxygen ions on the anatase are in the triangular position, which efficiently increase the absorption of organic molecules, whereas the titanium ions in the anatase phase are oriented in such a way to favour the reaction with the adsorbed species. Among others, ZnO (3.3 eV), SnO_2 (3.57 eV) and CeO_2 (3.19 eV) can be considered as alternative for TiO_2 for the degradation of organic pollutants due to their high adsorbing capacity (Shinde et al. 2017).

However, due to large bandgap of these metal oxide catalyst(s), it can only absorb UV light which limits the efficient use of its applicability in degradation of organic pollutants and dyes since only about 10% of the solar spectrum consists of ultraviolet light (< 400 nm). In the rest of the radiant energy emitted from the sun, about 50% lies in the infrared (IR) region (> 700 nm) and about 40% in the visible region (400–700 nm) (Qiang and James 2003). On the earth crust, sunlight consists of only 3–5% of UV light, which makes it insufficient for the efficient degradation of dyes (Wang et al. 2019). To make use of enormous potential of sunlight, researchers are concentrating on to develop materials, which can absorb lower energy photon especially of visible light to make the degradation of dyes more efficient (Nakata and Fujishima 2012; Saravanan et al. 2017). Although there are certain metal sulphides like CdS (2.42 eV) and PbS (0.37 eV) which can absorb visible light photon due to their relatively lower bandgap; however, these metal sulphides are not stable, toxic in nature and composed of rare earth element which limits its application for the degradation of dyes (Boldish and White 1998; Shiga et al. 2016). It has been suggested that the bandgap of the above metal oxide(s) can be tuned in the visible light wavelength by adopting some techniques, which may improve the structure for high photocatalytic degradation of dyes. The next section will discuss about those improvement methods.

Table 15.2 Influence of various parameters on the photocatalytic degradation of pollutants

Pollutant	Catalyst	Catalyst concentration (Optimized)	Pollutant concentration (Optimized)	pH range (Optimized pH)	Light source (intensity)	Removal	Reference
Crystal violet (CV)	TiO ₂	0.2 g	2.5 × 10 ⁻⁵ mol/L for CV in 50 mL	–	UV light 125 W Hg lamp	96.7%	Ren et al. (2014)
Azo dye 2-(2-naphthyl azo)-4,5-diphenyl imidazole	ZnO	0.03–0.60 g/100 mL (0.15 g/100 mL)	50–100 ppm (50 ppm)	4–11 (8.1)	UV light (8.44 mW/cm ²)	84.06%	Saad et al. (2018)
Methylene blue (MB)	TiO ₂	0–35 mg/10 mL (20 mg/10 mL)	5–15 ppm (15 ppm)	5.5	UV LED (395 nm)	–	Zulmajidi et al. (2017)
Gentian violet	TiO ₂ -P25	0.25–3 g/L (2 g/L)	2.5–20 mg/L (15 mg/L)	5.74	UV light (1.8 mW/cm ² at 365 nm)	Complete decolorization in 30 min	Bendjabeur et al. (2017)
Methylene blue	SiO ₂	0.05–0.2 g/20 mL (0.2 g/20 mL)	50–200 ppm (100 ppm)	1–11 (low pH-1 High pH-11)	UV light	Complete degradation in 90 s	Aly and Abd-Elhamid (2018)
Methylene blue	TiO ₂	0.2–1.2 g/L (0.2 g/L)	1–15 ppm (10 ppm)	3–13.3 (13.3)	UV light 24 W	85% in 60 min	Salehi et al. (2012)
Methyl orange	ZnO	0.1–0.8 g/L (0.8 g/L)	10–50 mg/L (30 mg/L)	2–10 (2)	UV light	99.7%	Chen et al. (2017)

15.5 Modification of Catalyst

In spite of the extensive R&D on TiO_2 as a photocatalyst for degradation of dyes and other organic pollutants, the low photo-quantum efficiency of TiO_2 is still a major problem. This may be due to the rapid recombination of photo-generated electron and hole. In order to inhibit the electron–hole recombination process and to tune the bandgap of catalyst to absorb the visible energy for high photocatalytic activity, the surface of the semiconductor catalyst can be modified in the following ways: (1) Making a composite with metal/metal oxides or with carbon based materials like activated carbon, graphite, graphene and carbon nanotubes (CNTs); (2) Doping of certain metal and non-metal in the structure of semiconductor photocatalyst; and (3) Surface sensitization by dye/polymer.

15.5.1 Modification by Making Composite

One of the possible approaches for inhibiting the electron–hole recombination and modifying the bandgap of catalyst to work in visible region of solar radiation is to make coupled semiconductor photocatalyst(s). Recently, many semiconductor composites like $\text{Ag}_2\text{O}/\text{TiO}_2$, $\text{CuO}@/\text{ZnO}$ core shell, CdS/TiO_2 , PbS/TiO_2 , CdS/ZnO , and so on have been reported (Liu et al. 2017; Mansournia and Ghaderi 2017; Aziz et al. 2019; Jana et al. 2016). It has been found that the photocatalytic activity can be enhanced by making composite system as compared to single component photocatalyst. This is because the composition of two-semiconductor photocatalyst having different bandgaps can inhibit the electron–hole recombination. Recently, Aziz et al. (2019) have reported the composites PbS/TiO_2 and CdS/TiO_2 for enhancing the photocatalytic degradation of azo-based dye (acid orange-56) in the visible light by using the above principle. It has been shown that the activity of composite (s) PbS/TiO_2 and CdS/TiO_2 is significantly enhanced towards acid orange-56 in the visible light, while anatase- TiO_2 alone did not show photocatalytic activity with the same conditions. This is because in the presence of visible light, there is rapid generation of electron–hole in the PbS and CdS due to their harmonized bandgap energy with visible light as compared to anatase- TiO_2 . Since the conduction band of TiO_2 is situated at lower position to the conduction band of PbS and CdS , the photo-generated electron in PbS and CdS transfer to the conduction band of TiO_2 . In this way, the electron–hole recombination process inhibits and thus the photochemical activity toward the acid orange-56 degradation increases (Aziz et al. 2019).

In another approach, the composite of semiconductor with carbon based materials like activated carbon, graphite, graphene and CNTs and graphitic C_3N_4 have been explored. These heterostructure(s) enhance the photocatalytic activity because of high electrical conductivity, high surface area, high adsorption capacity and increase in charge separation and transfer at the heterojunction. Recently, Lin et al. (2018) have reported the hybrid structure of reduced graphene oxide/ TiO_2 /graphitic carbon

nitride (g-C₃N₄) for the enhanced photocatalytic degradation of methylene blue (MB) under solar light irradiation. In this heterostructure, the porous structure of reduced graphene oxide (rGO) and g-C₃N₄ increase the adsorption and photocatalytic reaction sites by making excellent dispersion of TiO₂ nanoparticles on the heterostructure, while g-C₃N₄ increases the visible light absorption due to its lower bandgap. Furthermore, rGO helps to improve the photo-generated charge separation due to its high electronic conductivity. This ternary heterostructure has shown significant enhancement in the photocatalytic activity, which is about 17.2, 8.6 and 2.7 times more than that of g-C₃N₄, rGO/TiO₂ and TiO₂/g-C₃N₄. Similar reports comprising effect of composite materials with metal oxide(s) and carbon materials on the photocatalytic degradation of dyes and other pollutants are presented in Table 15.3.

15.5.2 Modification by Doping of Metal/Non-metal

The doping of certain metal/metal ion(s) into the semiconductor lattice is another approach to inhibit the electron–hole recombination and to extend the absorption of light in visible region. Many transition metals such as V, Cr, Fe, Ni, Co, Zn, W, Mo; and noble metals such as Pt, Au, Ag and Pd have been used as a dopant in the lattice of semiconductor to increase the charge separation (Garcia et al. 2017; Liu et al. 2013; Inturi et al. 2014; Sowmya et al. 2018). Inturi et al. (2014) have reported the doping of many transition metals (M = V, Cr, Fe, Co, Mn, Mo, Ni, Cu, Y, Ce and Zr) in the lattice of TiO₂ for the visible light photocatalytic degradation of acetonitrile. In their study, Cr doped TiO₂ showed the superior photocatalytic activity, which is 8–19 times higher than other metal-doped catalyst. It has been observed that during doping of Cr in TiO₂ lattice, Ti³⁺ species originate in the structure. The Ti³⁺ energy level lies in between the valence and conduction band of TiO₂, which helps to absorb the photon in visible region. On the other side, Cr nanoparticles may serve as trapping centre for the photo-generated electron in the conduction band of TiO₂. In this way, the doping of Cr in the TiO₂ inhibits the electron–hole recombination and increases the overall efficiency toward the acetonitrile degradation.

Doping/co-doping with non-metal(s) such as B, C, N and S in the semiconductor lattice can also increase the photocatalytic efficiency in visible light by red shifting the bandgap of semiconductor (Giannakas et al. 2016; Helmy et al. 2018). Jin et al. (2018) reported the efficient photocatalytic degradation of methyl orange (MO) on N doped anatase TiO₂ catalyst and with increasing concentration of nitrogen, the activity toward degradation increases, whereas bare anatase TiO₂ have no catalytic activity in visible light. Koltsakidou et al. (2018) reported the photocatalytic degradation of fluorouracil using TiO₂-P25 and N/S doped TiO₂ catalyst under visible light and found the best activity with codoped catalyst at the optimum molar concentration ratio of one.

Table 15.3 Influence of making composite with metal oxide and carbon material(s) on photocatalytic degradation of various pollutants

Pollutant	Light source	Catalyst	Comment	Reference
Methylene blue	Visible light	TiO ₂ /Ag ₂ O	In visible light. Composite TiO ₂ /Ag ₂ O (1:4) shows best activity compared to bare TiO ₂ and Ag ₂ O with complete degradation in 50 min. The rate constant of TiO ₂ /Ag ₂ O (1:4), TiO ₂ and Ag ₂ O toward degradation is 0.085 min ⁻¹ , 0.005 min ⁻¹ and 0.065 min ⁻¹ , respectively	Liu et al. (2017)
Methylene blue	Sunlight (100 mW/cm ²)	TiO ₂ /CdSe	The composite TiO ₂ /CdSe film shows high photocatalytic degradation of 81.77% in 180 min, whereas TiO ₂ film alone shows only 27.99% degradation of methylene blue	Lu et al. (2016)
Methylene orange	Visible light (500 W)	CdS/ZnO	The composite CdS/ZnO shows high activity of 94.6% towards methyl orange degradation compared to CdS and blank experiment, which have activity of 75.8% and 8.1% in 180 min. The rate constant of CdS/ZnO, CdS and blank for methyl orange degradation is 0.0142, 0.0079 and 0.0005 min ⁻¹ , respectively	An et al. (2015)
Rhodamine B	Visible light (1000 W halogen lamp)	CdS/ZnO	This report provides that the photocatalytic activity depends upon the mass ratio of components of composite. CZ1:1 shows complete degradation of Rhodamine B in 190 min, whereas within same time, only 25% and 40% dye degraded in CZ1:2 and CZ1:3, respectively	Jana et al. (2016)
Phenol	Visible light (300 W Xe lamp)	Bi ₂ O ₃ /g-C ₃ N ₄	Bi ₂ O ₃ /g-C ₃ N ₄ shows higher photocatalytic activity than Bi ₂ O ₃ toward phenol degradation despite having low content of Bi ₂ O ₃ (3%) in Bi ₂ O ₃ /g-C ₃ N ₄	He et al. (2018)
Methylene blue and 4-Nitrophenol	Visible light	ZnO/ZnSe	The optimized ZnO/ZnSe composite shows better activity toward photocatalytic degradation of methylene blue (100%) and 4-Nitrophenol (92.5%) in 360 min, whereas pure ZnO has lower photocatalytic activity	Liu et al. (2015)
Methyl orange (MO)	Visible light	SnO/activated carbon (AC)	The SnO/AC(3%) composite shows better photocatalytic activity than bare SnO for MO degradation which is 97.6% in 80 min	Liang et al. (2019)

15.5.3 *Modification by Dye/Polymer Sensitizer*

The photocatalytic activity of semiconductor in the visible light can also be influenced by using certain dye/polymer molecules such as reactive red dye 198 (RR 198), eosin-Y, merbromine, 2,7-dichlorofluorescein, curcumin, cobalt(II)-phthalocyanine-tetrasulfonate, chrysoidine G, tolylene diisocyanate and polymer such as poly(fluorine-co-thiophene) (PFT) as the sensitizers (Rehman et al. 2009; Buddee et al. 2014; Behjou et al. 2013). When visible light is incident, dye/polymer molecule get excited and the excited electron moves to the conduction band of the semiconductor where these electrons are trapped by molecular oxygen to form superoxide radical (O_2^-) which can further increase the rate of degradation of organic pollutants. The literature reports comprising effect of doping of various metals, non-metals and surface sensitizers (dyes/polymers) on the photocatalytic degradation of organic pollutants are presented in Table 15.4.

The above modification(s) in the structure of semiconductor catalyst especially TiO_2 have efficiently enhanced its activity in visible light. However, to apply a particular photocatalyst at the industrial scale, long-term stability and large-scale production have to be considered. Black TiO_2 having high visible light response and thus high photocatalytic activity can be another interesting alternative to be used in the industry. Black TiO_2 can be synthesized via hydrogenation of P25 TiO_2 and can have a very low bandgap of about 1.0 eV which is lower than the P25 itself. However, the method used for the hydrogenation of P25 generally requires hydrogen atmosphere at high temperature and pressure, which impose a safety issue during its preparation. However, recently, Wang et al. (2019) introduced a hydrothermal method to overcome the shortcomings of hydrogenation method to reduce the P25 TiO_2 with reducing agent like zinc (Zn) and aluminium (Al). The processed black TiO_2 from this method have very low band in the visible region.

15.6 Conclusion

Based on recent studies, this chapter dealt with the mechanistic understanding of various operating parameters such as catalyst physical parameters, pH, light intensity, catalyst concentration, pollutant concentration and presence of oxidizing agent, which effect the photocatalytic degradation of various dyes and other organic pollutants. The studies exhibit that these parameters can significantly influence the photocatalytic degradation process. Photocatalyst degradation process has emerged as an excellent method for the mineralization of wastewater pollutants. However, the finding of an appropriate low cost, scalable photocatalyst, which can absorb visible light or sunlight, is still a challenge. The future work should concentrate on this issue in a very specific mode to provide a low cost, non-toxic, scalable, durable and reproducible photocatalyst, which can increase the efficiency of photocatalytic degradation by working in sunlight as the light source.

Table 15.4 Influence of doping of various metal(s), non-metal(s) and surface sensitizer (dyes and polymers) on photocatalytic degradation of various pollutants

Pollutant	Light source	Catalyst	Doping conc. (%) (optimum)	Comment	Reference
Congo red	Sunlight	Ag-TiO ₂	0.005–0.5% (0.1%)	Ag-TiO ₂ with 0.1% Ag doping shows relatively better photodegradation activity of complete degradation in 80 min, whereas TiO ₂ without doping shows 59% degradation in 80 min	Sowmya et al. (2018)
Methylene blue (MB) and RR-241	Visible light (500 W)	Nd and Er doped ZnO	Nd-2% Er-5%	Doped ZnO shows better activity compared to undoped ZnO. In 10 min, 100% degradation for MB and 78.6% for RR-241 take place in the presence of 2% Nd/ZnO and 5% Er/ZnO, respectively	Raza et al. (2016)
DB 71 dye	Visible light (500 W)	Mn doped ZnO	1.5% doping of Mn	Mn doped ZnO shows highest photocatalytic activity of about 98.9% at neutral pH. It follows pseudo first-order kinetics	Thenmarasu Sivasamy (2019)
Methylene blue	Visible light (400 W)	Ni/co/Ce/Sb doped CdS	2% doping	Co-CdS shows best activity of 87% degradation, whereas Ni-, Ce-, Sb- and bare CdS show 73%, 76%, 70% and 68% degradation, respectively	Ertis and Boz (2017)
Bisphenol A	UV-Vis light (500 W)	Ag doped ZnO	3% doping of Ag	The Ag doped ZnO with 3% doping shows relatively much better photocatalytic activity as compared to bare ZnO. It follows first-order rate kinetics	Hoshiyama et al. (2016)
Methyl orange	Visible light	N-TiO ₂	3.8%, 13.6%	With increase in conc. of N, the photocatalytic activity increases which is due to the decrease in the bandgap with increasing N conc.	Jin et al. (2018)
5-fluorouracil	Blue light (16 W)	N-TiO ₂	—	The optimum N-TiO ₂ shows 88.8% photocatalytic degradation, whereas Degussa P25 TiO ₂ shows 61.5% degradation	Lin et al. (2015)

4-Nitrophenol	Simulated sunlight	C,N-TiO ₂	C-15.07% N-1.25%	The C,N-TiO ₂ shows better photocatalytic activity of 87% and rate constant 0.00487 min ⁻¹ , whereas anatase TiO ₂ shows 65% activity and rate constant of 0.00253 min ⁻¹	Osin et al. (2018)
Rhodamine B	Visible light	C,N,S doped rutile TiO ₂ nanorod and C,N,S doped anatase TiO ₂ nanoparticle	—	Bandgap become narrow due to ternary doping which support photocatalytic activity in visible light. Optimized CNS rutile TiO ₂ nanorod shows complete degradation in 60 min, which is better compared to anatase nanoparticles	Wang et al. (2017)
Phenol and Rhodamine B	Visible light	N, F codoped oxygen deficient TiO ₂	N-0.31% F-3.92%	Doping increase the activity of the material towards degradation, whereas P25 shows lesser photocatalytic activity towards degradation	Kang et al. (2018)
Methylene blue (MB) and orange II	Visible light	Curcumin sensitized TiO ₂	7.5% of Curcumin	The photocatalytic activity with Curcumin sensitized TiO ₂ for MB is high in basic medium, whereas for orange II, it is high in acidic medium	Buddee and Wongnawa, (2015)
Rhodamine B	Visible light (90 W)	Tetra (4-carboxyphenyl) Porphyrin(TCPP)-TiO ₂	0.05–1% (0.1%)	TCPP provide 93% degradation of Rhodamine B under visible light in 10 h	Ahmed et al. (2017)

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Chapter 16

Development and Application of the Integrated GIS-MODFLOW Model



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Prabhat Kumar Singh Dikshit**

Abstract Water scarcity is the major problem faced by today's world. Groundwater is the most valuable resource of drinking water due to the scarcity of good quality surface water. Groundwater occurs in hard rock layers whose thickness may vary from few meters to 100 m. Aquifer stores the groundwater and yielded the water at the time of pumping. A groundwater model was developed for Kanpur city, a fast growing City of Uttar Pradesh, India. Progressive increase in the land reclamation projects, continuous population growth and increasing industrial water demand, an efficient water resource management plan was needed for the city. Groundwater extraction is increasing excessively due to the high river water contamination. For the better management of groundwater, steady state groundwater flow model was conceptualized for 10 years from January 2007 to December 2017. This three-layer model was calibrated for 7 years to symbolize the actual field condition and validated for 3 years. In groundwater flow model preparation, Geographic Information System (GIS) techniques were integrated to simulate the groundwater flow. This integration of GIS and groundwater flow model was very helpful in evaluating the groundwater potential zones and generating the various possible scenarios for management and prediction of groundwater. The results of the current study confirm that the groundwater aquifer in Kanpur city is prone to significant water head reduction, especially in the high elevation zones. Therefore, there is need of an efficient integrated and sustainable management plan for the groundwater resources to minimize the impact of too much extraction of groundwater in the study area.

Keywords Groundwater modeling · MODFLOW · GMS · Water budgeting · GIS

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16.1 Introduction

A model is a theoretical portrayal or approximations that depict the physical framework utilizing scientific conditions. They may not be the correct representation of the physical frameworks or system. Groundwater model depicts the groundwater flow and transport processes utilizing mathematical equations based on certain assumptions. Assumptions are used in the modeling to simplify the modeling process (Olsthoorn 1985). Assumptions involved in the modeling are flow direction, boundary conditions, aquifer geometry and model domain, stratigraphy of the aquifer and soil type, aquifer parameters and identification of source and sink (Anderson and Woessner 1992; Bear and Verruijt 1987). After developing and representing the simplified form of hydro-geological framework sensible elective scenarios can be anticipated and tested on the framework (Scibek et al. 2007; Maxwell and Kollet 2008). The appropriateness or helpfulness of the model relies upon how intently the scientific conditions and mathematical conditions surmised the physical framework being modelled. For the accurate application of the model it is important to have through understanding of the physical framework and the assumptions involved in the derivation of the mathematical equations.

According to Furman (2008) and Barlow and Harbaugh (2006), the most commonly used numerical model to simulate groundwater flow is MODFLOW which is a three-dimensional model, originally developed by the U.S. Geological Survey (McDonald and Harbaugh 1988). However, there are also a number of more sophisticated models available such as Groundwater Modeling System (GMS) (Anon 2000), Finite Element subsurface FLOW system (FEFLOW) (Diersch 2009), Visual Modular three Dimensional Flow (Visual MODFLOW) (Anon 2000), a 2D and 3D geostatistics, uncertainty analysis and visualization software package (UNCERT) (Wingle et al. 1999) and Processing MODFLOW for Window (PMWIN, Chiang 2005). Among all of them MODFLOW code is widely used and various studies were done based on MODFLOW code (Omar et al. 2020; Nishikawa 1998; Ting et al. 1998; Umar et al. 2008; Asghar et al. 2002; Faunt et al. 2004; Wang et al. 2009) Harbaugh et al. (2000). This code was used with the combination of GIS techniques which can provide good visualization interface for the user (Omar et al. 2019).

The study concluded that groundwater modeling is important to understand and study the behaviour of the aquifer system and finding the groundwater level under various hydrological stresses.

16.2 Study Area

Kanpur Nagar is the second largest city of Uttar Pradesh, India and it is ranked 12th in the category of population in the India. Being the historical importance in the history and due to high population density, district has high groundwater stress. This study focuses on the Kanpur Nagar, which is surrounded by two rivers, i.e. the

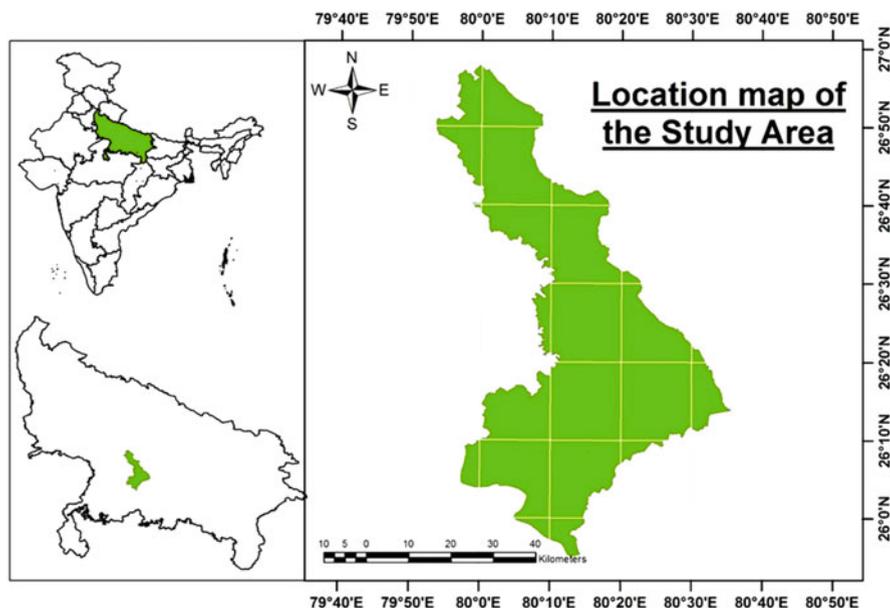


Fig. 16.1 Map showing the location of the study area

Ganga River in the north-east and the River Yamuna in the south. The study area lies between geographical coordinates $25^{\circ}55'$ to $26^{\circ}57'$ N and $79^{\circ}54'$ to $80^{\circ}35'$ E. In the south, district is surrounded by Hamirpur, Unnao district in the north-east and Bundelkhand lies just south. District lies in the central of the Indo-Gangetic plain which is very fertile doab region of the Ganges and Yamuna River. Figure 16.1 shows the position of the study area. For supply of the drinking water, water is intake from the Ganga River and Pandu River. Ganga water is pumped from Bhairon Ghat raw water pumping station but after the construction of Lav Khush Barrage (Ganga Barrage) water supply is done from here. It is sufficient to cater the needs of the town up to 2031 (Kanpur City Development Plan Under JNNURM n.d.).

Kanpur District experiences an atypical version of a humid subtropical climate with long and very hot summers, mild and relatively short winters, dust storms and a monsoon season. District lies in the northern plain of India, which witness large variations between summer and winter temperatures. Temperature in the study area can drop to a minimum of 7.3°C in the winters and maximum of 41.0°C in summers. Study area experiences severe fog in the month of December and January while hot dry winds, called loo, blow in the month of May and June. Rains appear between July and September almost at the end of regular monsoon season. Some rainfall is recorded during the harvest season of March–April. The average annual rainfall recorded over the study area is 885 mm. Crops of rabi and kharif are main crops in the study area. Major physiography of the study area consist of central Ganga alluvial plain due to which alluvial sand and loam are the major soil type in the study area.

16.3 Data Used and Adopted Methodology

Model development and accuracy of that model depend upon the availability and accuracy of the measured or recorded data. Development of groundwater flow model needs two types of hydro-geological data. First data defines the physical framework of the groundwater basin and second data describes its hydrological framework. For the development of groundwater modeling different data is collected from different agencies. In the present study, data are collected from CWC Lucknow, CGWB Lucknow, India-WRIS portal and IMD Pune. The data include well data, borehole data, rainfall data, population data, livestock data, groundwater water level data, river head and bottom elevation data. Various data are collected through field survey (Tables 16.1 and 16.2).

Field survey is very important for understanding the hydrogeology of the study area. Population related information is obtained from the national census data. Rainfall data (in mm) was obtained from the Indian Meteorological Department (IMD), Pune. Data related to types of soil were taken from the official website of the

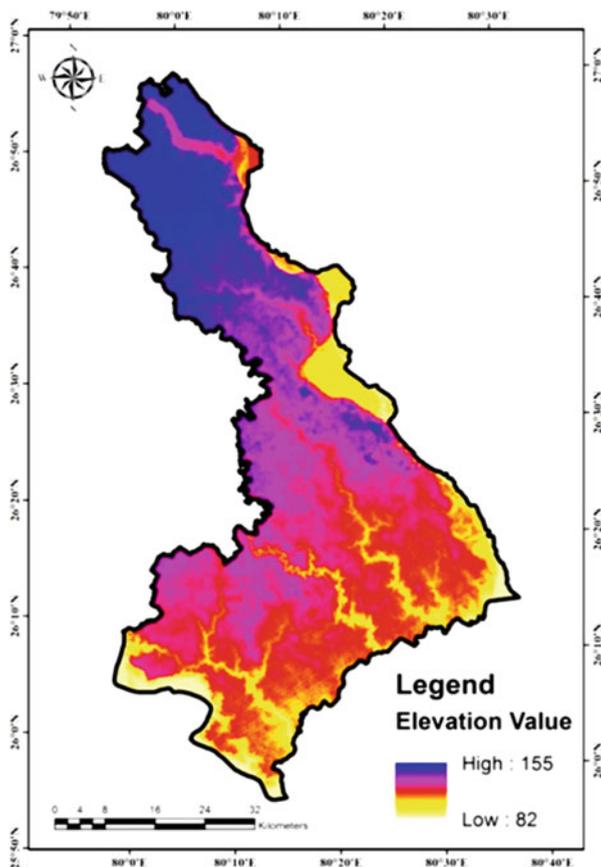
Table 16.1 Data used in the model development with their spatial and temporal details

Type of data	Location/area	Time/duration	Use
Climate data (rainfall)	Kanpur	2007–2015	Model input
Soil data	Kanpur Nagar	2007	Soil characteristics
Satellite imagery	79°55' E 25°50' N to 80°35' E 27°00' N	January 2007	Land use and land cover

Table 16.2 Detail of satellite imagery data used in the model

Year	Month	Path-row	Data description	Spatial resolution (m)
1995	January	143-42, 142-42,43	Landsat-5 TM	30
2000	March	143-42, 142-42,43	Landsat-5 TM	30
2005	November	143-42, 142-42,43	Landsat-5 TM	30
2008	December	143-42, 142-42,43	Landsat-5 TM	30
2010	January	143-42, 142-42,43	Landsat-5 TM	30
2011	February	143-42, 142-42,43	Landsat-5 TM	30
2013	March	143-42, 142-42,43, 141-42,43	Landsat-8 OLI_TIRS	30
2015	April	143-42, 142-42,43, 141-42,43	Landsat-8 OLI_TIRS	30
2017	October	143-42, 142-42,43, 141-42,43	Landsat-8 OLI_TIRS	30
2014	September	SRTM1N25E081V3, SRTM1N25E082V3, SRTM1N25E083V3	SRTM DEM of 1 Arc-Second	30

Fig. 16.2 DEM of the study area

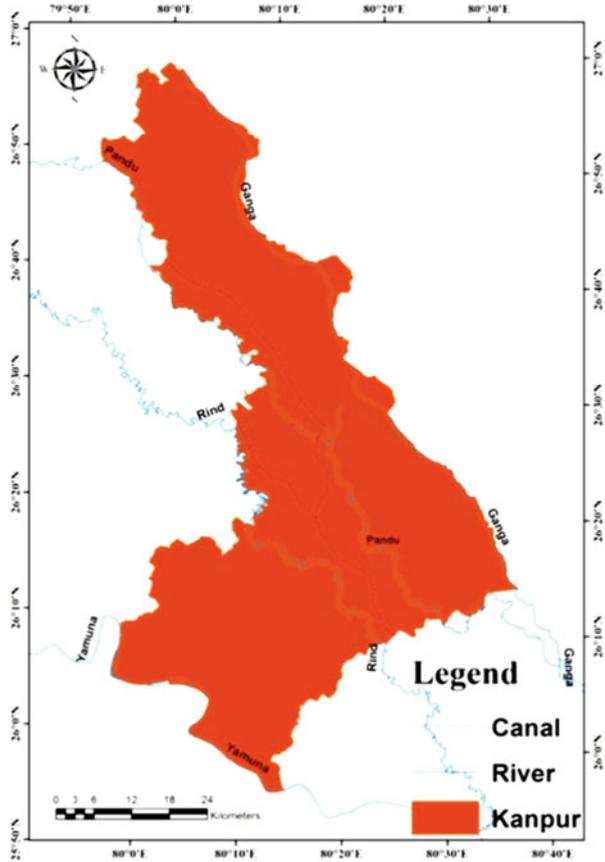


Department of Soil Survey and Soil Conservation. The elevation of study area is found by using DEM (Digital Elevation Model) of the study area. The DEM of study area is downloaded from the USGS (United States Geological Survey) site (<https://www.usgs.gov/>). Digital Elevation Model of the study area is shown in Figs. 16.2 and 16.3.

In order to develop, MODFLOW for the study area, it is first of all necessary to know the vertical stratification of the area. For this data was collected from Jal Nigam Kanpur. Borehole data provide the type of soil, their thickness and depth of the aquifer. For this, fence diagram was prepared based on the lithological logs as shown in Fig. 16.4. Fence diagram reveals the vertical and lateral disposition of aquifers in the study area down to depth of 150 m below the groundwater level.

Top layer of the area is surface clay which varies in depth from 3 to 6 m. Second layer comprises of fine sand and varies spatially in the nature. Below this layer clayey soil and sandy clay layer were found. At the bottom, a relatively hard and impervious bed is encountered. Due to this variability, for the model development, a conceptual model of three layers of each of thickness being 50 m is used in the

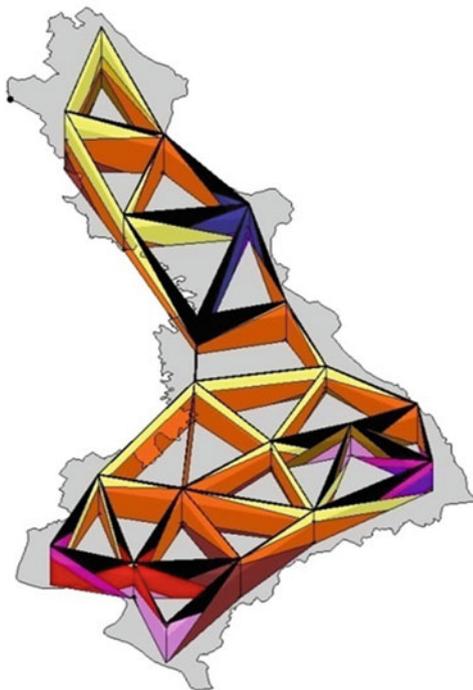
Fig. 16.3 River and canal network in the study area



present study. After developing the stratigraphy for the study area, solid data was prepared and interpolation of the solid data into the three layered MODFLOW model was done. Cross section in the soil data is showed in Fig. 16.5.

In the present study, the groundwater flow model is conceptualized as a three layered aquifer system spread over 15.70 km × 16.2 km area. The area is discretized into a three dimensional grid with single grid cell size of 50 m × 50 m. For the value of permeability, value was taken from the literature in and around Kanpur. The vertical permeability is considered as one tenth of the horizontal permeability (McDonald and Harbaugh 1988). Recharge to the groundwater was taken from the literature review. Recharge value was assigned to the MODFLOW to incorporate the influence of recharge in the study area. However, effect of the recharge is considered in the first layer of the model only. Specified flow boundary was given to the boundary of the study area other than the river boundary.

Fig. 16.4 Fence diagram for the study area



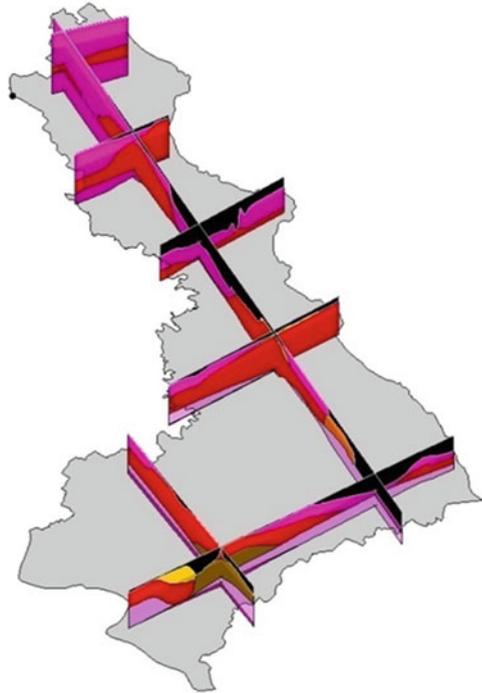
16.3.1 Model Calibration

In the present study, model calibration was done using three model parameters, namely horizontal hydraulic conductivity, vertical hydraulic conductivity and recharge rate. Model calibration is a process in which value of the input parameters was changed and tries to match the field conditions within an acceptable limit. After a number of trial runs, value of these parameters was adjusted in order to match the computed heads with observed heads.

16.4 Results and Discussion

In model improvement, steady state calibration comprised the matching of measured heads in the aquifer with hydraulic heads simulated by MODFLOW. The calibration of the model was done using 14 observation wells. Accuracy of the simulated water head was judged by comparing the mean error, mean absolute and root mean square (RMS) error calculated. RMS error can be defined as the square root of the sum of the square of the differences between computed and measured heads, divided by the number of observation wells. The absolute residual mean measures the average magnitude of the residuals and provides better indication of the calibration. In the

Fig. 16.5 Cross section of the solid data



final model, it was ensured that the model water head reasonably matched with the measured water head during the period of model developed. The simulated water head of the model indicates a prevailing trend of groundwater level in the inter stream region.

16.4.1 Water Budgeting

Groundwater flow modeling programs normally deliver water budgets for the model territory. In water budgeting, water accumulating in the cell was calculated and MODFLOW provides this data in the table form. The groundwater budget was computed from the groundwater flow model for the study area using zone budget.

Here, recharge from the rainfall is 2381310.277 m³/day and from other inflows it is 29354.268 m³/day. Outflow from model is 510817.913 m³/day. This outflow is from the constant head boundary. And discharge from the well is 2,303,000 m³/day. Loss of groundwater in the form of evapotranspiration is 6803.743 m³/day. The change in storage is -1.0667 means outflow is greater than inflow. These results indicate that there is immediate necessity for the arrangement of recharge of groundwater in the Kanpur District to save the groundwater for future generations.

16.5 Conclusion

Groundwater is the main resource of drinking water so the management of groundwater should be very high priority. Modeling of the groundwater is a complex phenomenon because in this various hydro-geographical features have to deal. Nowadays, groundwater flow model has proven to be a very useful tool more than a very long for addressing a range of groundwater problems. For this reason groundwater modeling is performed in the Kanpur District. Model calibration has also been performed by selecting three model parameters. Results show that the simulated values of the water head are in good-fitness of the measured data, which indicates that the model is trustworthy. The field monitoring was also incorporated in the study to verify the model predictions. The groundwater budgeting of the study area shows that total outflow from the area is more than total inflow into the area which indicate that the groundwater depletion in study area is taken place. Similar studies can be undertaken for other water stressed areas for the reliable water resources estimation so that better and efficient water resources planning and management can be done.

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Chapter 17

Salinization of Coastal Groundwater Resource in the Perspective of Climate Change



Somnath Bar, Binita Kumari, and Saurabh Kumar Gupta

Abstract Groundwater is around one third of global water withdrawals and serve drinking water. Coast is a most sensorial and dynamic geomorphic unit where marine, Aeolian, and terrestrial system meet. Coast is a potential area for human dwell, around 70% of world population live along the coast, and this population is growing exponentially to support the increasing population growth and development requires a large quantity of freshwater. In several areas groundwater resource is a subject of worry in respect to both quantity and quality. Groundwater salinization is considered a specific category of pollution that portends groundwater resources, because mixing a small quantity of saltwater with groundwater makes freshwater unsuitable and can result in abandonment of freshwater supply. Pumping or over extraction is considered the key reason of saltwater intrusion into coastal groundwater aquifers in several areas of the world although climate change and global warming have significantly accelerated sea-level rise and groundwater recharge.

Saltwater intrusion poses a major restriction to utilization of groundwater so saltwater intrusion should be prevented or at least have to be controlled. It is essential to practical measures and protect the available groundwater resources from pollution, saltwater intrusion, and contaminants which deplete quality. The modern computer modelling techniques can be used to design better groundwater withdrawal networks and methods to reduce the probability of sea-water intrusion and contaminations.

Keywords Groundwater · Coast · Salinization · Saltwater intrusion

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17.1 Introduction

Coast is a very sensitive transitional or ingredient zone between marine and terrestrial system. The most dynamic environment of the planet is coast. Coast is the meeting place of the hydrosphere, lithosphere, and the atmosphere, where wave, tidal energy is expanded to carry out erosion, transport, and deposition. The sensorial geomorphic unit coastal zone is subject to constant change minute by minute as waves break and currents move along shore; daily with high and low tides; monthly with tidal cycles; and over the longer term with change of climate and sea level. Due to the constant changing behaviour of the coast, major problems occur on geologic resources and coastal communities. As an impact of global warming, sea levels have risen through the twentieth century (Nicholls and Cazenave 2010). Coastal region's condition is declining due to the anthropogenic activity of the global population and undergoing environment decline, this issue being particularly acute in developing countries. Due to seawater intrusion advancements, existing pumping wells, exclusively adjacent to the coast, become salty and have to be uncontrolled, thus, reducing the value of the aquifer as a source of freshwater. Coastal metropolitan cities and towns increase out of control, like some generic experiment gone awry and Industries expansion with minor regard for environmental amenities. Resources are used and abused with thoughtless abandonment. Everywhere, it seems, coastal zones are under tremendous pressures (Laird 2009).

Contamination of freshwater aquifer is a global issue as it affects water quality, vegetation health, and soil environments along coastal areas. Deterioration of this freshwater resource threatens the sustainability of the water supply of coastal communities and their economic development (Cassardo and Jones 2016; Gain et al. 2012). Coastal regions face several hydrological problems like flooding due to cyclones and wave surge, and drinking freshwater scarcity due to saltwater intrusion in coastal aquifers. Groundwater is the largest source of freshwater and it is a ubiquitous source. Ground water plays a vital role in sustaining ecosystems and allowing human adaptation to climate variability and change (Scanlon et al. 2012). The coastal aquifers are very sensitive to saline sea-water intrusion and diffusion of pollutants due to placer mining, sea-level rise, and land use changes (Melloul and Collin 1998; Subba Rao et al. 2013). Groundwater of arid regions is frequently affected by high salinity due to evapotranspiration; it is the most common processes that cause salinization, mixing with seawater, rainfall concentration, and salts dissolution (del Pilar Alvarez et al. 2015). As an example of the salinization, groundwater has been reported even from highly populated coastal plains in temperate climate, e.g. the Polders in The Netherlands (Oude Essink et al. 2010), the Everglades in Florida (Langevin and Zygnerski 2013) and the Po Delta in Italy (Giambastiani et al. 2013).

As per the study on recent projection scenario of climate changes (IPCC 2014), the study showed the impact of pollution on groundwater resource has become much severe. Numerous studies tried to quantify the effect of relative sea-level rise (RSLR) on saltwater intrusion. Werner and Simmons (2009) have identified that the major

hydrogeological factors controlling RSLR impact saltwater intrusion in unconfined coastal aquifers, using a steady-state approach with an analytical solution, and these are also distinguished between flux-controlled and head-controlled systems and presented that sea-level rise is much challenging for head-controlled systems because inland water levels do not rise with rising sea level. In 2011, Chang et al. (2011) has found that for flux-controlled confined aquifers, sea-level rise may not have an impact on freshwater volumes. After Werner and Simmons (2009) and Werner et al. (2012), the study has extended to include confined aquifers and quantitative vulnerability indicators that can be calculated based on boundary condition type and hydro-geologic parameter values.

Both natural and anthropogenic processes played very crucial role in intrusion of sea water in coastal area. Sea-level rise is much associated with climate change (and also changes to atmospheric pressure, expansion of oceans and seas, and melting of ice sheets and glaciers). It is one potentially significant process that is expected to play a role in sea-water intrusion. Intergovernmental Panel on Climate Change (IPCC 2001) has predicted that by 2100, global warming will be the main cause of sea-level rise of between 110 and 880 mm, and it is usually understood that sea-level rise is expected to result in the inland migration of the mixing zone between fresh and saline water (FAO 1997). The rise in sea-water levels leads to increased saline water heads at the ocean boundary, and enhanced sea-water intrusion is the logical consequence. Two conceptual models are tested and may be measured to control the sea-water intrusion. Flux-controlled systems, where groundwater discharge occur to the sea is determined despite changes in sea level (groundwater level rise is proportionate with sea-level rise and hydraulic gradients are maintained), and second one is head-controlled systems which hydrogeologic controls (surface water bodies or bore fields) keep the inland head in the aquifer despite sea-level changes (Werner and Simmons 2009). They quantify the saline water–freshwater interface migration due to sea-level rise as a function of vital hydrogeological variables including aquifer thickness, recharge rate, hydraulic conductivity, and the rate of groundwater discharge to the sea.

17.2 Mechanism of Sea-Water Intrusion in Coastal Aquifer

Sea-water intrusion is a natural phenomenon that occurs as a result of the density difference between fresh and saline groundwater. Usually, the denser saline water forms a deep wedge that is separated from the freshwater by an ingredient zone of variable density. In some cases, this wedge can extend for many kilometres inland. (Kumar 2016) When groundwater is pumped from aquifers of land area that are in hydraulic connection with the sea, the gradients that are set up may induce a flow of saltwater from the sea towards the well. This migration of saltwater into freshwater aquifers under the influence of groundwater development is known as seawater intrusion. Saltwater intrusion can be induced in both unconfined and confined aquifers. To understand the mechanism of the processes involved, it is essential to

examine the nature of the saline water and freshwater interface in the coastal aquifer under normal condition. The most initial analyses were carried out independently by two European scientists (Ghyben 1888; Herzberg 1901) around the turn of the century. The assumptions were simple hydrostatic conditions in a homogeneous, unconfined coastal aquifer and they present that the interface between dense saltwater and less dense freshwater must project at an angle $<90^\circ$. Due to hydrostatic pressure conditions the weight of a unit column of freshwater extending from the water table to the interface is balanced by a unit column of saltwater extending from sea level to the same depth as the point on the interface. This is often called the *Ghyben-Herzberg* relation (Freeze and Cherry 1979). In both the hydrostatic analysis and the steady-state analysis assume the interface that differentiates fresh and saltwater in a coastal aquifer is a sharp boundary. There is a chance for saltwater and freshwater in diffusion zone around the interface to mix. Size of this zone is basically controlled by dispersive characteristics of the geologic strata. In where the zone is narrow, the methods of solution for a sharp interface may provide a satisfactory prediction of the freshwater flow pattern, but an extensive zone of diffusion can modify the flow pattern and the location of the interface and must be considered.

The main causes behind the saltwater intrusion in coastal aquifers are (1) Sea-level rise, (2) Subsidence of coast, (3) Decrease in Recharge, and (4) Increasing of pumping or ground water extraction. Once hydrodynamic coastal aquifer equilibrium has disturbed, it is very difficult to reverse because of the density differences (Light freshwater unable push the intrusive dense saltwater).

17.3 Modern Research Techniques in Coastal Groundwater Study

Coastal groundwater will rise with sea level, affecting water quality, the structural integrity of infrastructure, and natural ecosystem health. SLR induced groundwater rise has been studied in coastal areas of high aquifer transmissivity.

From last few decades, modelling has become a significant and very powerful tool in many branches of science. Models allow to test different hypotheses in a way that is non-destructive to the actual problem at hand. As many studies involving in sea-water intrusion, modelling has been used for several purposes.

One common goal of all these numerical and analytical models is to forecast and describe the movement of the transition zone of the aquifer where freshwater and saltwater meet and another goal of these modelling is to predict the degree and range of mixing in transitional zone.

Sea or Saltwater intrusion modelling studies can be categorized as Physical, Analytical and Numerical. Out of these three category numerical modelling is mostly used with availability of high configure computers (Kumar 2016).

17.3.1 Physical Modelling

Physical models have the additional advantage of providing visually understanding of the problem being studied, a crucial element when dealing with the lay population. Physical modellings have a unique identity as it allows the actual problem to down scale to manage and control. These models consist of minute physical analogues of the geology and hydrology of the condition being analysed. Custodio and Bruggeman (1987) has described that the physical models as an analogue which has similar dimensions as like prototype and in which every prototype element is reproduced, differing only in size. Physical modelling is very useful when numerical and analytical models are inappropriate for unavailability of long term historic and hydrological data. A simple example of these model is sand box type model where a container with sand filled porous media or bed and the movement of the fluid through the media occurs. Ion movement under an electrical gradient through an electrical solution is another type of model.

Another frequently used physical model is the Hele–Shaw analogue which employs two-dimensional groundwater movement and it consists of two transparent plates placed near together with a porous media in between to study the fluid flow in different hydraulic gradient (Kumar 2016).

17.3.2 Analytical Modelling

The analytic solution for the steady-state location of the freshwater–seawater interface developed by Strack (1976, 1989) is the basis for the method described by Werner et al. 2012. Analytical models include solving equations where a definite closed answer is reached at the end of calculations, offering ease of calculation and a simplified version of the real problem. First analytical model accurately presented by Custodio and Bruggeman (1987). The analytical models of sea-water intrusion in coastal groundwater of limited size are developed in an optimization methodology for determining the optimal pumping rates. These models are basically based on the sharp interface approximation and the Ghyben-Herzberg relation (Mantoglou 2003).

Analytical models are similar to numerical models, except that the equations involved can be solved exactly without the use of approximation methods. To address the equation, it is a must to assume some simple assumptions which provide a precise solution. Thus, this model is not suitable for complex flows and geometries that is why analytical models have inadequate use for sea-water intrusion modelling (Kumar 2016).

17.3.3 Numerical Modelling

Mostly, the seawater intrusion is extremely nonlinear process. For spatial and temporal simulations numerical modelling like finite element method or finite difference method are needed to figure out nonlinear equations of flow through saturated or unsaturated media (Javadi et al. 2013). The groundwater flow movement is unsteady in subject to Darcy's law under temperature and pressure where input and outputs are spatially and temporally varies. Hydraulic dispersion and molecular diffusion are main phenomena for sea-water intrusion (Lu et al. 2013). Numerical modellings are amalgamation of mathematical algorithms that present hydraulic and chemical facts. Partial differential equations relate the parameters example as head and water flow. The first efforts to model the density dependent miscible seawater and freshwater were accomplished by Henry (1964) and Pinder and Cooper (1970). After that numerical modelling of sea-water intrusion has been conducted by Cantatore and Volker (1974), Cheng (1975), Christensen (1978) and several other studies in the last few decades. According to Atkinson et al. (1986), the categories of algorithm which are commonly employed for numerical modelling are finite difference methods, finite element methods, and the method of relaxation. FEFLOW (finite element subsurface FLOW system) is a 3D groundwater flow model, which can simulate transient or steady-state, fluid density coupled or linear, and flow and mass, flow and heat or completely coupled thermohaline transport processes in subsurface water resources (Diersch and Kolditz 2002).

17.4 Coastal Groundwater Salinization Under Climate Change

As earlier mention that the main causes of sea-water intrusion are sea-level rise, subsidence of coast, decrease of recharge and increasing of groundwater extraction, much of the reasons circulated around climate change or extensive variability of climatic phenomena. Climate change has a significant intensive effect on the hydrological cycle by affecting precipitation, evapotranspiration, and soil moisture, etc. In hydrological cycle evaporation and precipitation are much intensified in the perspective of climate change. Some part of the globe may face significant reduction of precipitation and the main alteration is time cycle of wet and dry season (IPCC 2000). Some studies from the past decade show that coupled climate change with hydrological modelling studies indicates that different areas face water resources stress due to climate change. The most stressed country is in southern and northern Africa, around Mediterranean and Middle East, Central America, a large part of Europe, South Asia and Indian subcontinent. These studies also predicted for 2025 and above mentioned countries will growing to get affected by climate change and water resource stress. By the year 2050s and 2080s, other countries in southern

Africa will derive into the stressed class and pressures will grow much rapidly in Africa and parts of southern Asia and Eastern Europe (Arnell 1999).

Coastal aquifer is an important sources of freshwater and saltwater intrusion. Climate variability has significantly altered rate of recharge and thus affects the availability and quality of freshwater. As Ranjan et al. 2006 mentions that coastal aquifer salinization is a function of reduction of groundwater research and as result in crisis of fresh groundwater resources.

17.4.1 Effect of Sea-Level Rise

Sea-level rise is a key indicator of climate change. In the twentieth century, sea level has experienced a rising rate of 0.06 m per decade and since 1950s in every successive decade has faced an increased rate of sea level (Gehrels 2009). IPCC (about climate change) has found that from 1993 to 2010, sea level rose by about 3.2 mm per year and it is expected that this in future sea level will probably rise upto 1 m (Etkin 2015).

As Etkin (2015) mentions the causes of sea-level rise are Thermal expansion of ocean for global warming, Continental ice melting, and change of land water storage. Since 1993–2007, ~30% of sea level rise was reason of thermal expansion and ~55% due to ice melting and this contribution has increased ~80% after 2007 (Cazenave and Llovel 2009). The major physical impacts of sea-level rise are inundation of lowland islands, increasing flood occurrence and submergence of coastal area, Saltwater intrusion in surface and subsurface waters (aquifer), increasing rate of erosion and coastal habitat destruction, etc. (Noone 2013).

Sea-level rise exacted grater hydrostatic on coastal freshwater aquifer which leads to intrusion of saline water into the fresh groundwater thus adversely affects groundwater resources. Ghyben-Herzberg define that the freshwater and saltwater interface is dependent on the position of groundwater table above sea level. Sea-level rise pushes freshwater layer to move upward to get an equilibrium and freshwater aquifer become thinner and diluted (Kundzewicz and Döll 2009).

17.4.2 Effect of Decreasing of Ground-Water Recharge

The global precipitation pattern is largely influenced by the global circulation patterns controlled by climate change. The episodic recharge as a result of frequent, high-intensity precipitation events includes the bulk of groundwater recharge in an arid region, climate change and alterations in precipitation intensity has affect groundwater continuity and recharge (Cassardo and Jones 2016). Precipitation is a very important part of hydrological cycle so it can be expected that the groundwater aquifer will be affected by fluctuation of recharge (which basically encompasses changes in precipitation and evapotranspiration). The groundwater flux scenario is

the function of some natural components (like precipitation regime, climatic variability, soil and landscape condition) and human interactions (like agriculture tillage, irrigation, and channel or river flow regulation for different economic purpose) (Kumar 2010).

Groundwater recharge is a key variable for effective groundwater management (Bredehoeft 2002; Pandey et al. 2011; Wada et al. 2010), specifically in dry or arid regions where recharge is little (Richey et al. 2015; Todd Jarvis 2013). The increasing fluctuation and variability of climatic components adversely impact upon the other natural setups like forest cover, soil (moisture regime texture, structure, composition, etc.), river flow, salinity of sea water, etc. and these all naturally setups shows effect on groundwater recharge.

17.5 Impact of Coastal Subsidence

The downward displacement of the land relative to sea level is defined as Coastal Subsidence and it's frequently strike in deltaic regions associated with riverine and estuarine sedimentation. Subsidence could occur for several reason like tectonics activities, consolidation of Tertiary, Pleistocene, and Holocene deposits, extraction of groundwater, and hydrocarbons and increasing loads due to sedimentation or urban development (Etkin 2015). Surface fluid pressure decreased with declining groundwater recharge and increase pumping or over extraction, as consequent subsidence of land. Although anthropogenic subsidence is a major contributor relative to sea-level rise in the coastal zone, the maximum rate of this subsidence ($\sim 0.1\text{--}1\text{ cm year}^{-1}$) exceeds the natural subsidence rate of unconsolidated sediments and the global sea-level rising rate is $\sim 0.3\text{ cm year}^{-1}$ (Ingebritsen and Galloway 2014). The Combining prediction rates of sea-level rise with an extrapolation of historical subsidence rates suggest a total drop of between 0.6 and 1.2 m by the middle of this century (Etkin 2015).

17.5.1 Possible Ways of Mitigation

Several different measures have been used to control seawater intrusion and to protect the groundwater resources. The key concept of protection is to increase the volume of fresh groundwater and reduce the volume of saltwater. In 1974, Todd has discussed various aspect to prevent sea-water intrusion such as reduction of abstraction rates or pumping, surface barriers construction, relocation of wells, natural and artificial recharge abstraction of salinity, and combination of injection and abstraction systems (Todd 1974). In order to reduce the abstraction rates it aims to decrease the pumping or extraction rates and reduced use of groundwater replacing other waters (Scholze et al. 2002) and the relocation of wells goals to move the wells further from inland (Al-Rashed and Sherif 2001). In subsurface barriers method is to

prevent the influx of saltwater into the basin (Harne et al. 2006). A subsurface physical barrier is a method employed to control saltwater intrusion. The mixed physical barrier system is a recently developed barrier system to control seawater in a coastal aquifer. It includes an impermeable cutoff wall and semi-permeable surface dam (Abdoulhalik et al. 2017). The artificial recharge increases the level of water table, using surface spread method for unconfined and recharge well for confined aquifer and this source of the injected water are surface water, treated wastewater desalinated water (Papadopoulou et al. 2005). Extraction of brackish water to reduce salinity of the aquifer (Sherif and Hamza 2001) and the combination of above two methods can deduce saline water and increase freshwater volume (Rastogi et al. 2004). As Abd-Elhamid and Javadi 2008 discussed a method of Abstraction, Desalination and Recharge (ADR), it depends on three steps like abstraction of brackish water from the saltwater aquifer, desalination of brackish water using RO treatment process, and recharge of the treated water into the aquifer. The ARD method is it return the mixing zone in original status of aquifer which leads the system to reach into dynamic equilibrium of fresh and saltwater.

17.6 Conclusion

The coastal regions are often the most densely populated areas in the world. The availability and accessibility of flat land, communication arteries, easy water transportation, tourism potentiality, good soils and high productivity of organic matter attract people. Around 70% of world population dwell in coastal area and for the growing population growth and development require a large quantity of freshwater. As population of coastal area is growing exponentially, the need for greater groundwater withdrawals is sure to increase. It is a giant challenge to support the need of water because the availability of freshwater is constant. Throughout the globe, arid and semi-arid climatic regions are suffering from freshwater shortage problem. Saltwater intrusion is a major problem in coastal regions all over the world. Overexploitation or pumping is considered the key reason of saltwater intrusion into coastal groundwater aquifers in several areas of the world and the sea-level rise accelerates the intrusion process and groundwater affords about one third of the total freshwater consumption throughout the world. Saltwater intrusion poses a major restriction to utilization of groundwater, so saltwater intrusion should be prevented or at least must be controlled. It is essential to take practical measures and protect the available groundwater resources from pollution, saltwater intrusion and contaminants which deplete quality. The modern computer modelling techniques can be used to design better groundwater withdrawal networks and methods to reduce the probability of sea-water intrusion and contaminations.

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Chapter 18

Impact of Climatic Variabilities on Water Resources, Consequences, and Recommendations



Abhishek, Tsuyoshi Kinouchi, and Manik Goel

Abstract Climate change has affected almost all the hydrological events globally. The streamflow patterns and groundwater recharge estimates follow closely the predicted precipitation changes. The uncertainties in direction and magnitude of these changes are inconsistent even between similar regional scenarios. Decline in the streamflows and groundwater recharge further poses stress on water availability and food security within an economy. The trend of reduced quantity of water resources is directly proportional to the deterioration of the associated quality. The magnitude of impact of climate change on surface and groundwater resources also depends on the system characteristics and the implementation of adaptation strategies. These nonclimatic stressors have greater impact than the climatic factors in some regions.

Keywords Climate change · Regional water resources · Water quality · Anthropogenic stressors · Numerical modelling

18.1 Outline

Increasing demand on groundwater resources induced partly from the population growth and partly from the climatic shift toward a drier climate has been witnessed globally over the past few decades. As the climate is becoming drier, it is creating pressure on surface water resources leading them to dry in some parts of the world or stressing the groundwater resources beyond the limits of natural replenishment.

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This chapter is comprised of the following major topics:

1. Interconnectivity of the climate change with groundwater.
2. Direct and indirect impacts of climate change on groundwater resources.
3. Current status of the mitigation strategies adopted worldwide.
4. Data-driven prediction of climate change and its benefits for resources management.
5. Future recommendations.

18.2 Groundwater and Climate Change

Groundwater is a major source of the water supply throughout the world. The dependency on groundwater is further increased in the economies lying near the equator and hence experiencing the higher temperatures. For example, in India, more than 80% of rural water supply and over 60% of irrigation are dependent solely on the shallow and deep groundwater resources. It also governs the crop production and food security for the agrarian economies like India with a total share of 70% in food grain production. As per the data, India accounts for 16% of the world's population on 2.45% of the world's land surface and possesses about 4% of the world's freshwater resources out of which only 38% are groundwater resources (Kumar 2012; Shah 2009).

Impact of future climate change, under the current and projected scenario of industrialization and increasing food, energy, and water demands, will be more severe and may hamper the economy's growth dominantly if preventive measures are not practiced within safe time.

Climate change greatly affects the water resources of a region both on landscape and watershed levels. It includes the variations in the surface water, groundwater, and soil moisture storage and associated quality parameters.

A detailed description of all these aspects is as follows.

18.3 Impacts of Climate Change

Change in spatial and temporal variability of the climatic factors (e.g., precipitation) directly affects the components of the hydrological cycle and its constituent components. The perturbations in these hydrological components have manifold impacts on the water resources directly and indirectly. Some of the major effects of climate change and its associated parameters are described as in the following sections.

18.3.1 Hydrological Cycle

The variability in the climate shows the direct and quick, and indirect and prolonged response to the surface and subsurface phenomena, respectively, of hydrological cycle. The response of extreme weather can be directly observed as the prolonged events of droughts and floods depending on the antecedent moisture conditions and aquifer characteristics. This disturbance in the hydrological events further affects the soil moisture, groundwater, dependency, and availability of water resources.

18.3.2 Soil Moisture

The quantity of water stored in the vadose zone, termed as soil moisture, plays a crucial role in crop production, agricultural water management, evapotranspiration rates, runoff generation, groundwater recharge, and so on. The localized effects of climate change on the soil moisture pattern are governed partly by the climate-change induced variability and partly by the constituent properties of the soil (Barron et al. 2010). The water storage capacity and infiltration rates are, apart from soil types, sensitive and prone to change by the physical phenomena such as water logging, intensity and frequency of precipitation and/or snowfall events, which in turn are caused by climate change.

18.3.3 Surface Water

Surface water resources are exposed and directly linked with the hydrological parameters. The one-to-one response of the variability in temperature, precipitation, wind, and other weather parameters can be observed in the surface water resources. Diurnal fluctuations in the stream and spring flows can be analyzed as the direct response of the climatic factors provided that the interaction with the subsurface remains constant over the study—domain and period.

18.3.4 Groundwater Quantity

Groundwater resources can be broadly classified as unconfined and confined aquifer depending on the physical and geological characteristic properties of the soil matrix. The unconfined aquifers, also termed as shallow aquifers, are recharged by

infiltration from rainfall events or from the surface water bodies and hence have profound and quick impact of the change in the climatological factors. The unconfined aquifers composed of macro fissures and preferential flow paths generated from the root decay in the rhizosphere zone reveal much rapid and amplified response to climate change. Furthermore, the changes in the surface phenomena such as evaporation, transpiration, runoff, and others also affect the recharge to the unconfined aquifers. On the contrary, the confined aquifers are relatively deeper and hence have slow recharge from the far-situated recharge zones. Moreover, the seasonality induced from climate change has dominant impacts on recharge rates in the arid and semi-arid regions because of their prevailing moisture conditions and the major recharge patterns.

Groundwater resources are indirectly affected by climate change through a number of secondary channels. Climate change alters the pattern of surface water availability, which further results in the increased pumping of the groundwater and thus triggering the already stressed GW resources. Moreover, the seasonal distribution of rainfall patterns affects the recharge rates both at the diffuse (recharge across the landscape) and localized (recharge across floodplains and rivers) scale (Barron et al. 2010; Shah 2009). The level, nature, connectivity to the shallow aquifer systems, and type of surface water–groundwater interaction as determined by the underlying soil properties, regardless of being site-specific, also play a vital role in the GW recharge (Zaveri et al. 2016). Land use land cover (LULC) patterns also have an impact on the GW resources, which is described in a separate section.

Unconfined aquifers, among all groundwater systems, are the most sensitive to climate change, especially when these are already stressed. An assessment of the major aquifers of national importance in Australia revealed that the majority of them, apart from being sensitive to climate change, are having a projected reduction in the GW resources.

18.3.5 Groundwater Quality

Groundwater quantity and quality go in parallel in an aquifer system. Climate change does not only affect the groundwater recharge rates, that is, the quantity but also impairs the GW quality. The quality aspects become of paramount importance in coastal region, where coastal aquifers serve as the freshwater sources. Rising sea levels due to the temperature changes, reduced recharge rates, and high pumping rates may impose the threat of saltwater intrusion into coastal aquifers. Once the GW resources are polluted, it is very challenging to clean the aquifer systems as it is difficult to clean the soil matrix unlike in the case of surface water, where only the water needs to be treated. In case of the low-lying coastal regions, the vulnerability to the quality degradation increases manifold.

The shallow coastal aquifers, for example, in some Caribbean islands, over pumping have caused the saline water intrusion diminish the available freshwater lens, which will further be worsened if there is any sea level rise due to the climatic factors. The physics and hence the link of sea water and aquifer water is governed by the existing hydrostatic equilibrium and is studied by Ghyben–Herzberg analytical relation (Todorovic and Verruijt 1968):

$$z = \frac{\rho_f}{(\rho_s - \rho_f)} h,$$

where h and z are the thickness of freshwater above and below sea level, respectively, and ρ_s and ρ_f are the densities of saline water and freshwater, respectively. At 20 °C, the equation simplifies to

$$z = 40 h,$$

where $\rho_s = 1.025 \text{ g/cm}^3$ and $\rho_f = 1.000 \text{ g/cm}^3$.

This relation implies that for an unconfined coastal aquifer, there will be 40 m of freshwater below sea level for every meter of fresh water above sea level.

18.3.6 Land Use Land Cover (LULC)

A shift in the climate types found in some studies has highlighted the occurrence of land use land cover (LULC) pattern changes due to the projected precipitation and temperature trends. This LULC change further intensifies in the current (or projected) arid and semi-arid climates because in such areas the GW recharge reduction is followed by a shift to perennial vegetation practices, which further lowers the recharge rates. Sole contribution of rainfall reduction to the recharge rates is a potential factor that is further added up by the land use land cover changes: this is the arena that needs to be studied in detail. If there happens to be a paradigm shift of woodland environment to a grassland environment, the water holding capacity in the shallow root zones can be increased significantly, which can contribute to the GW recharge even in the prolonged dry periods.

18.3.7 Economy

Although monetary measures of the hydrological changes, ecosystems, and associated human health are difficult to calculate, market impacts of climate change can be

quantified in terms of GDP of an economy. A report on heat stress on the decent work and labor productivity by the International Labour Organization (2019) claimed that a total increase of temperature not exceeding 1.5 °C, by 2030, will cause a yearly loss of 2.2% in the production equivalent to USD 2.400 tn. As per the assessment, the agricultural sector is supposed to be most affected with a share of 60%, followed by the construction sector with a share of 19% of the total estimated/projected loss. These results are further supported by IPCC (2007) who concluded that temperature variations of ± 2 °C, measured against 1990 levels, can fluctuate the world GDP by a few percent. Further studies by Godard (2008) using the basic economics of risk premiums (IPCC 2007) revealed that unmitigated climate change could result in a reduction in welfare equivalent to a persistent average fall in global per-capita consumption of at least 5%.

18.3.8 Water Availability and Demand

The available water resources in the form of runoff and groundwater recharge are estimated to be about 40,000 km³ per year (United Nations 2007), while the global annual water consumption is only about 10% of available blue water resources. However, water scarcity has been observed in many parts of the world due to temporally variable and spatially uneven (inhomogeneous) distribution of freshwater resources and growing water demand.

The volume of available freshwater resources is determined as a result of the natural water cycle involving precipitation, evapotranspiration, recharge, melting of accumulated snow and glacier, and so on in addition to water technology such as recycling and desalination. Long-term trends from 1950 to 2010 in annual mean observed precipitation are characterized over many regions worldwide, including Africa, Southeast Asia, eastern Australia, and southern Europe in terms of drying, and central USA, Argentina, and northern high-latitude areas in terms of increased wetness (Dai 2013). Yearly streamflow for most of the world's large rivers (one-third of the top 200 rivers ranked by river flow are having statistically significant trends during 1948–2004) and for continental discharge showed large variations, with higher number of rivers showing downward trend as compared with those having upward trend (Dai et al. 2009). However, both of the recent trends are less attributable to global warming and more related to internal climate variability. In the future, average precipitation changes in a much warmer world are expected to be nonuniform with noticeable increase in some regions and others with decreases or being unaltered (Stocker et al. 2013). Consistent to that of the projected precipitation patterns, runoff is likely to be decreased in southern Europe and the Middle East and increased in high northern latitudes (Stocker et al. 2013). Glaciers will continue to shrink and severely affect the availability of freshwater resources in some regions.

The sea level rise may increase the salinity in surface and groundwater, and available freshwater will be reduced in coastal regions.

Agriculture was the largest user of water, accounting for about 70% of total global freshwater demand, followed by the demand for electricity generation, domestic and manufacturing in the order of magnitude (OECD 2012). Projected global water demand between 2000 and 2050 is expected to increase by 55% between 2000 and 2050, and the increase in demand will come primarily from the aforesaid sectors (OECD 2012). The demand for irrigation is strongly dependent on irrigation efficiency and future expansion of irrigated areas.

Increased future water demand will exacerbate basin-scale water stress, especially in densely populated areas in rapidly developing economies (Fant et al. 2016; Koutroulis et al. 2019). The population of these stressed river basins is expected to mark 3.9 billion in 2050 as compared with 1.6 billion in 2000 or more than 40% of the world's population (OECD 2012). In addition, degradation of water quality due to increasing wastewater and pollutant will limit the available surface and subsurface water resources. Thus, renewable and nonrenewable groundwater abstraction will continue to increase to compensate the shortage against demand (Wada and Bierkens 2014). The effectiveness and costs of a range of adaptation options were investigated to reduce the future gap between water demand and water supply on a global to regional scale (Straatsma et al. 2020) (Table 18.1).

18.4 Data-Driven Approaches and Benefits (Numerical/Empirical Modelling)

An ample of methods incorporating surface water, soil moisture, and/or well data have been suggested and practiced for estimating the groundwater recharge rates under projected climatic behavior. But unavailability of the field data at high temporal and spatial scale remains a challenge, and hence numerical modelling approach is adopted for simulating the recharge. Through numerical modelling, we can alter the real field input conditions as the forcing parameters to our model and get the output for further analysis. However, the modelling approach has limitations associated with the accuracy of the output owing to the complexities involved in the recharge processes, heterogeneity of the soil media, and other physical variations in the real field conditions. In data scarce regions, where validation of the numerical model becomes difficult, only general inference trend can only be drawn from the modelling studies.

Yet a significant number of existing studies involving the landscape-scale hydrologic models suffer from the validation (Barron et al. 2010). Such uncertain and inconsistent model outputs cannot be used for accurately downscaling the hydrological parameters of interest. Therefore, in the recent past, there has been a shift

Table 18.1 Summary of the research conducted to assess the impact of climate change on the water availability

References	Title	Objective	Methodology adopted	Key findings
Immerzeel et al. (2010)	Climate change will affect the Asian water towers	Study the climate change impact on upstream snow and ice reserves of Indus, Ganges, Brahmaputra, Yangtze, and Yellow river basins	All five river basins are assessed for the climate change on the basis of three factors: (1) existing importance of meltwater in over-all hydrology of river basin; (2) perceived cryospheric changes; and (3) climate change impacts on food security	The Himalayas, also termed as Asia's water towers, are endangered by changing climate, with a nonuniform effect on food security and water availability among various river basins. Severity of the climate change impacts is large for the Indus and Brahmaputra basins owed to their heavy population density and subsequent greater dependence on irrigated agriculture
Bangash et al. (2013)	Ecosystem services in Mediterranean river basin: climate change impact on water provisioning and erosion control	Assessment of basin-scale water provisioning and erosion control services for the changing climate in the densely populated Mediterranean Llobregat River basin (NE Spain)	InVEST models are evaluated for the ecosystem services of hydropower and potable water availability, and erosion control at the annual scale	The study concluded that drinking water provisioning is expected to decrease by 3–49%, while total hydropower production would decrease by 5–43%. Erosion control is also expected to be reduced by up to 23%, indicating that costs for treating the water and dredging the reservoirs will also increase
Seidl et al. (2017)	Forest disturbances under climate change	The paper aims to the global synthesis of climate change effects on	Generally, majority of forest disturbances cause are sensitive to	The study discovers that the boreal biome and the coniferous

(continued)

Table 18.1 (continued)

References	Title	Objective	Methodology adopted	Key findings
		important abiotic agents such as fire, drought, wind, snow, and ice; and biotic agents such as insects and pathogens	climate. However, quantification of disturbance dynamics in response to external change remains incomplete, particularly regarding large-scale patterns, interaction effects, and dampening feedbacks	forest are having most pronounced disturbance from the climate change impacts. Indirect and induced climatic effects such as vegetation cover may reduce the long-term disturbance sensitivities to climate, but the direct interaction between the various agents is likely to amplify the disturbances. The study recommended that both the ecosystems and the prevailing society should be prepared for an increasingly disturbed future of forests
Versini et al. (2016)	Climate change impact on water resources availability: Case study of the Llobregat River basin (Spain)	Water resources of Llobregat basin supplying the Barcelona region are analyzed for the impact of climate change	The study adopted a “top-down” approach to produce hydro-climatic ensembles. Future water availability is estimated using small spatial scale hydrological simulations. The output is coupled with an uncertainty analysis focused on both GCM and hydrological model errors	The study reveals that due to changing climate scenario, there will be a decline of up to 40% in water resources with more frequent drought extremes. Additional uncertainty analysis revealed the high variability of the results in annual water availability (from 147 hm ³ /year to 274 hm ³ /year), thus making accurate projections difficult

(continued)

Table 18.1 (continued)

References	Title	Objective	Methodology adopted	Key findings
Eekhout et al. (2018)	Why increased extreme precipitation under climate change negatively affects water security	Climate change impacts are assessed by regional scale hydrological and soil erosion model, jointly assimilated with regional climate model projections	Climate change impact on the distribution of water between green water (soil) and blue water (surface water) compartments was assessed	The research demonstrates the significance of accounting for the fact that water redistribution between green and blue water will get disturbed, increased soil erosion, and reduced water security due to increased precipitation with an ultimate serious implications for design of climate change adaptation measures

from numerical models to the empirical models for better understanding of the climate change and its consequences on hydrology. The empirical model outperforms the numerical models as they do not need the high-resolution ground data for calibration and validation. Nevertheless, the applicability of the empirical models is limited to the specific sites and the original environmental conditions for which it was developed and needs to be corrected with the different corrections as per the user's interest area and domain.

18.5 Current Status on Climate Change Adaptation Measures (Institutes Involved, and Short Description of Their Ongoing Projects) (Table 18.2)

Table 18.2 Summary of the projects undertaken to mitigate the climate change impacts on various hydrological and socioeconomical domains

References	Project description	Project coordinator	Objectives	Expected results
Zheng et al. (2016)	Current status and future projections of the vulnerability of thermoelectric power generation with implications of climate change and power planning	China	Water and electricity conflicts occurring all over the China were analyzed for their locations, severity, and relation to climate change	Climate change-induced decrease in water resources is expected to intensify the existing vulnerability in most of the selected regions, with the highest in Yellow River basin. For ensuring power security, less-vulnerable watersheds highlighted in this study are recommended as the potential sites for future installment of the power plants
http://b4est.eu/	B4EST: Adaptive BREEDING for productive, sustainable, and resilient FOR ESTs under climate change	“Institut National de La Recherche Agronomique (INRA), France”	The projects aim to enhance forest survival, resilience, health, and productivity under changing climatic conditions, including natural disturbances. It also targeted for a balanced ecosystem having preserved genetic diversity fostering a competitive EU bio-based economy	It results in a high degree of data and knowledge integration, involving multiple and new target traits and their trade-offs; genomic information; temporal and spatial assessments in a wide range of environments; stakeholder demands; and forest owner and manager risk perception and acceptability of new breeding strategies
http://www.projectbingo.eu/	BINGO: Bringing Innovation to Ongoing Water Management—a	Laboratório Nacional de Engenharia Civil	The main objective of BINGO is to reduce the uncertainty of	It will try to develop a new global strategy of dealing with

(continued)

Table 18.2 (continued)

References	Project description	Project coordinator	Objectives	Expected results
	better future under climate change	(LNEC) Lisbon, Portugal	near-term climate predictions and developed a response strategies that may help society to better manage the remaining uncertainty	climate action and management of the integrated water cycle, encapsulated several dimensions, thus setting up a scalable model, to be followed by others, in Europe and all over the world
https://www.coacch.eu/	COACCH: CO-Designing the Assessment of Climate Change Costs	Fondazione Centro Euro-Mediterraneo sui Cambiamenti Climatic (Fondazione CMCC), Italy	The prime objective of COACCH is to develop an enhanced down-scaled assessment of the risks and costs of climate change in Europe that can be accessed directly for the different needs of end users all over the world from the research, investment, and the decision-making community	A new challenge-driven, solution-oriented, and transparent, advanced knowledge on climate change impacts and policy directly usable for the policy making, research, business, and investment communities
https://www.solace-eu.net/	SOLACE: Solutions for improving Agroecosystem and Crop Efficiency for water and nutrient use	Institut National de la Recherche Agronomique (INRA), France	SOLACE long-term goal is to design novel agroecosystem management strategies and novel crop genotypes to improve water and nutrient (i.e., N and P) use efficiency. It will ultimately assist in dealing with the challenge of more frequent combined limitations of water and nutrients in the	The mentioned breeding and management strategies will help the end users in co-design and co-assessment so as to enhance the overall system resource use efficiency. The findings of SOLACE will be distributed to a broad spectrum of stakeholders, including policy-makers

(continued)

Table 18.2 (continued)

References	Project description	Project coordinator	Objectives	Expected results
			coming decades in European agriculture	
https://parivesh.nic.in/	Climate Change Adaptation in Rural Areas of India (CCA-RAI)	German Federal Ministry for Economic Cooperation and Development (BMZ) and Ministry of Environment and Forests (MoEF)	The risk of climate variability and changes has been a prime concern for the central and state governments of India. An integrated adaptation toward climate change in the policy decisions and rural development programs to reduce the climate threats	It provides a comprehensive approach for vulnerability and risks examination associated with climate change, and to help policy-makers and practitioners

18.6 Conclusions and Future Recommendations

Despite numerous studies on the impact of climate change in surface water resources, there is a lack of attention toward the groundwater. Therefore, a number of solutions are proposed here in order to deal with this pressing issue by getting involved in training, research, and management activities at all levels:

1. Unmanaged and mismanaged practices, such as overexploitation of the resources and lack of transparent planning framework, make an aquifer more vulnerable to climate change by means of additional uncertainty. Strategic use of water resources and an even distribution of the integrated WR management practices incorporating the climate change-associated risk should be adopted for ensuring a safe future supply.
2. All the existing management and mitigation strategies should be updated in accordance with the projected climate. This also includes the updating of the existing tools and instrumentation for supporting the water resources planning efficient for the adequate analysis under future climate conditions. The existing models of surface water, groundwater, and all associated entities should go through a climate change audit to ensure their fit-for-purpose status. This can be done effectively and timely by taking into active participation of the academic institutions, bureaucrats, policy-makers, and the local community.
3. More rigorous and localized studies should be emphasized to understand the behavior of the aquifer systems rather than the general outcomes of the regional studies over an entire state or nation. Although the aquifers extend beyond the

local scales, working on whole to part, the scenario analysis, and the possible consequences of the present data of census, use of the available resources and projected stress should be done for making specific recommendations. If not possible for all aquifers, such studies should be commenced at least for the high priority aquifers considering the number of dependent people and current status of the resources.

4. Amid ongoing inability of the current models to mimic replicate real field conditions for further analysis, there is a need for development of an extensive numerical framework with more robust model setups enabling more accurate prediction and hence making it feasible/viable to implement the management strategies in a timely manner.
5. In order to get a higher success rate of the management policies and to reduce the overexploitation of the available water resources, the local community participation plays an important role. The community should be made aware about the proper usages, distribution, allocation, and the ongoing government planning of the resources the community is using. Basic research and training activities should be employed from time to time for this purpose and for undoubtedly enhancing the availability of quality resources timely for the future generation.
6. All the climate-induced hydrological components should be looked into a holistic approach with the nonclimatic changes such as health and economy of a region. We should not keep the society and the components with which it interacts as separate entities in our planning and management activities and mitigation strategies.
7. Artificial recharge of the aquifers through the process of Managed Aquifer Recharge (MAR) is a pragmatic and sustainable approach for augmentation of the groundwater storage to increase the water availability and to enhance the climate change adaptation. It involves modifying the landscape and/or building the infrastructure (e.g., recharge wells) for recovering the overexploited aquifers leading toward a green and sustainable ecosystem.

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