Environmental Chemistry for a Sustainable World 70

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Remediation of Heavy Metals

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Foreword

Water will become more and more vital in the context of climate change, pollution, industrialisation, and the future circular economy. Epidemiological and eco-toxicological studies have shown that heavy metals have adverse impacts on living organisms in both terrestrial and aquatic environments, in particular with genotoxic, carcinogenic, mutagenic, and teratogenic effects, even at trace levels. Heavy metals are both of natural and human origin, yet the human activity sources are rising fast with industrialisation. Unlike organic pollutants, heavy metals do not degrade in nature and thus must be removed, or their toxicity must be inactivated. Remediation methods include ion exchange, membranes, reverse osmosis, filtration, electrodialysis, precipitation, electrochemical process, biological treatments, coagulation/flocculation, and adsorption.

This book presents advanced knowledge on the sources, analysis, abatement, and remediation of heavy metals, with focus on water and wastewater. Adsorbents include nanomaterials, adsorbents, biowaste, and chelating materials, whereas techniques include nanotechnology assisted treatments, membrane adsorption, advanced oxidation processes, and eco-engineering. Chapter 1 gives an overview of the most used analytical methods for the determination of heavy metals in water, with special emphasis on modern developments regarding detection techniques, sample preparation, and their combinations. Additionally, the importance and latest developments related to the speciation analysis of heavy metals are discussed in depth, along with relevant examples and future perspectives in the field. Chapter 2 discusses the use of by-products and waste from olive tree cultivation, olive recollection, and olive oil extraction as low-cost materials in the removal of heavy metals from aqueous media. Chapter 3 discusses different types of magnetic sorbents for heavy metal ion remediation. The focus is on eco-friendly ferrite magnetic nanocomposite sorbent having a high remediation rate. Case studies are illustrated based on oil palm fibres, cellulose, and Ceiba pentadra as the recently developed metal-oxide composites based on agrowastes. Chapter 4 details two-dimensional materials for heavy metal removal. The major focus is given to communicate structures, mechanisms, and applications of the two-dimensional materials for heavy metal removal. Chapter 5 addresses electrodialysis-based processes, focusing on electroplating and mining

Natural landscape in New Caledonia showing the absence of plants on reddish soils that contain naturally high contents of nickel, cobalt, chromium, and manganese. Observed living plants have developed unique strategies to live in the presence of toxic metals. (Copyright: Eric Lichtfouse 2015)

activities. The feasibility of recovering nickel, copper, zinc, and chromium for reuse in electroplating processes, as well as copper and zinc recovery from mining processing solutions, is discussed.

Chapter 6 discusses the adsorption-mediated removal of heavy metal ions from contaminated water using novel metal oxide nanostructures. High surface area, surface charge, and porosity in metal oxides are the prime requisites for efficient adsorption and removal of metal ions. The quantification of adsorption is described with Freundlich and Langmuir isotherms. Chapter 7 presents the application of organic and inorganic ion exchange materials for the removal of heavy metals from water resources and industrial wastewaters. Fundamentals of the ion exchange process and examples on the removal of various heavy metals with ion exchangers are discussed. Chapter 8 outlines conventional wastewater treatment and potential low-cost methods for the removal of toxic heavy metals from wastewaters. Advanced approaches include bionanotechnology, emerging membrane technology, and low-cost sorbents using zeolites and metal organic frameworks for efficient and economical techniques. Chapter 9 presents nanomaterials as adsorbents for remediation of water laden with heavy metal cations, with numerous examples. Chapter 10 reviews the origin, fate, and health hazards of the riverine contaminants, and then the application of ecoengineered systems for remediation of the polluted rivers.

Laboratory scale and on-site hybrid integrated treatment technologies for river bioremediation are detailed. Chapter 11 discusses ballast water releases from ships and their impacts on the local marine environment as the result of transporting various invasive aquatic species. Management options and available treatment techniques, which can be ship or port based, are reported.

Chapter 12 details sources and effects of hexavalent chromium pollution with a focus on carcinogenic properties. Cr(VI) removal techniques are presented, for example chemical and electrochemical methods, ion exchange with membrane separation, adsorption, biosorption, nanozerovalent iron adsorption, and microbial remediation. This chapter also highlights the advantages and disadvantages of popular chromium removal processes and recent advances in microbial remediation of Cr(VI). Chapter 13 discusses the impact of heavy metals on biological systems, and metal removal using various technologies. Chapter 14 discusses the merits and demerits of conventional processes used for the removal of heavy metals from water. Recent advances in removal are explained in detail, with focus on opportunities and challenges. Chapter 15 presents different modification techniques used to increase the adsorption capacity of sugarcane bagasse, with emphasis on process parameters such as initial concentration of metal, pH, and amount of biosorbent in mono- and multi-component systems. Adsorption capacity, isotherm models, and kinetic models are reported. Chapter 16 reviews the use of chelating materials such as membranes, nanomaterials, polymers, resins, surfactants, chitosan, covalent and metal organic frameworks, and hybrid materials to remove heavy metals from water. Chapter 17 presents metal sources and transportation in environmental media, and mitigation strategies.

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About the Editors

Inamuddin is an assistant professor in the Department of Applied Chemistry, Zakir Husain College of Engineering and Technology, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, India. He has extensive research experience in multidisciplinary fields of analytical chemistry, materials chemistry, electrochemistry, renewable energy, and environmental science. He has worked on different research projects funded by various government agencies and universities and is the recipient of the Department of Science and Technology, India, Fast-Track Young Scientist Award and the Sir Syed Young Researcher of the Year Award 2020 from Aligarh Muslim University. He has published about 190 research articles in various international scientific journals, 18 book chapters, and 145 edited books with multiple well-known publishers. His current research interests include ion exchange materials, sensor for heavy metal ions, biofuel cells, supercapacitors, and bending actuators.

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Eric Lichtfouse is Professor of Environmental Chemistry and Scientific Writing at Aix Marseille University and Xi'an Jiaotong University, and chief editor and co-founder of the journal *Environmental Chemistry Letters*. He has invented carbon-13 dating following the discovery of various temporal pools of a single individual organic substance in soils. He has published the book *Scientific Writing for Impact Factors*, which includes a new tool – the Micro-Article – to identify the novelty of research results. He has received the analytical chemistry prize from the French Chemical Society, the grand prize of the Universities of Nancy and Metz, and a journal citation award by the Essential Indicators. He is world XTerra vice champion and has won the ITU cross triathlon world bronze medal in the age category.

Tariq Altalhi, PhD, joined the Department of Chemistry at Taif University, Saudi Arabia, as assistant professor in 2014. He received his doctorate from the University of Adelaide, Australia, in the year 2014 with Dean's Commendation for Doctoral Thesis Excellence. He became head of the Chemistry Department at Taif University in 2017 and vice dean of the Science College in 2019, a position he still holds. In 2015, one of his works was nominated for the GreenTec Awards from Germany, Europe's largest environmental and business prize, amongst top 10 entries. He has co-edited various scientific books. His group is involved in fundamental multidisciplinary research in nanomaterials synthesis and engineering, characterisation, and their application in molecular separation, desalination, membrane systems, drug delivery, and biosensing. In addition, he has established key contacts with major industries in the Kingdom of Saudi Arabia.

Chapter 1
Analytical Methods for the Determination of Heavy Metals in Water

Mauricio Llaver, María N. Oviedo, Pamela Y. Quintas, and Rodolfo G. Wuilloud

Abstract The presence of heavy metals in aqueous systems is a topic of continuous concern in the scientific community due to their high toxicity, coupled to their increasing applications and irresponsible waste management, which demand for a tight control and evaluation of their impact on natural systems. In this respect, analytical chemistry plays a fundamental role for the development and application of more efficient methods and techniques for their quantification. Nevertheless, challenges related to low concentrations, species distributions and complex matrices can only be overcome with novel, effective and cost-efficient methods that lead to reliable results.

This chapter presents an overview of the most used analytical methods for the quantification of trace heavy metals in aqueous samples. It includes an in-depth discussion of atomic spectroscopic and spectrometric techniques, electrochemical analytical tools, ranging from potentiostatic to chemiluminescent methods, and chromatographic and bio-based techniques for heavy metal determination. Additionally, a section dedicated to the growing field of sample preparation is also presented, paying special attention to novel liquid-liquid and solid phase microextraction techniques based on the use of modern solvents and nanomaterials. Throughout the chapter, special emphasis is made on recent developments aimed to the improvement of the sensitivity and limits of detection and on the importance of speciation analysis, a fundamental yet still undervalued aspect of the integral evaluation of the presence and impact of heavy metals in waters.

Keywords Heavy metal · Analytical chemistry · Preconcentration · Nanotechnology · Water · Speciation analysis · Sample preparation · Green chemistry · Atomic spectroscopy · Electrochemistry

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1.1 Introduction

The rapid evolution of technology and industry is, without a doubt, one of the defining aspects of modern-day society. Although its influence in our everyday life is ever present, its impact on the environment is usually ignored or understated by the general public. Even though natural sources of chemical, physical and pathogenic polluting agents exist, anthropogenic influence from human activities has a much more significant impact on water, soil and air contamination (Rhind 2009). In particular, water bodies are extremely susceptible to direct contamination from industrial, urban and agricultural activities. An estimate of 2 million tons (the approximate weight of the entire human population) of sewage and industrial and agricultural waste are discharged into the world's water every day (WWDR 2003); among these, the problem of heavy metal waste disposal is of paramount importance, since their applications in technological industries are continually growing (Sharma 2014). Even though there is not a widely accepted definition for the term, "heavy metals" is usually applied to a group of metal elements which are known to be toxic to humans and ecosystems at low concentrations (Dufus 2002). Furthermore, the health threats represented by heavy metals exceed aqueous organisms, since they have the tendency of bioaccumulating in organisms; thus, by means of trophic chains, contamination is transferred to non-aqueous organisms.

Therefore, it is clear that the detection and quantification of heavy metals in water samples is one of the main areas of interest in analytical chemistry. Precise and accurate measurements allow for the evaluation of the present situation and historical records permit the estimation of future trends concerning contamination and necessary courses of action for its control. Furthermore, it is widely known that the toxicity, bioavailability and environmental transport mechanisms of several heavy metals (e.g. arsenic, mercury, lead) are highly dependent on their oxidation state, thus making the determination of each metal species fundamental, independently of the total concentration of the metal or metals under study (Bakirdere 2013). Moreover, the total concentration of heavy metals in aqueous samples is usually below the parts per million (ppm, mg/L) or parts per billion (ppb, μg/L) levels (Crompton 2015). This, in addition to the fact that the concentration of each species is only a fraction of the total, translates into the need of highly sensitive and selective analytical methods for the quantification and speciation analysis of heavy metals and, in several cases, the development of sample pre-treatment methods prior to said determinations.

In this chapter, an overview of the analytical techniques that have been most used for the determination of heavy metals in aqueous samples is presented. Special emphasis will be made on recent developments concerning modern environmental aspects, such as nanoparticle contamination. Furthermore, several novel sample preparation techniques are discussed.

1.2 Total Concentration and Speciation Analysis

Heavy metal analysis in waters has been very well benefited from innovative analytical methodologies. Up to date, this has evolved from the identification and quantification of the total concentration of a given element to the identification, separation and quantification of the different chemical species. The term *speciation* has become extremely popular and is frequently used in studies related to the distribution of a chemical element in its different forms or *species* (Templeton and Fujishiro 2017). Therefore, the development of highly selective and sensitive analytical methodologies for the identification and determination of toxic and/or essential elemental species constitutes one of the main demands on modern analytical chemistry (Clough et al. 2018). The knowledge on the different chemical species of an element, as well as their stability and dissociation kinetics is of vital importance, due to the high dependence between elemental species and toxicity, bioavailability, bioaccumulation, mobility and biodegradability (Achterberg et al. 2019). To cite an example, tellurium -an increasingly popular element for the construction of solar panels- is widely recognized as a toxic heavy metal, but the fact that the toxicity of its tetravalent species is ten-fold higher than that of its hexavalent species is not much discussed in the literature (Zare et al. 2017).

The concept of speciation thus turns out to be extremely important in water pollution studies, since it provides information related with the bioavailability and toxicity of a given element (Cornelis and Nordberg 2007). It is evident that the determination of the different chemical forms in which an element can be present in water samples is a fundamental need in order to obtain exact results on the risk of exposure to certain toxic elements and, on the other hand, to establish nutritional requirements for those which are essential at low concentrations (Bakirdere 2013). Such is the case of chromium, which exists in nature in two stable oxidation states: Cr(III) and Cr(VI), with completely different biological and physiological properties. Cr(III) is essential for living organisms, playing an important role in metabolic processes, enhancing the activity of enzymes stimulating the synthesis of cholesterol and fatty acids. On the other hand Cr(VI) is a toxic and carcinogenic agent, which makes the differential quantitation of these species of paramount importance (József et al. 2019).

Consequently, the ongoing development and application of cutting-edge analytical methodologies involves the coupling of highly efficient sample preparation methods, e.g. solid and liquid microextractions or chromatographic methods, with sensitive elemental detection techniques, such as atomic absorption spectrometry or inductively coupled plasma-mass spectrometry. These are crucial activities in modern analytical chemistry in order to achieve a high level of elemental speciation analysis based on the identification and quantification of species at trace concentration levels (μg/L or even lower) (Kocot et al. 2016). In all cases, a great distinction of different chemical species is needed by means of physical, chemical or biological processes, for an unequivocal identification.

1.3 Health and Legislation

Heavy metals contaminate drinking water sources through natural processes such as weathering, decomposition of plants and animals remains or natural forces like volcanoes, earthquakes or storms (Azimi et al. 2017). However, nowadays, anthropogenic activities represent one of main causes of water pollution (Paul 2017). Heavy metal pollution of water has become one of the most important modern environmental problems due to the environmental stability of metal ions. Heavy metals can be classified into essential and non-essential based on their biological functions (Izah et al. 2016). Metals such as Cu, Zn, Fe, Mn, Mo, Ni and Co are essential micronutrients to maintain various biochemical and physiological functions in living organisms when they are present at very low concentrations; however, they become noxious when they exceed certain threshold concentrations (Jaishankar et al. 2014). On the other hand, non-essential metals such as Hg, Ag, Pb, Cd and As are highly toxic trace elements (Tiimub et al. 2015).

Water is considered a vital substance in the environment. Safe drinking water is defined by the World Health Organization (WHO) Guidelines as water that does not represent any significant risk to health over a lifetime of consumption (WHO 2008). Consequently, legal regulations to control the permissible limits of heavy metals in drinking water for human consumption are fundamental. The heavy metals discussed in this section are those declared as a high priority for human health, according to the World Health Organization (WHO 2008). However, permissible levels for other heavy metals, established by different regulatory bodies, are presented in Table 1.1.

Cadmium is the seventh most toxic heavy metal as per the Agency for Toxic Substances and Disease Registry ranking (Jaishankar et al. 2014). Exposure may cause serious damage like high blood pressure, renal dysfunction, bone degeneration and also cancer (Zare et al. 2018). Therefore, the maximum permissible level of Cd ions in drinking water allowed by the United States Environmental Protection Agency (U.S. EPA) standards and the World Health Organization is only 0.003 mg/L (Awual et al. 2018), while the European Union (EU) established a maximum of 0.005 mg/L (Izah et al. 2016).

Chromium is one of the most common naturally existing elements in the earth crust. Due to its wide applications in industrial processes -mainly in the manufacture of steel or tannery- large quantities of chromium compounds are discharged into the environment (Kaprara et al. 2015). Both acute and chronic exposure to Cr(VI) can cause severe health problems, ranging from simple skin irritation to lung cancer (Zare et al. 2018). According to the World Health Organization and the European Union, the maximum allowed amount of Cr in drinking water is 0.05 mg/L (EU 1998; WHO 2018), whereas the United States Environmental Protection Agency declared a maximum permissible concentration of 0.1 mg/L (Catalani et al. 2015).

Mercury is one of the most hazardous elements for human health because of its relative solubility in water and living tissues and its tendency to bioaccumulate in

Table 1.1 Maximum tolerated levels of heavy metals in drinking water, expressed in mg/L.

Regulatory agency	Cd(II)	Cr total	Hg (inorganic)	Pb(II)	As (total)	Se (total)	Al(III)	Ni(II)	Mn(II)	Fe (total)	Zn(II)	Cu (total)
U.S.EPA	0.005	0.100	0.002	0	0.010	0.050	0.200	–	<0.050	0.300	5.0	1.3
EU	0.005	0.050	0.001	0.010	0.010	0.010	0.200	0.020	0.005	0.200	2.0	2.0
WHO	0.003	0.050	0.001	0.010	0.010	0.040	0.100–0.200	0.070	0.400	0.300	3.0	1.0

U.S.EPA United States Environmental Protection Agency, *EU* European Union, *WHO* World Health Organization the human body (Mergola et al. 2016). The World Health Organization and the European Union recommend a limit of 0.001 mg/L for inorganic mercury concentration in drinking water, while the United States Environmental Protection Agency permissible limit is 0.002 mg/L (U.S.EPA 2018; WHO 2005a).

Lead is a trace element in the earth's crust and it can cause severe dysfunctions in the neurological, hematological, gastrointestinal, musculoskeletal, cardiovascular, renal and reproductive systems (WHO 2010), to which young children are particularly susceptible to. The United States Environmental Protection Agency has set a zero-tolerance policy towards Pb in drinking waters (U.S.EPA 2018). On the other hand, the maximum tolerance level determined by the World Health Organization (WHO 2004) and the European Union (Izah et al. 2016) is 0.01 mg/L.

Arsenic is a toxic element, known as class (I) human carcinogen and ubiquitous in the environment in both inorganic and organic forms (Kumar et al. 2016). Inorganic forms of As, arsenite and arsenate, are mainly found in the environment dissolved in water, making drinking water the main ingestion source for humans. The World Health Organization recommends a limit of 0.010 mg/L of arsenic in drinking water; however, the water sources of millions of people in the world exceed this limit (Ameer et al. 2017).

Selenium is a nutritionally essential element but excessive ingestion brings severe risk and damage to human health (He et al. 2018). The maximum permissible limit suggested by the World Health Organization (WHO 2011) and the European Union (He et al. 2018) in drinking water is 0.010 mg/L, while the United States Environmental Protection Agency (U.S.EPA 2018) sets the limit at 0.050 mg/L.

Drinking water is the principal source of aluminum human exposure (Panhwar et al. 2016). Sources of aluminum in water include raw water and aluminum-based coagulants (Zhang et al. 2016). The maximum permissible level of aluminum in drinking water is 0.0200 mg/L according to the World Health Organization (WHO 2003). The same level was recommended by United States Environmental Protection Agency (U.S.EPA 2012) and the European Union (EU 1998) (Table 1.1).

The primary source of nickel in drinking water is leaching from metals, such as pipes. However, nickel may also be present as a consequence of the dissolution of nickel ore-bearing rocks. Ni in high concentrations can be toxic to the skin, kidneys, lungs and liver (Büyükpınar et al. 2017). The World Health Organization sets a threshold limit for Ni of 0.070 mg/L in water (WHO 2005b). However, the European Union (Izah et al. 2016) has established an even lower maximum permitted level at 0.020 mg/L (Table 1.1).

Manganese, another ubiquitous element in the environment, comprises about 0.1% of the earth's crust (Gerke et al. 2016). Ingestion of elevated Mn concentrations from drinking water may cause neurological disorders which might adversely affect the developing brain of infants (Dion et al. 2018) and a compensatory decrease in gastrointestinal absorption as well as an increase in biliary excretion (Bouchard et al. 2018). Therefore, the World Health Organization established a guidance level for manganese in drinking water at 0.5 mg/L (WHO 2004). Nevertheless, lower levels have been established by the European Union (Izah et al. 2016) and the United States Environmental Protection Agency (U.S.EPA 2004).

As it is possible to observe, the heavy metal concentrations established as limits are, for the most part, very low. In addition, due to the fact that some of these legal thresholds are near or below the limits of quantification of several well-established analytical techniques, such atomic absorption spectrometry, the development of preconcentration techniques, which can improve limits of detection up to three orders of magnitude, is continually gaining importance to achieve accurate and precise determinations.

1.4 Sample Preparation for Elemental Analysis of Heavy Metals

Despite the selectivity and sensitivity of many modern analytical techniques, there is a crucial need for sample treatment before heavy metal analysis. This is a consequence of their usually low concentrations in water samples and of the high levels of concomitants present along with the analytes of interest. Sample preparation can overcome these drawbacks by including both preconcentration and clean-up steps. Thus, the concentration of the analyte is increased prior to its determination and potentially interfering species occurring in the sample matrix are separated (Camel 2003).

Liquid or solid phase extractions are the most common sample preparation techniques. They are based on the selective partition of the analyte to a low volume or mass of the extractant phase and its separation from the original sample (Wilson et al. 2000). These techniques are continually evolving towards the development of new and more efficient and selective extractants and methods with the aim of miniaturizing the systems to make them more environmental and economically sustainable (Płotka-Wasylka et al. 2016a).

1.4.1 Solid-Phase Extraction

Solid-phase extraction encompasses a family of techniques for sample treatment which use a solid sorbent to selectively retain metal ions. The analytes can be directly measured or back-extracted (or eluted) prior to their determination by a suitable detection technique. For heavy metal extraction and preconcentration, ion exchange and chelation with O, N and S-containing groups provide the main interactions for analyte retention on solid sorbents (Camel 2003). Ionic exchange sorbents usually contain cationic or anionic functional groups that can exchange the associated counterion (Rossi et al. 2017). Meanwhile, chelating retention can be achieved either by adding a chelating agent to the sample prior to solid-phase extraction with an appropriate sorbent or by functionalizing the solid extractant with a chelating moiety (Ribeiro and Masini 2018). Trends regarding the most applied

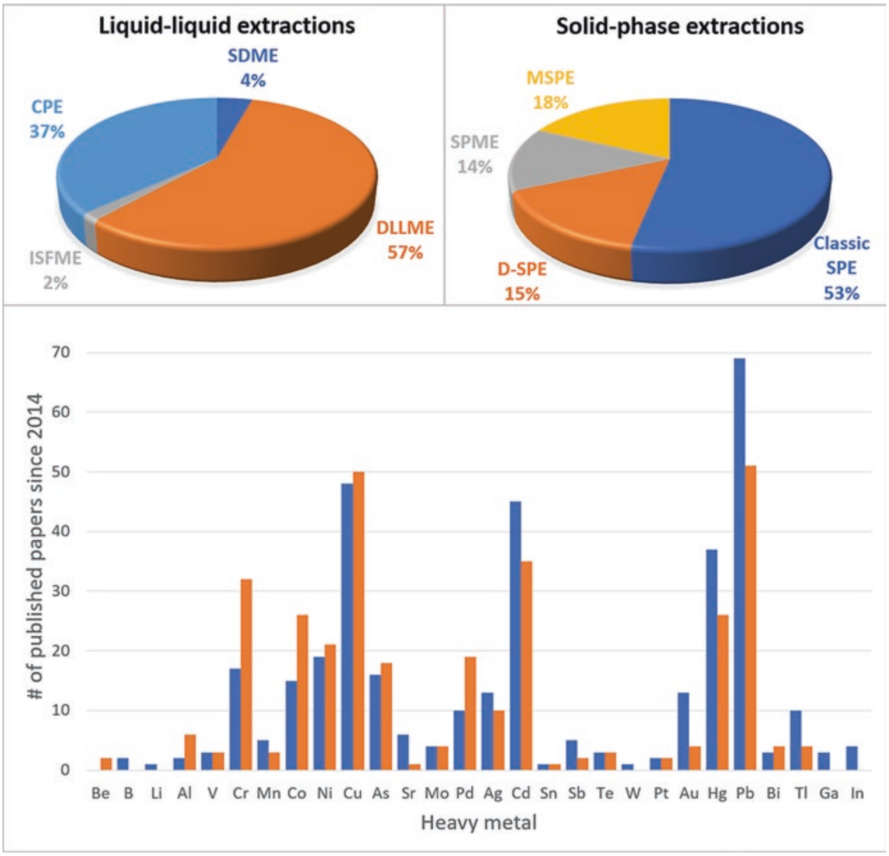

Fig. 1.1 Distribution of works published on solid-phase and liquid-liquid extraction for metal determination from 2014 until July 2019. *MSPE* Magnetic solid-phase extraction, *SPME* Solid-phase microextraction, *D-SPE* Dispersive solid-phase extraction, *SPE* Solid-phase extraction, *SDME* Single-drop microextraction, *CPE* Cloud point extraction, *ISFME* In-situ solvent formation microextraction, *DLLME* Dispersive liquid-liquid microextraction

solid-phase extraction techniques and the heavy metals they have been applied to, during the last 5 years, are presented in Fig. 1.1.

1.4.1.1 Classic Solid-Phase Extraction

Classic solid-phase extraction is one of the simplest sample preparation techniques for preconcentration and extraction of heavy metals from aqueous samples. Solid-phase extraction is based on the affinity between the analyte, present in a liquid matrix, and a solid sorbent packed in diverse geometries, being the most common a column, a cartridge or, more recently, a disc (Płotka-Wasylka et al. 2016b). A classical solid-phase extraction methodology includes four steps: (i) equilibration of the column or cartridge with a solvent, (ii) loading of the sample, which percolates through the packed sorbent that retains the analyte, (iii) washing of the sorbent to remove impurities and (iv) elution and collection of the analyte (Ramos 2012). The main advantages of solid-phase extraction are its ease of operation and its selectivity. On the other hand, the aforementioned steps, along with additional stages which are sometimes necessary, such as pre-treatment for samples with suspended solids, usually yield low analytical frequencies. Nevertheless, this has been partially overcome by the automatization of the technique, which improves the frequency of analysis and reproducibility (Calderilla et al. 2018).

1.4.1.1.1 Modern Sorbents for Classic Solid-Phase Extraction

Most innovations in the field of solid-phase extraction for heavy metal extraction and preconcentration stem from the development and application of novel sorbents. Nanomaterials, with physical features less than 100 nm in one or more dimensions, play a leading role, since they present several advantages such as: high surface-to-volume ratio, the possibility of surface functionalization and favorable thermal features (Pyrzynska 2013). Consequently, the extraction efficiency of solid-phase extraction has been greatly enhanced by the application of nanomaterials, which provide a higher number of interaction sites than other solid sorbents. Carbon nanomaterials such as nanotubes, graphene and fullerenes (Herrero Latorre et al. 2012), dendrimers, which are a unique class of spherical polymeric macromolecules formed by a nanoscale hierarchical self-assembling process (Sajid et al. 2018) and metal oxide nanoparticles, particularly silica and alumina (Hua et al. 2012), have been applied for solid-phase extraction of heavy metal ions in diverse aqueous samples.

Furthermore, physically and chemically modified nanomaterials are an attractive alternative, since their modifications enhance functionality, usually in terms of selectivity. Chemical modifications with functional groups such as amines, amides, esters, thiols and carboxylic acids can provide chelating and/or ion exchanging properties to nanosorbents, increasing their efficiency for heavy metal retention. Also, physical functionalization with polymers and surfactants has been carried out to improve the extraction capability and physical stability of nanosorbents for solid-phase extraction (Płotka-Wasylka et al. 2016b). A specifically interesting case is that of ion-imprinted polymers, in which metal recognition sites are obtained from the self-assembly of some ligand(s) around the template ion prior to crosslinking. This enables the binding sites to match the charge, size and coordination number of the target metal ion. High selectivity, good stability, simplicity and low cost can be important benefits derived from the application of ion-imprinted polymers and they have done a great contribution for the selective separation and preconcentration of heavy metal ions (Wan Ibrahim et al. 2014).

A novel alternative for heavy metal solid-phase extraction has also been provided by biosorption processes; that is: the use of biomass for the retention of metal ions. The binding characteristics of microorganisms are attributed to superficial functional groups which provide features like selectivity, specificity and easy release for posterior determination. Also, amino acids and peptides which act as synthetic analogues of natural metallothioneins -present at the cell walls of microorganisms- have been immobilized onto solid supports, e.g. carbon nanotubes, controlled pore glass, silica gel polyurethane foam, and introduced in solid-phase extraction systems.

1.4.1.1.2 Micro Solid-Phase Extraction

Micro solid-phase extraction is a modern alternative to classic solid-phase extraction which aims to the miniaturization of the technique. Micro solid-phase extraction devices can be prepared by inserting a very small amount of sorbent -in the order of mg- inside a porous membrane sheet, sealing its edges with heat to form a small bag. This sorbent-containing bag is then cleaned and conditioned in a suitable solvent, where it is stored until further use. When needed, the micro solid-phase extraction device is air dried and added to the stirred water sample solution for an optimal amount of time. The device is then removed, rinsed, dried and transferred to a small glass or vial for elution with a reduced volume of solvent (Basheer et al. 2006). Micro solid-phase extraction solves a common drawback from classic solid-phase extraction, which is the high consumption of reagents and solvents during the conditioning and elution phase, making it a much cleaner and sustainable method. Also, common back-pressure problems in classic solid-phase extraction due to excessive packing of the sorbent phase are avoided by this approach. Furthermore, due to the protection of the porous membrane, micro solid-phase extraction is much more resistant to interferences in samples with high organic loads and suspended solids, such as natural waters, which need additional previous clean-up steps in classical solid-phase extraction techniques (Sajid 2017).

1.4.1.2 Dispersive Solid-Phase Extraction

Dispersive solid-phase extraction involves the use of a solid sorption material that is dispersed into the sample to achieve an intimate contact between the phases, thus increasing sorption kinetics. The sorbent must be then separated from the sample matrix by centrifugation or filtration. The high extraction efficiency achieved with modern meso- and nanostructured extractants help to reduce the amount of sorbent to a few milligrams, thus giving place to a miniaturized version of dispersive solid-phase extraction: dispersive micro-solid phase extraction (Chisvert et al. 2019). The main advantage of dispersive techniques with respect to classic solid-phase extraction, and more specifically online solid-phase extraction methods, is the avoidance of the backpressure built up inside a column or cartridge filled with the sorption material. These drawbacks are more significant when nano-sized particles are used due to a greater compaction of the packing material, which can be easily overcome when the sorbent is dispersed. Modern improvements to dispersive solid-phase extraction and dispersive micro-solid phase extraction are mostly related either to novel dispersion methods or sorbents.

1.4.1.2.1 Dispersion Techniques

Vortex and ultrasound are the most traditional mechanical dispersion techniques. Their simplicity and applicability still make them the most used alternatives, despite the fact that they generate an increase in temperature during extraction that might affect the thermodynamics of the sorbent-analyte interaction, especially when ultrasound stirring is applied. Modern approaches to mechanical dispersion include the development of air-assisted dispersive micro-solid phase extraction, in which the sorbent is dispersed by a stream of air bubbles generated by repeated suction and injection of the sample with a syringe (Rajabi et al. 2016), and disposable pipette tip extraction, where the sorbent is confined in a modified pipette tip by two filters and the sample is suctioned and ejected to and from the sorbent for efficient dispersion (Bordin et al. 2016). An interesting approach for the chemical dispersion of the solvent, effervescence-assisted dispersive micro-solid phase extraction, was developed in 2011 (Lasarte-Aragonés et al. 2011). The basis of this technique is the use of a tablet that includes the sorbent, a carbon dioxide source such as Na_2CO_3 and a proton source. Thus, the generation of the CO_2 bubbles produces turbulence in the sample solution, dispersing the sorbent for the extraction of analytes (Sorouraddin et al. 2019).

1.4.1.2.2 Modern Sorbents for Dispersive Solid-Phase Extraction and Dispersive Micro-Solid Phase Extraction

Nanostructured Materials

Extraction efficiency markedly depends on the effective contact surface area of the sorption material. In this sense, nanostructured materials are ideal sorbents for dispersive solid-phase extraction and they have largely contributed to the miniaturization of this technique. Carbon-based nanomaterials such as multi-walled carbon nanotubes (Krawczyk and Jeszka-Skowron 2016) and graphene oxide (Ruiz et al. 2019) have been applied for the preconcentration of heavy metals in aqueous samples without any surface functionalization or chelating agents. This phenomenon is possible thanks to direct electrostatic interaction between metal cations and the negatively charged -COO^- and -O^- functional groups covering the surface of these nanomaterials that are obtained after partial oxidation. Furthermore, these surface groups can act as complexing moieties for the selective extraction of some metals, while some of them can even show selectivity to certain oxidation states (Feist 2016). Additionally, graphitic carbon nitride is receiving a great deal of attention nowadays, since its chemical properties resemble those of graphene, but its synthesis is much more environmentally friendly, thus reducing the ecological impact of its use. Furthermore, the presence of nitrogen-containing surface functional groups positively affects its dispersibility in water and its extraction capabilities, since amine and amide groups are well-known complexing agents for metal ions (Speltini et al. 2016).

Layered double hydroxides are two-dimensional nanostructured materials that consist of metal hydroxide positively charged layers with intercalated anions. Their use for heavy metal preconcentration has been reported taking advantage of the flexibility provided by the interchangeable intra-layer anions, which can selectively interact with metal cations to retain them between the hydroxide layers (Asiabi et al. 2017).

Metal-organic frameworks are some of the most modern sorbents applied in dispersive solid-phase extraction preconcentration techniques of various analytes, including heavy metals (Tahmasebi et al. 2015). They are hybrid solids consisting of metallic cores coordinated to organic linkers and show ideal properties for dispersive micro-solid phase extraction: (i) high chemical stability due to a crystalline structure, (ii) high surface area for interactions thanks to their nano-scale porosity and permeable channels and (iii) tuneability, permitting the design of task-specific metal-organic frameworks when different metals and linkers are combined: around 20,000 metal-organic frameworks have been synthesized and characterized (Rocío-Bautista et al. 2017).

Ion-imprinted polymers are a growing family of compounds and represent the state of the art in the field of ultra-selective extraction of heavy metals thanks to their artificial recognition sites for specific metal cations (Kakavandi et al. 2017). Their highly crosslinked polymeric nature makes them durable and they can be reused without loss of activity or stored for long periods of time without losing the affinity for the target ion. As in classic solid-phase extraction, they are progressively making their way into dispersive methodologies, while their features are being continually improved, particularly in terms of selectivity and stability (Branger et al. 2013).

Hybrid Materials

Hybrid materials can be obtained from the combination of a solid sorbent, usually in the nanoscale, and a functionalizing agent. The resulting composite material retains some of the properties of the original, such as the high surface/mass ratio of nanomaterials, with improved characteristics derived from its functionalization (Chisvert et al. 2019). The functionalization can proceed via two mechanisms: physical or chemical. Physical functionalization does not involve covalent bonding between the components of the hybrid sorbent; instead, Van der Waals, electrostatic and hydrogen bonding forces generate the desired union. The main advantage of physisorbed composites is their ease preparation, since time and reagent-consuming chemical reactions are avoided. On the other hand, covalent bonding is the defining characteristic of chemically functionalized materials. They require more complex synthesis procedures but are usually much more stable, since no loss of the functionalizing agent is observed after repeated use. Also, a much better control of the functionalization degree can be achieved (Martinis et al. 2017).

Chemical functionalization with complexing agents is a common approach for the preconcentration and speciation analysis of heavy metals by dispersive techniques, since many chelating reagents, such as pyrrolidine dithiocarbamate and diethyldithiocarbamate, are selective not only in terms of the identity of the metals, but also in terms of their oxidation state. Thus, the surface of different nanomaterials including carbon nanotubes (Rohanifar et al. 2018), graphene (Yavuz et al. 2018) and metal oxide nanoparticles (Biata et al. 2018) has been modified for selective preconcentration and speciation analysis of heavy metals.

Ionic liquids comprise a new generation of alternative solvents which have found great usefulness in the development of efficient separation and preconcentration techniques. Besides their applications in liquid-liquid extraction, ionic liquids are widely recognized as agents for the functionalization of nanomaterials. This combination gives rise to a whole new family of sorbents with synergistically improved properties, combining the high surface provided by the nanomaterials with the exceptional extraction properties of the ionic liquids (Martinis et al. 2017). Chemically and physically coupled nano-ionic liquid hybrids have been used for the preconcentration and speciation analysis of several heavy metal ions in water samples. Examples include the use of a task-specific IL physically adsorbed on multi-walled carbon nanotubes for the preconcentration of Pb(II) (Saljooqi et al. 2014) or the use of a phosphonium ionic liquid grafted onto multi-walled carbon nanotubes for the preconcentration and speciation analysis of As (Grijalba et al. 2015).

1.4.1.3 Magnetic Solid-Phase Extraction

Among the different approaches in solid-phase extraction, the use of magnetic materials is becoming increasingly important and popular because of their advantages over classic solid-phase extraction and dispersed extractants. Magnetic solid-phase extraction consists of the use of a magnetic (nano)material which is dispersed into the sample solution for the retention of target analyte/s and then easily and swiftly recovered by means of an external magnetic field. This technique avoids common drawbacks observed in classic solid-phase extraction, such as clogging of the sorbent column in online solid-phase extraction, and one of the most time-consuming steps in dispersive techniques: phase separation by centrifugation and/or filtration (Capriotti et al. 2019). Furthermore, the rapid advances in the synthesis of nanomaterials bring higher versatility to the obtained magnetic nanoparticles in terms of shape, size, sorption capacity and potential for functionalization. Improved extraction efficiency, higher enhancement factors, lower limits of detection and excellent reproducibility have been achieved based on the properties of magnetic nanomaterials (Hemmati et al. 2018).

1.4.1.3.1 Advanced Magnetic Sorbents

Magnetic nanoparticles usually consist of magnetic elements such as iron, nickel, cobalt or their oxides and alloys with ferromagnetic or superparamagnetic properties. Ferromagnetic particles have a permanent magnetism, while superparamagnetic particles are attracted to magnetic fields, but do not retain any residual magnetism after the field is removed. Among magnetic nanoparticles, the superparamagnetic iron oxides magnetite (Fe_3O_4) and, more recently, maghemite (γ-Fe_2O_3), have received much attention due to their ease of synthesis, the facile tuneability of their size dispersion and their high capacity for surface functionalization (Giakisikli and Anthemidis 2013). Pure inorganic magnetic nanoparticles, such as neat Fe_3O_4 or γ-Fe_2O_3, tend to form aggregates easily, which results in changes in their magnetic properties. In addition, their lack of selectivity makes them unsuitable for work with complex matrix samples, such as river or sea waters, while they tend to dissolve in acidic media. As a consequence, the protection of the magnetic core with an adequate coating has proven to be an efficient approach not only to solve this problem, but also to prevent particle aggregation and to provide specificity towards a specific analyte (Xie et al. 2014). Ferrites, with the formula $MeFe_2O_4$ (Me = Mn, Mg, Zn, Cu, Ni, Co), exhibit stronger superparamagnetic properties than magnetite and maghemite and have also been applied for preconcentration of heavy metals in waters, but no surface modifications were required (Stefanova et al. 2012).

Among the most widely used coatings for magnetic iron nanoparticles, silica (SiO_2) has proven to be an excellent alternative, since it has low cost, it is chemically inert and thermally stable and provides reactive silanol superficial groups which are hydrophilic and can be readily modified with other functional groups or materials (H. Lu et al. 2007). Thus, for example, the selectivity of silica-coated magnetic nanoparticles can be enhanced by including a silanation functionalized agent which might include amino, thiol or carboxylic groups, among others (Kazemi 2016; Mahmoud et al. 2016). A vast array of modifiers, ranging from ionic liquids (Martinis et al. 2017) to complexing agents (Behbahani et al. 2016) have been chemically and physically immobilized onto silica-coated magnetic nanoparticles for heavy metal preconcentration in waters. Other inorganic oxides, such as alumina (Al_2O_3) (Tavallali et al. 2013) and zirconia (ZrO_2) (Wu et al. 2012), have also been used as protective coatings in magnetic sold-phase extraction methods, although not as intensively as silica

Carbon-based nanostructured materials do not have intrinsic magnetic properties, but can be coupled to magnetic nanoparticles, retaining their unique retention characteristics and adding magnetic features useful for their isolation. Graphene, graphene oxide and carbon nanotubes have found several applications in sample treatment for heavy metal determination in water samples. Magnetized graphene and graphene oxide can be easily obtained by co-precipitation methods with iron oxides and have found diverse applications making use of their exceptional ultrahigh specific area of up to 2630 m^2 g^{-1}, according to theoretical calculations. Both magnetized nanomaterials have proven successful for the preconcentration of diverse metal ions in varied water samples both as-obtained and with further functionalization (Li et al. 2018a). Carbon nanotubes combined with magnetite nanoparticles are also a heavily featured modern material for magnetism-based extractions, both in their pristine, hydrophobic state, which allows for interactions with complexed metal ions and/or after an oxidation step that yields negatively charged surface groups to interact directly with metal cations (Herrero-Latorre et al. 2015).

As previously mentioned, most of the sorbents used for dispersive solid-phase extraction can be subsequentially magnetized. Layered double hydroxides obtained by co-precipitation of the corresponding cations in alkaline media and in the presence of magnetic nanoparticles yield electrostatically-bound composites which have been applied for the efficient preconcentration and speciation analysis of heavy metals (Abdolmohammad-Zadeh and Talleb 2014). Metal-organic frameworks have also been introduced in the field of magnetic extractions. Direct physical mixing of metal-organic framework crystals with magnetic nanoparticles results in good magnetic hybrids, but *in-situ* growth of magnetite nanoparticles in the presence of stable metal-organic framework crystals or layer-by-layer nano-metal-organic framework growth over bare or protected magnetic nanoparticles lead to higher yields. The tunable characteristics of metal-organic frameworks allow the design of sorbents with the desired degree of specificity for single or multi-analyte determinations (Taghizadeh et al. 2013). Still, if high selectivity is sought, ion-imprinted polymers are the most adequate sorbents. Their magnetization usually requires a SiO_2-protected magnetic nanoparticle, given the appropriate anchoring surface silica represents for ion-imprinted polymer binding (Shakerian et al. 2016). Selective and efficient magnetic-solid phase extraction using these magnetized polymers have been reported for many heavy metals (Hemmati et al. 2018).

Finally, in view of the need to progressively fulfill the principles of Green Chemistry in search of a more environmentally sustainable practice of analytical chemistry, the development of magnetized biosorbents has gained significant progress in these last years. The use of microorganisms and biopolymers has been able to meet these expectations in the fields of heavy metal preconcentration and speciation analysis, both in their natural state and coupled to magnetic carriers. Surface modifications of magnetic nanoparticles with chitosan, a readily available, nontoxic and biodegradable biopolymer are, by far, the most reported. Chitosan presents a great affinity for metal ions due to the presence of large numbers of amino and hydroxyl groups in its structure, thus making it an excellent extractant by complexation (Cui et al. 2014).

1.4.2 Liquid-Liquid Extraction

Liquid–liquid extraction is widely used as a sample preparation technique for separation and preconcentration of inorganic and organic analytes from water (Anthemidis and Ioannou 2009). This technique is based on the distribution of different molecules of a sample solution between two immiscible phases. Liquid-liquid extraction has been traditionally performed by partitioning solutes between an aqueous phase and organic solvents, which are expensive, toxic, flammable and volatile, resulting in the production of hazardous waste (Ghaedi et al. 2009). Consequently, novel extractant phases are being continuously developed with the aim of miniaturizing and diminishing the environmental impact of the techniques. The most important families of novel liquid-liquid extraction phases will be discussed in the next section. A summary of the most applied techniques, along with the distribution of reported works categorized according to the heavy metal they have been applied to, is presented in Fig. 1.1.

1.4.2.1 Modern Solvents Used in Liquid-Liquid Extraction

1.4.2.1.1 Non-ionic or Zwitterionic Surfactants

Surfactants are a group of substances that decrease the interfacial tension of immiscible liquids, facilitating the emulsification of these fluids. In their structure they present two regions, one formed by a hydrophilic head group and another by a hydrophobic tail group. Zwitterionic surfactants are a class of surfactants which bare two charges in their structure, a positive charge, generally from an ammonium group, and a negative charge, generally in the form of a carboxylate group. On the other hand, surfactants that do not possess any surface charges are called non-ionic surfactants. These solvents have either polyether or polyhydroxyl moieties as polar hydrophilic groups. In polar solvents, these molecules are associated forming micelles such that their hydrophobic tails huddle in the core of the micelle, and the hydrophilic head groups project outwards to the polar solution.

Surfactants have been widely used as emulsifiers and dispersants in extraction processes. Several methods of extraction of heavy metals in water have been reported using these compounds, such as cloud point extraction, in which the stability of the solubilized micellar aggregates decreases as the temperature increases. These solvents, in contrast to organic solvents, generate less environmental impact since lower volumes are required for extraction processes (Hébrant 2009).

1.4.2.1.2 Ionic Liquids

In last decades, ionic liquids have started to be considered as potentially alternative solvents in line with the precepts of Green Chemistry, thanks to their special features like low vapor pressure at room temperature, high viscosity, dual natural polarity, high thermal stability and wide range of miscibility with water and other organic solvents. Hence, the use of ionic liquids avoids many environmental and safety problems associated with organic solvents. Moreover, they represent an excellent replacement for organic compounds in extraction processes, since the partition mechanism that produces the transfer of analytes from the aqueous phase to the ionic liquid phase is similar to that when traditional organic solvents are involved (Marciniak 2010). In most works, co-reagents for ion metals are used to diminish their polarity and favour their partition towards the ionic liquid phase (Martinis et al. 2014).

The most widely used ionic liquids in analytical chemistry usually comprise an organic cation, e.g., imidazolium, phosphonium, pyrrolidinium, pyridinium or quaternary ammonium and appropriate anions: hexafluorophosphate, tetrafluoroborate, alkylsulfates, alkyl sulfonates, chloride or bromide (Palacio and Bhushan 2010). Moreover, these solvents have been deemed “designer solvents”, due to the fact that they can be synthesized with tailored properties, such as greater selectivity, lower aqueous solubility or better biodegradability, by adequately combining different anions and cations.

Recently, a new family of ionic liquids known as magnetic ionic liquids has become the subject of interest in several analytical applications. These compounds are synthesized by the incorporation of an element with magnetic properties such as iron, manganese, cobalt or dysprosium, as part of the anion or cation of the ionic liquid. Magnetic ionic liquids strongly respond to external magnetic fields, apart from possessing the unique and tuneable physicochemical properties of ionic liquids (Santos et al. 2014). This accounts for one of their main advantages, since the separation from the liquid matrix can be easily performed by an external magnetic field, thus eliminating time-consuming steps such as centrifugation and/or filtration for phase separation (Clark et al. 2016).

1.4.2.1.3 Deep Eutectic Solvents

Deep eutectic solvents are another kind of ionic solvents, formed from a eutectic mixture of Lewis or Brønsted acids, such as urea, glycerol, sugars, carboxylic acids and bases, e.g. choline chloride, Vitamin B4 (Yilmaz and Soylak 2016). Due to the formation of eutectic mixtures, these compounds generally have much lower melting points than the individual components. These solvents are low-cost alternatives to traditional volatile organic compounds since they can be easily prepared starting from natural compounds and purification steps are not necessary. Deep eutectic solvents have similar properties to ionic liquids, such as high conductivities and high solubilities for a wide range of solutes, as well as some advantages over them, such as lower toxicity and higher biodegradability (Smith et al. 2014). Moreover, the synthesis of ionic liquids is more expensive and usually results in a higher environmental impact in comparison with the synthesis of deep eutectic solvents, which makes use of less toxic reagents such as amino acids, sugars, natural acids (Pena-Pereira and Namieśnik 2014).

1.4.2.2 Novel Liquid-Liquid Microextraction Techniques

Classic liquid–liquid extraction has many disadvantages, such as emulsion formation and the use of large sample and organic solvents volumes, making it time-consuming, expensive and significantly damaging to the environment (Anthemidis and Ioannou 2009). Consequently, simplified and miniaturized versions of the liquid-liquid extraction technique have been developed. These microextractions involve a non-exhaustive miniaturized sample preparation methodology using a very small volume of extracting phase relative to the sample volume. The main advantages of these techniques are the lower time consumption and the reduction of waste production without sacrificing precision and accuracy (Martinis et al. 2014).

1.4.2.2.1 Dispersive Liquid-Liquid Microextraction Techniques

Dispersive liquid–liquid microextraction is based on the use of an organic solvent such as chloroform, dichloromethane or acetonitrile as a third component for a better dispersion of the extractant, due to its high miscibility in both the extractant and aqueous phases. This increases the surface area between the extraction solvent and the aqueous sample, achieving a faster equilibrium and decreasing the required volume of extractant and the extraction time. After centrifugation, the preconcentrated analytes can be determined by various instrumental techniques. Nevertheless, this technique has some drawbacks, since it is difficult to automate and the identity of the third component -usually an organic solvent as disperser- increases its environmental impact (Rezaee et al. 2010).

Temperature-assisted dispersive liquid-liquid microextraction is an interesting alternative to dispersive liquid–liquid microextraction. In this technique, a specific temperature is applied to increase the solubility of the solvent phase and enhance the contact between the extraction and sample phases. Then, a cloudy solution is formed when the mixture is cooled in an ice bath and the separation of both phases occurs. Its main advantage with respect to dispersive liquid–liquid microextraction is that it does not require the use of a dispersant, making it more environmentally friendly. The main drawback of this methodology is related to the time invested during the heating and cooling steps, and the fact that it is limited to thermally stable analytes and extraction solvents (Martinis et al. 2014). However, this last limitation has been solved with the application of ionic liquids in temperature-assisted DLLME (Sadeghi and Moghaddam 2012).

Ultrasound-assisted dispersive liquid-liquid microextraction is another modification of dispersive liquid–liquid microextraction. This technique involves the application of ultrasound for the efficient dispersion of the extraction phase in the sample matrix, which leads to a faster equilibration of the phases and shorter extraction time. In addition, there is no need to use organic solvents as dispersants, since the high energy produced by the ultrasonic stirring is enough for the adequate dispersion required. (Rezaee et al. 2010). On the other hand, special care must be taken, since ultrasound stirring usually increases the temperature of the sample solutions and this effect can compromise the chemical stability of some chelating reagents used in the preconcentration of metals.

In recent years, magnetic ionic liquids have been used as extraction solvents in liquid–liquid extraction techniques in aqueous systems, giving rise to magnetic dispersive liquid-liquid extraction. These solvents have been efficiently applied in several magnetic dispersive liquid-liquid microextraction techniques, due to their ability to separate from the sample solution with an external magnetic field, decreasing the duration of the sample preparation stage (Clark et al. 2016). A novel magnetic dispersive liquid–liquid microextraction method using 1,3-(propyl-1,3-diyl) bis-(3-methylimidazolium) bis-(tetrachloroferrate) as a dicationic magnetic ionic liquid was investigated by for the analysis of trace of gold and silver in water samples followed by electrothermal atomic absorption spectrometry (Beiraghi et al. 2015).

1.4.2.2.2 In-Situ Phase Separation Techniques

Cold-induced aggregation microextraction is a simple, rapid and much safer method compared to dispersive liquid–liquid microextraction (Shemirani and Majidi 2010). In this technique, a small amount of extraction solvent, such as an ionic liquid, is added to the sample solution, where it is mixed with a non-ionic surfactant which acts as an emulsifier, improving its dispersion. Then, the resulting solution is cooled in the ice bath, decreasing the solubility of the extractant phase. After centrifugation, the extractant phase is separated from the aqueous solution and settles to the bottom of the conical centrifuge tube, where it can be easily separated for the final determination of the analyte. In this last stage, the surfactant prevents the adherence of the fine drops of ionic liquid to the wall of the used vessel (Baghdadi and Shemirani 2008).

In-situ solvent-formation microextraction is a simple, suitable and robust method for the extraction and preconcentration of several analytes from sample solutions containing high concentrations of salts (Baghdadi and Shemirani 2009). This methodology consists on the addition of an ion pairing agent, such as sodium hexafluorophosphate ($NaPF_6$), to the sample solution containing very small amounts of a water-soluble ionic liquid, such as 1-hexyl-3-methylimidazolium tetrafluoroborate ($[C_6mim][BF_4]$). This results into the formation of a cloudy solution caused by fine droplets of a hydrophobic solvent, product of the metathesis reaction between the water-soluble ionic liquid and the added anion, such as $[C_6mim][PF_6]$. After centrifugation, the fine droplets of the extraction phase settle at the bottom of the glass centrifuge tube and can be easily separated for analyte determination (Martinis et al. 2010).

1.4.2.2.3 Cloud Point Extraction

A novel alternative to traditional liquid–liquid solvent extraction is the use of aqueous polymeric solutions as environmentally safe liquid–liquid extraction media. Colloidal-sized clusters known as micelles are formed when surface-active agents are dissolved in aqueous solution. During their formation, the surfactant micelles can entrap several hydrophobic substances, isolating them from the solution. When the critical micelle concentration is reached, the solubility of the surfactants in aqueous solution decreases above a good-defined temperature named cloud point temperature, resulting in their separation from the aqueous matrix of the sample (Pytlakowska et al. 2013).

Therefore, any metal ion either directly or complexed, can be extracted into the micelles of the surfactant-rich phase, giving rise to the cloud point extraction technique (Zheng et al. 2019). Cloud point extraction is a simple, rapid, inexpensive and non-polluting technique that has been employed, for example, for the preconcentration and determination of nickel and manganese in water using p-nitrophenylazoresorcinol and Triton X-114 as chelant and extractant, respectively, prior to determination by flame atomic absorption spectrometry (Şahin et al. 2010).

1.4.2.2.4 Non-dispersive Microextraction Techniques

In the single-drop microextraction technique, a droplet of the extraction phase is suspended at the tip of a micro syringe needle and directly immersed in a stirred solution or placed in close contact with its headspace for the extraction of analytes (Jeannot et al. 2010). This technique is inexpensive, requires a minimal volume of extraction solvent and high sensitivity can be achieved (Jain and Verma 2011). Nevertheless, this technique has some drawbacks such as: limited surface area and, consequently, low interfacial contact between sample and extraction solvent, and a limited stability of the drop suspended from the needle. To solve these problems, an alternative termed hollow fibre liquid phase microextraction has been proposed. In this case the extraction solvent is contained inside a hollow fibre which is affixed to the tip of a syringe needle (Wang and Wang 2014). Since the drop is mechanically protected, the sample can be vigorously stirred without any loss of extraction solvent.

1.4.2.3 Liquid-Liquid Extraction in Flow Analysis

During the last decades, a new analytical approach based on flow techniques for automation, optimization and miniaturization in sample pre-treatment has been developed. Batch methods have several disadvantages, being usually labour intensive, time-consuming and involving large amounts of chemicals that could be harmful to the operator, expensive and environmentally unfriendly (Silvestre et al. 2009). Flow techniques are well known for reducing the consumption of reagents and waste generation, limiting the intervention and exposure of the operator and improving both the reproducibility and the frequency of analysis. Traditionally, these methodologies comprise three stages: in the first step, either a discrete or continuous sample flow is pumped or suctioned into a carrier stream, which may also contain a reagent such as a chelating agent. Next, the extractant immiscible phase is injected into the sample stream, generating a single flow which passes through an extraction coil, where the mass transfer between both phases occurs. Finally, a phase separator splits the phases into individual streams, being the one that contains the analyte directed towards the detector for analysis (Silvestre et al. 2009).

Although possessing several advantageous characteristics, this technique has not been widely applied for routine heavy metals analysis due to the critical instrumentation needed and the challenges represented by flow phase separations, which are intrinsically complicated and can appreciably affect the reproducibility, stability and robustness of the method (Adam and Anthemidis 2009). To cite a successful application example, an efficient flow injection-ion chromatography system has been reported by (Ho et al. 2010) to automate pre-treatment procedures for several trace metals in water samples by inductively coupled plasma mass spectrometry.

1.5 Analytical Techniques for Heavy Metal Detection

The aim of this section is to discuss different available methods for the quantification of heavy metals in waters. They have been grouped into two main families: spectroscopic and electrochemical techniques and a final section including widely used techniques that do not exactly fit into any of the other two.

1.5.1 Spectroscopic Techniques

Absorption, emission and fluorescence measurements, as well as mass spectrometry and even molecular absorption are the tools discussed in this section, which aims to provide a general overview of the most applied spectroscopic techniques for heavy metal determinations in waters (represented in Fig. 1.2).

1.5.1.1 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy is one of the most widely used lab scale methods for the quantification of heavy metals. The fundamental principle of atomic absorption spectroscopy is the excitation of isolated atoms from the ground state to an excited state using radiation of a specific wavelength. Then, the amount of energy absorbed during this excitation -which is proportional to the concentration of atoms present in the sample- is measured (Malik et al. 2019).

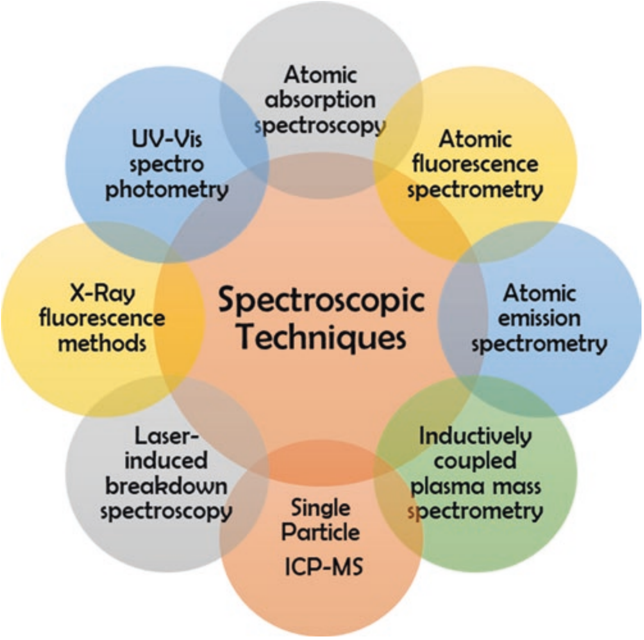

Fig. 1.2 Most applied spectroscopic techniques for heavy metal determination in water samples. (*ICP-MS* Inductively coupled plasma-mass spectrometry)

To be analyzed at the atomic level, the sample needs to be atomized first. Thus, the sample must be volatilized and decomposed in such a way as to produce gas-phase atoms and ions. This phenomenon is achieved with the use of plasmas, flames and electrothermal atomizers (Sikdar and Kundu 2018). In addition, hollow cathode or electrodeless discharge lamps of the same element to be measured are the most widely used single line sources to excite the atoms or ions with a pre-selected precise wavelength for monoelemental measurements. The type of atomizer defines the name of analytical techniques: direct flame and graphite furnace (or electrothermal) atomic absorption spectrometry are the most classical techniques. Alternatives such as glow-discharge (Büyükpınar et al.), hydride generation and cold-vapor have also found applications in the field. For example, cold vapor atomic absorption spectrometry is a routine method commonly used to determine mercury in various types of samples due to its low cost, simplicity and high sensitivity and selectivity (Mohajer et al. 2017).

Vapor generation may be defined as a process whereby volatile or semi-volatile analyte species are synthesized from non-volatile precursors to permit their subsequent transfer from a condensed phase to the gas phase (Sturgeon 2017). In this sense, vapor generation techniques for atomic spectroscopy sources yield the advantages of efficient separation of the analyte from a matrix without adverse interference effects (Jia et al. 2019). Particularly, in photochemical vapor generation, the analyte is converted into a volatile species by action of ultraviolet radiation. In this technique, a photochemical agent in the liquid phase, such as formic or acetic acid, is necessary. Photochemical vapor generators usually make use of a low-pressure mercury ultraviolet lamp emitting primarily 254 nm radiation (Šoukal et al. 2018). Photochemical vapor generation has been successfully applied to metals such as As, Sb, Sn, Bi, Se, Te, Hg and Pb (Sturgeon 2017).

When sample atomization is performed by electrothermal atomic absorption spectroscopy, the temperature in the furnace can reach values over 3500 K. Such a high temperature, significantly exceeding even the flame temperature of acetylene/nitrous oxide mixtures, results in a significant reduction of the detection limit compared to the flame atomic absorption method (Grochowski et al. 2019). Furthermore, the high temperature allows higher reproducibility, alas with longer analysis time when compared to flame atomization (Malik et al. 2019).

Although atomic absorption spectroscopies usually present very good limits of detection for heavy metals, sample treatment steps are sometimes necessary in order to preconcentrate the analytes or to eliminate matrix effects prior to analysis (de Andrade et al. 2017). In this context, the use of nanoparticles is gaining great interest in atomic absorption techniques. Their use has been enormously facilitated by the fact that electrothermal atomization allows for the direct introduction of several analyte-containing nanoparticles for measurements, thus avoiding additional digestion and/or dilution steps (Choleva et al. 2019).

1.5.1.2 Atomic Fluorescence Spectrometry

Atomic fluorescence spectrometry is similar to atomic absorption spectroscopy in the sense that it involves the excitation of vaporized atoms or ions to excited states after the absorption of electromagnetic radiation of a specific wavelength. The main difference stems from the fact that in fluorescence measurements it is not the absorbed radiation that is measured but, instead, the emitted characteristic fluorescence of the element in study. Thus, in order to discriminate emitted light from incident light, the excitation source is placed at a 90° angle with respect to the optical axis of the detector. The intensity of the fluorescence radiation depends on four factors: the intensity of the excitation source, the concentration of atoms in the atomizer, the quantum efficiency of the atoms and the extent of self-absorption. Although, if saturation is avoided, fluorescence is directly proportional only to the concentration of atoms in the atomizer and, therefore, to the concentration of the metal in the sample (Sanchez-Rodas et al. 2010).

Modern developments in atomic fluorescence spectrometry are mostly related to sample introduction. Hydride generation has been demonstrated to be the most widely applied technique coupled to atomic fluorescence and it is based on the mixing of the aqueous sample or the eluate resulting from a sample preparation procedure with a reducing agent, typically $NaBH_4$. Several elements, including As, Bi, Cd, Ge, Pb, Se, Sb, Sn, Te and Zn are able to form gaseous hydrides, which are subsequently separated using a gas-liquid separator and flushed into the measurement cell by an inert gas. During this process, hydrogen is also formed as a breakdown product of $NaBH_4$ and can be swept along with the hydrides into the atomization cell, where it serves as fuel for the atomization flame. Importantly, hydride formation is usually selective towards the lowest oxidation state species of several metals, thus serving as a species selective step (Hill and Fisher 2017). Mercury, due to its high vapor pressure, can be determined by means of direct gaseous atom trapping in a gold trap which works as a preconcentration step, and posterior release by heating followed by transport towards the measurement cell (Puanngam et al. 2012). Plasma induced (He et al. 2014), electrochemical (Hanna and Jones 2011) and photochemical vapor generation -recently significantly enhanced by the use of nanomaterials (Zou et al. 2019)- have also been applied, but at a much smaller scale.

The main disadvantages of atomic fluorescence spectrometry are related to signal quenching by other molecules in the atomization source and spectral and chemical interferences, which must be thoroughly studied if they affect sensitivity. Furthermore, non-specific emission from excited species at the atomizer is also a common problem, albeit minimized when working with hydride generation as sample introduction method (Sanchez-Rodas et al. 2010). Atomic fluorescence spectrometry is usually regarded as superior to atomic absorption spectroscopy and close to inductively coupled plasma-mass spectrometry in terms of sensitivity for several heavy metals, being simpler and cheaper than the latter, but lacking its multielemental intrinsic nature.

1.5.1.3 Atomic Emission Spectrometry

Atomic emission spectrometry, sometimes referred to as optical emission spectrometry, is the measurement of the light emitted when thermally excited atoms decay to lower-energy orbitals to determine their concentration (Ferreira et al.). Since the emitted wavelengths are element-specific, atomic emission spectrometry is a highly selective method for the quantification of heavy metals. In contrast with fluorescence techniques, excitation in this technique is not achieved by means of a specific lamp, but with a high-temperature atomization source (Michalke and Nischwitz 2013). Because higher temperatures yield higher emission intensities, strong excitation sources are necessary, making inductively coupled plasma an ideal source of excited atoms, since temperatures in the 6000–10,000 K range are achieved in the generated plasma. Thus, the combination of inductively coupled plasma-atomic emission spectrometry is, by far, the most used approach for elemental emission measurements (Biata et al. 2018). Other excitation sources such as glow discharge (Cheng et al. 2019), flame (Fernández-Sánchez et al. 2019) and microwave-induced plasma (Broekaert 2006) can also be applied for the determination of heavy metals in water samples by atomic emission spectrometry.

Modern advancements in atomic emission techniques for water analysis are related mostly to the sample introduction, since liquid samples must reach the excitation source as aerosols and completely evaporate without producing serious disturbances of the analytical signal. It is therefore necessary to achieve droplets below

10µm in diameter in order to maximize the aerosol transport and evaporation efficiency. Most efforts in this direction involve the design of nebulizers that maximize the fraction of suitable droplets to improve the mass flux that can be introduced into the excitation source, lowering the limits of detection and improving the resolution of the analytical signs (Almagro et al. 2006).

Since all the atoms in the sample are simultaneously excited, atomic emission spectrometry can be used for multielemental analysis with sensitivities like those obtained by atomic absorption spectroscopy, which is a major advantage in comparison to this technique (Sperling 2014). On the other hand, mass spectrometry has progressively replaced atomic emission spectrometry as the preferred detection method after using the inductively coupled plasma thanks to its better limits of detection, which has made it the technique of choice for direct and hyphenated trace-analysis since its introduction. However, atomic emission techniques are still routinely used, since they present higher tolerance towards saline content, which is important in samples such as sea or wastewater, and since it allows for the monitoring of some non-metal elements such as C, S, P and Cl, which are difficult to determine with mass spectrometry (Michalke and Nischwitz 2013).

1.5.1.4 Inductively Coupled Plasma-Mass Spectrometry

Inductively coupled plasma-mass spectrometry is probably the most widely used technique for the determination of heavy metals. Its workings are similar to those of inductively coupled plasma-atomic emission spectrometry in terms of the atomization plasma. The particularity of mass spectroscopy detection is that the ions from the plasma have to be extracted, usually by means of a quadrupole through a series of cones, into a mass spectrometer which measures their mass-to-charge ratio, yielding signals with intensities proportional to the number of generated ions.

This technique shows sensitivities similar to those of electrothermal atomic absorption spectroscopy, which is, in general terms, a cheaper and more low-maintenance technique (Ferreira et al. 2018). However, inductively coupled plasma-mass spectrometry has unique advantages, such as wide lineal ranges for most metal elements, multielemental capabilities and isotopic information (Meermann and Nischwitz 2018). Atomic emission spectrometry is in general less sensitive than mass spectrometry, although with more robustness towards highly saline samples. Furthermore, inductively coupled plasma-mass spectrometry can detect trace element-containing species, even for elements distributed amongst a large number of species (Rosen and Hieftje 2004).

Despite all these advantages, there are some difficulties that are often encountered when using plasma-related techniques. High concentrations of some organic solvents or salts can result in plasma instability as well as in a build-up of carbon residue in the sampling cone which ultimately contaminates the instrument. These problems can be alleviated to some degree by addition of oxygen to the nebulizer-gas flow or, if analyte concentrations are high enough, by diluting the samples prior to measurements with water or dilute acid (Ammann 2007).

1.5.1.4.1 Single Particle Inductively Coupled Plasma-Mass Spectrometry

Currently, with the continuously increasing field of nanotechnology, concerns have been raised about an increase in the probable environmental and health risks from nanoparticles (Leopold et al. 2016). So, the development of new techniques capable of providing accurate and robust quantification and characterization of nanoparticles is necessary (Montaño et al. 2016). In response to these demands, inductively coupled plasma-mass spectrometry operated in single particle mode has been developed (Hsiao et al. 2016). This technique is suited to differentiate between an analyte in solution and the analyte as nanoparticles without any prior separation, simplifying analysis while eliminating complex sample preparation steps (Laborda et al. 2016). This allows it to provide information on the size and size distribution of nanoparticles, as well as their quantity and dissolved concentration of the metal (Hsiao et al. 2016).

Single particle-inductively coupled plasma-mass spectrometry involves the introduction of the nanoparticle-containing samples into the inductively coupled plasma-mass spectrometry system and the rapid collection of data. Very short measurement times are necessary to ensure the detection of individual particles as ion pulses (Montaño et al. 2016). The number of detected pulses is related to the total number of nanoparticles in the sample, while the intensity of the pulses depends on the size of the nanoparticle (Fréchette-Viens et al. 2019). For instance, this approach has been described as a tool for the analysis of diverse metal nanoparticle/metal ion systems in water samples, such as: Ag (Newman et al. 2016), Ti, Ag, and Au (Donovan et al. 2016), Cu (Keller et al. 2018) and, Pb, Fe, Sn, Cu, Ag and Ti (Venkatesan et al. 2018).

1.5.1.5 Laser-Induced Breakdown Spectroscopy

Laser-induced breakdown spectroscopy (LIBS) is a novel technique of atomic emission spectroscopy that uses the micro plasma generated by a pulsed and focused laser beam onto a very small area of the sample as the vaporization, atomization and excitation source (Li et al. 2018b). After thermal equilibrium has been established, the plasma cools down and characteristic emission lines from the elements present in the sample are detected by a spectrometer (Sikdar and Kundu 2018).

The success of laser-induced breakdown spectroscopy stands mostly on advantages such as: multi-element analysis, fast response, portability for field work, robustness which avoids substantial sample pre-treatment and simple and easy to use instrumentation (Jantzi et al. 2016). However, due the fluctuation of the laser energy, discrepancy of resolution of spectrometers, matrix effects and inhomogeneities of the laser-induced plasma, among others, it usually presents low sensitivities and detection limits when compared to other atomic spectrometric techniques, especially for liquid sample analysis (Galbacs 2015).

In the direct analysis of water samples by laser-induced breakdown spectroscopy, splashing severely interferes with light collection by the optics system, deteriorating analytical sensitivity and reproducibility (Cremers et al. 2006). To solve this problem, Zhao and co-workers developed a graphite enrichment method for the on-line determination of heavy metals in industrial wastewater. With this approach, limits of detection were reduced to ppb level for Pb, Ni, Cd, Cr, Zn and Cu (Zhao et al. 2019). Other simple, robust and inexpensive alternative for laser-induced breakdown spectroscopy elemental analysis of water droplets and aerosols is acoustic levitation (Contreras et al. 2018). This approach can be used for trapping and pre-concentrating single-liquid droplets and has been applied for the determination of Cd, Hg, Pb, and Ba in water samples.

To further enhance emission signals, nanoparticle enhanced laser-induced breakdown spectroscopy has been proposed. This technique is based on the deposition of silver or gold nanoparticles on the sample surface before the laser irradiation. In this case, the plasma is generated at the surface of targets where spherical metal nanoparticles have been deposited (De Giacomo et al. 2016a). This increases the number of electrons emitted in the plasma that, in turn, greatly enhance the emission of radiation. In this context, the application on aqueous samples is possible after the deposition of the nanoparticles on a conductive substrate, requiring only a few microliters of sample for the determination (De Giacomo et al. 2016b).

Laser-induced breakdown spectroscopy can also be combined with laser-induced fluorescence. In this case the atoms are resonantly excited from the ground state to a higher state with a tunable laser and the fluorescence emissions from the upper states are selectively monitored. This technique coupled to laser-induced fluorescence allows to decrease four to five orders the limit of detection obtained by direct analysis. This technique has been recently applied for analysis of Pb and Cu in waters (Kang et al. 2017; Wang et al. 2019).

1.5.1.6 X-Ray Fluorescence

Energy dispersive X-ray fluorescence spectroscopy is a well-established technique for quantitative determinations of the elemental composition of aqueous and solid samples. It is based on the excitation of the sample with primary X-radiation which displaces inner-shell electrons from the atoms. These electron voids are then filled by electrons from outer shells, which emit energy in the form of X-ray fluorescence in the process. Since these energies are characteristic of each element and proportional to the amount of atoms present, the detected signals contain both quali- and quantitative multielemental information about the composition of the sample, represented by the wavelength and the intensity of the signals, respectively. Its main advantages are that it is a clean and fast non-destructive technique, which is universally applicable, including its use in field analysis with portable instruments (Zhou et al. 2018). However, the sensitivity of energy dispersive X-ray fluorescence makes it unsuitable for the analysis of minor and trace elements, which motivated the development of related techniques with improved analytical features.

Total-reflection XRF is one of these derived techniques, in which the incidence angle of the primary X-ray beam on the sample surface is below 0.1°. Consequently, most of the incident beam is reflected, minimizing the penetration of the incident radiation in the sample and reducing the spectral background. Furthermore, when thin layers are used, the intensity of fluorescence is practically double, since the sample is excited by both the primary beam and by its reflection on the posterior surface. These two factors allow the achievement of detection limits up to 0.1μg/L, two to three orders of magnitude below those of traditional energy-dispersive X-ray dispersive fluorescence (Dalipi et al. 2017). Since total-reflection techniques can be applied to both liquid and solid samples, their application to water analysis can be performed both directly (Borgese et al. 2014) or on a solid sorbent after a preconcentration step, with further improvements on the limits of detection for sub-μg/L heavy metals (Nourbala-Tafti et al. 2017).

1.5.1.7 UV-Vis Spectrophotometry

UV-Vis spectrophotometry is one of the most classical analytical techniques for the quantification of analytes in aqueous samples. It is based on the irradiation of a liquid sample with light in the ultraviolet-visible wavelength range and the measurement of the amount of light absorbed by the sample. Spectrophotometric measurements follow the Beer-Lambert law, which describes the relation between the absorbed intensity and the concentration as lineal, resulting in a simple and rapid method for the determination of analyte concentrations. Heavy metal UV-Vis spectrophotometric methods rely on the formation of colored complexes between metal ions and reagents such as dithizone for Co, Ni, Cu, Zn, Ga, Pd, Ag, Cd, In, Pt, Au, Hg, Tl, Pb and Bi (Maratta et al. 2016) or thiocyanates for Ti, Fe(III), Co, Mo and W (Filik et al. 2004), among others (Okoye et al. 2013). Since the limits of detection obtained by this technique are, at best, around 0.01 mg/L -well above those obtainable by atomic spectroscopic methods-, coupling with preconcentration is common in order to achieve the detection and quantification of trace metal analytes (Rajabi and Razmpour 2016).

The main advantages of UV-Vis spectrophotometric measurements are its ease of application and its cost-effectiveness, which makes it one of the most ubiquitous techniques for routine analysis in laboratories around the world. Furthermore, this technique allows for some degree of speciation analysis of multivalent heavy metals, since several chromogenic reactions are selective towards a specific oxidation state, such as the cases of selective determinations of Cr(VI) using diphenylcarbazide (Lace et al. 2019) and V(V) using Gallamine blue (Gürkan et al. 2017).

1.5.2 Electrochemical Techniques

Spectroscopic techniques are widely used for heavy metal quantifications but have limitations such as elevated costs of acquisition and maintenance of the equipment, added to the usual need of sample preparation, which increases the risk of contamination of samples (Feldmann et al. 2009). Therefore, electrochemical techniques have been of interest to analysts due their ease of application, low cost and low consumption of reagents. Moreover, contamination of the sample by reagents or during sample storage or handling is decreased (Pujol et al. 2014). These techniques are based on the use of an electrolytic cell formed by an electrolyte and electrodes. As electrons are transferred from the electrode to the analyte, or vice-versa, ions circulate in solution to balance the charge and close the electrical circuit (Elgrishi et al. 2017). The usual configuration of an electrochemical experiment is presented in Fig. 1.3a. Electrochemical techniques are classified into: amperometric, voltammetric, potentiometric, impedance measurement, galvanostatic and electrochemiluminescent techniques, according to the different electrical signals generated (Fig. 1.3b).

1.5.2.1 Potentiostatic Techniques

Potentiostatic techniques are based on the application of a fixed potential between the working and the reference electrode, by means of a potentiostat. This methodology allows the measurement of the analyte concentration, which is correlated to the resulting current. Moreover, these techniques are classified into three main categories: amperometry, chronocoulometry and voltammetry (Bansod et al. 2017).

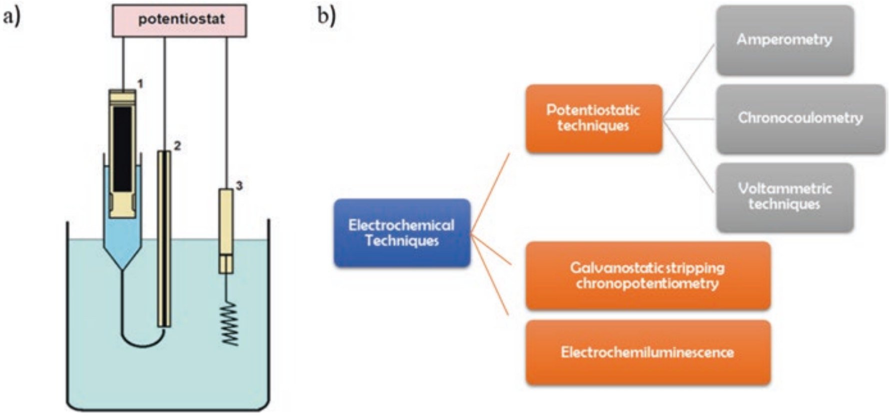

Fig. 1.3 (**a**) General setup for electrochemical detection of heavy metal ions in water samples. These configurations usually comprise three types of electrodes: the half reaction of interest occurs on the surface of the working electrode (2), whose cell potential is measured compared to the reference electrode (1) and a third electrode known as the counter electrode (3) (Modified after *P. Zanello*, *Inorganic Electrochemistry: Theory, Practice and Application. 2003, Royal Society of Chemistry, London, UK*). (**b**) Overview of the most applied electrochemical techniques for heavy metal ions in water samples

1.5.2.1.1 Amperometry

Amperometry involves the measurement and recording of the electrical current signal at a certain fixed potential between the working and reference electrode. The resulting current is generated due to the reduction or oxidation of electroactive analytes on the surface of the working electrode, and its intensity is proportional to the concentration of the analyte (Su et al. 2011). The main advantages of this technique are its low limit of detection, high reproducibility, high sampling frequency, large lineal working range and inexpensive instrumentation, added to the fact that it can be easily coupled to flow injection systems (Tag et al. 2007). However, amperometric detection has some drawbacks, being the biggest disadvantage its low selectivity when several electrolytes are present in the sample. Chronoamperometry is a faster type of amperometric technique in which a potential is applied in a single step and the resulting current is recorded in a short period of time, without the need of stirring the measured sample (Ngamchuea et al. 2014).

One of the most important characteristics of amperometric techniques is that the capacity of the sensors is strongly influenced by the material used to build the electrodes (Felix and Angnes 2010). Initially, inert metal electrodes made of Pt, Au or C were used. However, more disposable and cheaper screen-printed electrodes have been used recently, involving modern alternatives such as nanomaterials (Vidal et al. 2013). Furthermore, the development of novel amperometric biosensing techniques using biologically modified electrodes for qualitative or quantitative measurements has grown significantly in the last decades. For example, an efficient and selective amperometric biosensor technique for quantitative determination of As(III) and Cd(II) ions in water samples was performed using a platinum electrode modified with ruthenium(II)-tris(bipyridyl), graphene oxide and acetylcholinesterase (Gumpu et al. 2018).

1.5.2.1.2 Chronocoulometry

Chronocoulometry consists in the application of a controlled potential and the subsequent quantification of the resulting transferred electric charge, calculated by taking the integral of the current as a function of time (Inzelt 2010). This technique presents greater advantages compared to chronoamperometry, since signals rise with time and integration is able to improve the signal-to-noise ratio (Kim et al. 2007). It is a simple and precise technique which, nevertheless, needs a high current efficiency, reason why it is not widely applied in electrochemical analysis (Choi et al. 2015).

In order to improve the sensitivity and selectivity of chronocoulometric techniques, nanomaterials have been used for the coating of electrochemical sensors and biosensors (Zhu et al. 2014) due to their specific electronic, mechanical and chemical characteristics, providing greater advantages for the analysis of heavy metals. The use of nanomaterials increases the electrode surface area and mass-transport rate and improve electron transfer when compared to conventional materials (Aragay and Merkoçi 2012). Recently, electropolymerization has also been used extensively for the preparation of modified electrodes, due to the high electronic conductivity, high sensitivity, and greater electrocatalytic activity obtained compared with unfunctionalized electrodes (Venkataprasad et al. 2018). Deoxyribonucleic acid has also been widely used for the coating of heavy metal sensors, due to its capability to form metal complexes with selected nucleic acid bases (Hasanjani and Zarei 2019).

1.5.2.1.3 Voltammetric Techniques

These techniques comprise the family with the most applications used for in situ identification and measurement of heavy metals ions in several environmental samples (Lu et al. 2018). Voltammetric techniques involve the measurement of the electric current at several potential points in a current-voltage curve, being different to the fixed potential measurement which characterizes amperometric techniques. The driving force of the redox reaction involved comes from the potential applied to the working electrode, which allows to control the electrolyzed chemical species on the electrode surface. These techniques are suitable to decrease the background current, thus improving limits of detection. In contrast to other electrochemical techniques, voltammetric techniques can be applied to turbid and coloured solutions, which is an important advantage. In addition, as well as with other electrochemical techniques, voltammetric electrodes can be subjected to modifications, allowing enhanced selectivity for analysis (Silva et al. 2014).

Voltammetry is subclassified in different sub-techniques: polarographic or differential pulse voltammetry techniques involve the use of a dropping mercury electrode with a constant flow of mercury drops to obtain current-potential relations. Employing mercury drops as electrodes continually generates usable, fresh and uncontaminated electrode surfaces for use over a range of applied potentials. A simple and effective method for the determination of Co(II) was carried out based on a second derivative wave of catalytic adsorptive polarography produced by complexing the metal with dimethylglyoxime and nitrite onto the dropping electrode (Zhu et al. 2019).

Linear sweep voltammetry implies the measurement of the current as a function of a potential that is linearly varied with time (Savizi and Janik 2011). This detection method is simple and more selective than differential pulse and square wave techniques. Moreover, kinetic behaviour studies of ions in solutions for an extensive range of analyte concentrations can be performed with this technique (Khun and Liu 2009).

Square wave voltammetry is based on the application of a combined square wave and staircase potential in the working electrode. The resulting square-shaped staircase potential applied results in a highly sensitive response with minimal background currents, which makes it faster and more effective than other voltammetric techniques for low analyte concentrations (Mirceski et al. 2013). Square wave voltammetry has been used in several electrochemical processes, for example, for the determination of heavy metals in thin-layer chromatography (Lovrić 2010).

Cyclic voltammetry consists in the application of potential cycles to an electrode submerged in an electrolytic solution and the measurement of the resulting current. The controlled potential applied through the working and reference electrodes is considered as an excitation signal which is usually repeated several times. In a first step the potential is varied linearly; then, the direction of the sweep is reversed and the potential returns to its initial value. The voltage extremes in which the inversion occurs are called change potentials and the intensity of current is directly proportional to the concentration of the analyte. This technique has been widely used for the study of systems containing reversible electroactive species.

Stripping voltammetry has been used extensively for elemental analysis due to its high selectivity, low cost and versatility. This technique is subdivided into anodic stripping voltammetry, cathodic stripping voltammetry and adsorptive stripping voltammetry. Anodic stripping voltammetry is a widely used electrochemical technique for quantitative determination of metals ions, since it is highly sensitive and has a high signal to background ratio (Herzog and Beni 2013). Usually, mercury electrodes have been used in this technique to improve sensitivity and reproducibility. However, due to the high toxicity of this metal, the use of these electrodes is restricted. Therefore, new alternatives have been used, such as Au, Ag and Bi electrodes (Bansod et al. 2017). Anodic stripping voltammetry is divided into two steps; a pre-concentration step, where the analyte is electrodeposited onto the electrode surface, and a second step, in which the analyte is reoxidized and stripped out of the electrode by applying a reverse potential. The quantitative analysis is related to the peak current, while the peak potential provides qualitative information about the analyte in the sample. A simple and sensitive analysis of Hg(II) in environmental water samples by square wave anodic stripping voltammetry on screen-printed gold electrodes was reported by (Bernalte et al. 2011).

1.5.2.2 Galvanostatic Stripping Chronopotentiometry

Galvanostatic measurements are electrochemical methods based on the measurement of the potential of a system during the application of a constant current. Although there are not many current works reporting the use of these techniques for heavy metals determination, galvanostatic stripping chronopotentiometry has been applied for trace metal determinations in complex samples such as waters with high organic loads (Malik et al. 2019). This technique is based on a two-step process. The first step involves the preconcentration of the metal by deposition on the working electrode with a constant potential. The second step involves the oxidative stripping of the deposited metal by a chemical oxidant or by constant current, while measuring the potential of the working electrode as a function of time to quantify the metal ions (Matar et al. 2010). In stripping chronopotentiometry there is no current at the working electrode during the stripping phase of the analysis, thus avoiding the interference of electroactive particles present in the system. Furthermore, this technique has been demonstrated to be suitable for multicomponent analysis, having good selectivity and adequate sensitivity (Štroffeková et al. 2008).

1.5.2.3 Electrochemiluminescence

Electrochemiluminescence is a kind of luminescence produced during electrochemical reactions in solution (Richter 2004). It involves the production of reactive intermediates from stable precursors at the surface of an electrode, which then react to produce an electronically excited state emitting light upon relaxation (Valenti et al. 2016). Electrochemiluminescence excitation is caused by energetic electron transfer reactions (redox or enzymatic) of electrogenerated species (Bansod et al. 2017). In this technique, luminescence is initiated and controlled by switching an electrode voltage. This characteristic allows the improvement of the selectivity, because varying the electrode potential it is possible to control the species that are reduced and/or oxidized on the electrode surface (Bertoncello and Ugo 2017).

In this regard, electrochemiluminescent detection of heavy metal ions is widely used along with metal nanostructures and electrodes of nanometric size, which have been increasingly applied in the last years. Among them, carbon nanomaterials have received considerable interest for electrode modification due to their high conductivity, large surface area and electrocatalytic superiority in many electrochemical reactions (Fiorani et al. 2019). Furthermore, these functionalized electrodes have greatly increased the sensitivity in comparison to bare electrodes (Sun et al. 2017). Alongside, quantum dots possess great characteristics, such as a large surface area–volume ratio, good interfacial properties with high surface reaction activity, high electron-transfer efficiency and excellent biocompatibility, which makes them ideal for electrochemiluminescence (Pedrero et al. 2017). Also, they make easy the introduction of functional groups to their surface, giving rise to selective interactions for the detection of different metal ions (Zou et al. 2015). Recently, the use of graphitic carbon nitride nanomaterials for this technique has also increased. These nanomaterials show important properties, such as high film-forming capacity and excellent catalytic and electronic properties (Sun et al. 2017). Silica nanoparticles are also receiving considerable attention lately for the construction of platforms for electrochemiluminescence due to their biocompatibility and low cost (Bertoncello and Ugo 2017), added to their porous properties and their surface chemistry, which allows easy modification and functionalization (Chen et al. 2019).

1.5.3 Other Methods

1.5.3.1 Ion Chromatography

Within the chromatographic techniques, the use of ion chromatography for determination of multiple cations and anions in solution is a field of increasing interest (Michalski and Nischwitz 2018). Ion chromatography allows for the analysis of metals with low-cost and little time of analysis. Furthermore, it requires small sample volumes and minimal preparation, yielding high sensitivity, selectivity and resolution (Liu et al. 2015). Briefly, this is an analytical technique that separates ionic species by combining the chromatographic and ionic equilibrium theories into one application (Weiss 2016). There are several ionic equilibrium mechanisms for analyte separation, including ion exchange, ion-pairing and ion-exclusion. In ion chromatography, a column packed with a resin is used as a stationary phase and an eluent as a mobile phase (Chow and Watson 2017). The stationary phase can have cationic or anionic exchange properties, thus binding positively and negatively charged species, respectively.

As the sample is injected onto the column, the analytes are retained on the resin surface and are then subsequently displaced by the eluent ions as the elution solution is added to the column (Liu et al. 2015). Owing to diverse ion sizes and relative charges, the analytes are separated from the column at different times during the elution, being the different ion-resin affinities the basis of the separation. Also, the interaction between the solvent and the analyte can have an impact on the order in which the analytes are eluted. This sequential elution results in a temporal separation which allows individual ion quantifications, usually by conductimetric detection (Weiss 2016). Furthermore, ion chromatography allows for the speciation analysis of several metals, distinguish between different oxidation states. As an example, As(III) and As(V) using IC followed by UV detection have been analyzed in aqueous solution (Shaw and Haddad 2004).

1.5.3.2 Surface-Enhanced Raman Spectroscopy

Surface-enhanced Raman spectroscopy is a technique that involves the enhancement of Raman scattering signals from species adsorbed on roughened metal surfaces and nanoparticles, especially on Au and Ag nanostructures that act as substrates. The enhancement comes because of the highly localized increase of electromagnetic fields near the surface of nanostructures, particularly around edges or between adjacent nanoparticles. Enhancement factors can be as high as 10^6–10^{10}, which leads to an enormous increase of analytical sensitivity, allowing for limits of detection in the low ng/L range (Borah et al. 2015). Due to the high sensitivity, unique molecular fingerprints that characterize Raman spectroscopy and nondestructive data acquisition, this technique is becoming one of the most widely used spectroscopic tools for the detection and identification of several chemical species, including heavy metals. The most critical aspect of performing a Surface-enhanced Raman spectroscopy experiment is the choice and/or fabrication of the substrate. Many factors -which include shape, size and interparticle distance of the nanomaterial, as well as its dielectric environment- must be chosen carefully. Traditional substrates include electrodes roughened by oxidation-reduction cycles, island films, colloidal nanoparticles and surface-confined nanostructures (Haynes et al. 2005).

Sensors based on this approach are one of the most important nano-optical-based detection strategies for chemical speciation of heavy metal ions in water at trace levels. Nanostructured substrates modified with selective anchors allow for the specific interaction with heavy metal ions, keeping them close to the signal-enhancing surface, allowing their amplified determination (Shaban and Galaly 2016). Following this approach, several heavy metals have been determined by using, for example, 2-mercapto-isonicotinic acid-functionalized Au nanoparticles (Tan et al. 2012), a nanoporous alumina membrane functionalized with carbon nanotubes (Shaban and Galaly 2016) or Au nanoparticles functionalized with citric acid (Frost et al. 2015), among others. Also, since surface-enhanced determinations are sensitive to structural features, the speciation analysis of some heavy metals can be performed by means of this technique (Guerrini et al. 2014).

1.5.3.3 Bio Methods

Immunoassays, which represent the bio-approach towards the determination of heavy metals in waters, comprise a currently growing field of interest. They offer significant advantages over more traditional methods of heavy metal ion detection, being a quick, inexpensive, easy to perform and reasonably portable alternative, with an inherent high specificity (Blake et al. 1998). The idea behind immunoassays relies on an antibody that is developed to have a high degree of selectivity towards a specific chelated target metal ion. This high specificity of the antibody is coupled to a sensitive colorimetric reaction which is proportional to the initial concentration of the metal analyte, which can be subsequently quantified either by showing a visual result or by means of a spectrophotometric measurement (Sarkar 2002). The development and advances in the monoclonal antibodies synthesis field have led to the development of immune-based analysis of several heavy metals, as well as of their speciation distribution: Cr(III) (Zhou et al. 2013), Cd(II) (López Marzo et al. 2013), Hg(II), Pb(II) and Ni(II) (Blake et al. 1998) are some of the reported cases.

There are three key properties that are desirable in a metal-specific antibody. The first of them is that the antibody should exhibit little or no ability to bind the metal-free complexant, since the assay requires a molar excess of chelant over metal ion. The second one is the efficient binding with the target analyte complex, since this affinity defines the ultimate sensitivity of the method. Metal complex-antibody systems with dissociation constant values in the 10^{-9}–10^{-8} M range are usually considered ideal and allow to achieve limits of detection in the low µg/L. The final desired characteristic is the selectivity towards the target complex. A tenfold difference between the affinity of the antibody for the metal-chelant complex of interest and the affinity for other metal ion complexes likely to be present in the sample matrix is usually considered enough. However, if this ideal behavior cannot be achieved, masking agents that specifically bind the interfering metals and remove them from the antibody binding reaction can be used (Blake et al. 1998).

1.6 Conclusions and Future Perspectives

Analytical chemistry plays a fundamental role in relation to the study and control of heavy metal contamination in water by providing the tools to determine their identity and concentration. In a context of increasing technological and scientific demand of these elements without many certainties about their fate in the environment and their impact on life, precise, sensitive and cost-effective alternatives for their monitoring are highly required. Thus, valid analytical methods with increasingly better limits of detection, sensitivities and robustness must be continually developed and improved, and this is possible only based on the innovations from various fields of science, ranging from modern measurement equipment to novel tailor-made materials.

There are several challenges associated to the task of quantifying heavy metals in waters. Many of them stem from the low concentrations into which heavy metals are found in the environment, thus requiring extremely sensitive methods for their accurate determination. Moreover, this situation is even more challenging when speciation analysis is performed, because species represent only a fraction of the total element concentration. To this end, developments related to detection techniques are continually evolving to achieve lower limits of detection.

Spectroscopic techniques such as atomic absorption, emission and fluorescence spectrometries have been demonstrated to be useful alternatives for the highly selective determination of heavy metals in waters. Advances in the fields of sample introduction and atomization, including the application of nanomaterials science and photochemistry, keep refreshing the application of these techniques for routine heavy metal analysis. Nevertheless, the development of inductively coupled plasma-mass spectrometry has meant a significant leap in the field of spectroscopic determinations by providing excellent sensitivities, limits of detection and extended lineal ranges, coupled to the identificatory power of mass spectrometry, albeit with a still high instrumental cost. On the other hand, electrochemical techniques are less expensive alternatives with a vast array of variants to suit the needs of a myriad of analytical problems, although their main drawback stands on their usually low selectivity and laborious sample preparation to obtain accurate results. Recently, the application of nanotechnology to the field of electrochemical analysis has revolutionized its advancement; carbon nanotubes, graphene and metal nanoparticles represent only a fraction of the nanomaterials that have been applied to improve the analytical performance of these methods.

Another common problem faced by analytical chemists is the interference from the sample matrix in the determination of the desired element or elements. Modern developments in materials science and organic chemistry are being extensively applied in the development of sample preparation methods. For instance, neat or functionalized nanomaterials, ionic liquids, metal-organic frameworks and ion-imprinted polymers are being actively used thanks to their advantages in terms of selectivity and efficiency to separate and preconcentrate heavy metals from various aqueous matrices. Liquid-liquid and solid-phase microextraction techniques have been developed for the preconcentration of practically all heavy metals, and several of them have also been applied for the separation of elemental species, thus becoming useful tools for speciation analysis.

Despite the enormous number of alternatives, both in terms of sample treatment and instrumental determination options, the main and irreplaceable tool for a reliable analytical determination is still the criterion of the analyst. Given the benefits and drawbacks of each technique or method, along with their costs and availability, the right choice is always dependent on each specific analytical need. It is thus in the hands of the analytical chemist or technician to properly evaluate the problem and set the goals of an analysis, in order to create a standpoint from which to choose the most convenient alternative amidst the many alternatives hereby presented. Finally, the inherent evolving character of the field of heavy metal analytical chemistry assures that more notorious advantages will continue to surface thanks to the introduction of novel technologies and materials. This will come not only with analytical improvement in mind, but also with the aim to minimize the impact of their application in the environment. Novel nanomaterials, more powerful optical systems and recyclable solvents are only some of the fields which will lead the way to the development of faster, better, greener and more reliable ways of identifying and quantifying heavy metals in our environmental, waste and drinking water.

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Chapter 2
Olive-Oil Waste for the Removal of Heavy Metals from Wastewater

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Abstract Spain is the world's largest olive growing country. Olive oil is considered a very healthy product, particularly in Mediterranean areas. Olive oil is produced from the olive that is the fruit of the olive tree. However, industries dedicated to olive-oil production (olive mills, olive pomace extraction plants, between others) generate a great amount of solid residues and by-products. On the other hand, contamination of water by heavy metals is an important problem on a global scale. In an effort to provide solution to these problems, by-products and waste from the olive tree cultivation, olive recollection and olive oil extraction have been explored as low-cost materials in the removal of heavy metals from aqueous media. The aim of this chapter is provide a summary of main results of recent research studies on this topic. In a great extent, the revised materials in this chapter were particularly native materials without any prior treatment. Also, the characterization of these residues and by-products has been reviewed and commented.

Keywords Biosorption · Heavy metals · Olive cake · Olive pomace · Olive-oil production · Olive stone · Olive tree pruning

2.1 Introduction

Water is a scarce and valuable resource. Using it rationally is an obligation of all people, to ensure the next generations a livable world. The use of water is both a right and a responsibility, and has economic, social and environmental value. Each country, each company, each person, must be aware that quality water is a natural resource necessary for economic development and essential to support any way of life.

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However, pollution of aquatic environments remains a problem of special interest. This contamination is produced by the presence of compounds or elements that normally would not be without the action of man, or by an increase or decrease in the normal concentration of existing substances due to anthropogenic action. Specifically, various activities related mainly to mining and industrial activity have generated waste, which either due to ignorance or poor management has caused episodes of pollution in air, water and soil. A clear example of this type of contamination is heavy metal spills into the environment (Gupta and Ali 2013; Azimi et al. 2017).

Heavy metals are found in the environment naturally, but the problem arises when their concentration increases due to the spillage produced by human activities. These heavy metals enter the food chain so that their presence above the necessary limits can cause significant problems in living beings (Domenech and Peral 2008; Caviedes Rubio et al. 2015; Malik et al. 2019).

Water pollution prevention measures should be based, in general, on the use of techniques that minimize the generation of waste and on the substitution of hazardous compounds with others of less danger, as well as on the application of recovery techniques and recycling of the substances used in the production process itself. However, it is rarely possible to suppress metal spills with the introduction of prevention measures at source. Therefore, they must be combined with the use of final wastewater treatment techniques.

Wastewater treatment is a complicated process, since the water to be treated usually has a very variable composition and characteristics. Therefore, there are few processes that allow the decontamination of effluents while meeting requirements such as economic costs, flexibility in terms of effluent quantity and pollutant load or sufficient selectivity in terms of decontamination of the metals considered.

Several authors have carried out reviews of the main treatment technologies for the removal of metals from industrial effluents. Among these technologies are physicochemical processes, adsorption, chemical precipitation, electrochemical process, ion-exchange or membranes filtration process (Fu and Wang 2011; Lakherwa 2014; Azimi et al. 2017; Malik et al. 2019).

In recent years, interest in more innovative technologies that are being studied and have certain advantages over conventional ones has increased. This is the case of biosorption, an unconventional method to take out heavy metals from aqueous solutions, based on the property that some types of biomass has to accumulate these pollutants by different types of mechanisms such as physical adsorption, complexation and ionic exchange. Frequently, natural materials that are completely renewable, that present a low cost, that their handling does not pose an additional risk and that can be disposal by incineration are used as biosorbents (Rahimizadeh and Liaghat 2015).

A summary of the advantages and disadvantages of the main technologies for wastewater treatment and biosorption is included in Table 2.1.

A large number of biosorbents that are effective for the separation of heavy metals are currently studied. Typical biosorbents include non-living biomass (waste from various agro-industrial activities, crustacean shells) and algae biomass or

Table 2.1 General characteristics of the main heavy metal decontamination technologies (Ronda 2016)

Technology	Advantages	Disadvantages
Chemical precipitation	Simplicity of operation Low operating cost	The active agent cannot be recovered for reuse Problems with low metal concentrations Final waste difficult to eliminate
Membranes tecnologies	Pure effluent Automated process Possible metal recovery	High energy cost Membranes are especially deteriorable (low average life rate) Applicability only at low metal concentrations
Organic extractions	Selectivity	Requires the use of large amounts of organic agents extractants Applicability only at high metal concentrations
Ionic exchange	Effective Pure effluent Possible metal recovery	High installation cost Resins are vulnerable to oxidation by chemical agents The process is strongly affected by the presence of other cations
Electrochemical process	Possible metal recovery	High energy cost Applicability only at high metal concentrations
Adsorption	Conventional Highly effective at very low concentrations Adsorbent (activated carbon)	Not selective Applicability principally at for low metal concentrations High dependence on pH
Biosorption	Process not governed by biological limitations Process fast Efficient in metal removal Metals can be easily released and recovered	Fast saturation of the biosorbent High dependence on pH Organometallic species are not susceptible to degradation Metal state valence cannot be altered biologically

microbial biomass (bacteria, fungi and yeasts) (Rahimizadeh and Liaghat 2015). Some examples of biosorbents have been used in recent works such as marine algae and *Prosopis Juliflora* (Prasanna and Supriyasubrahmanian 2019), sugar beet shreds (Blagojev et al. 2019), Irish *Fucus vesiculosus* (Brinza et al. 2019), waste fish scale (Rajesh et al. 2018), walnut shells (Shruthi and Jeevitha 2018), fruit waste (Ugya et al. 2018), olive stone and pinion shell (Calero et al. 2018).

In this work a review of the use of waste derived from the olive industry as biosorbents for the removal of heavy metals from aqueous solutions is carried out.

The continuous historical expansion of olive cultivation has marked the landscape, economy and culture of Spain. Olive oil is especially important in Andalusia region. In the 2018/2019 campaign, global olive oil production is expected to exceed 3 million tonnes. In Spain, an increase in olive oil production is estimated to be 23.3% compared to last year. Andalusia will be the main producing region, with production forecasts of 86% of all olive oil nationwide and 44% globally. The area of olive for mill has experimented a progressive increase in recent years (93,600 ha in 10 years), currently exceeding 1.5 million hectares (Junta de Andalucía 2018).

Although the main product derived from the olive grove is olives and its oily juice, it is clear that the agricultural management of the crop leads to the production of significant quantities of pruning. On the other hand, the processing of olives to produce olive oil in mills generates large by-products such as wet olive pomace that is generally intended for different uses. The technique most used includes (1) drying, (2) extraction of waste oil in extractors that use hexane (with or without prior olive stone separation) and, finally, (3) combustion of the oil-free olive pomace (called olive cake) for energy purposes or (4) composting.

A diagram of the olive processing is shown in Fig. 2.1, which includes all the products, by-products and waste that are generated and the amounts expressed in percentage of the total. The data for the olive tree pruning have not been included since this is very variable and depends on several aspects such as the age of the tree or its production. It has been estimated that a hectare of olive groves produces on average 1.7 tons of waste per year (Moya and Mateo 2013). Therefore, the olive pruning residue can represent an amount greater than 4 million tons according to the approximately 2.5 million hectares occupied by olive growing in Spain.

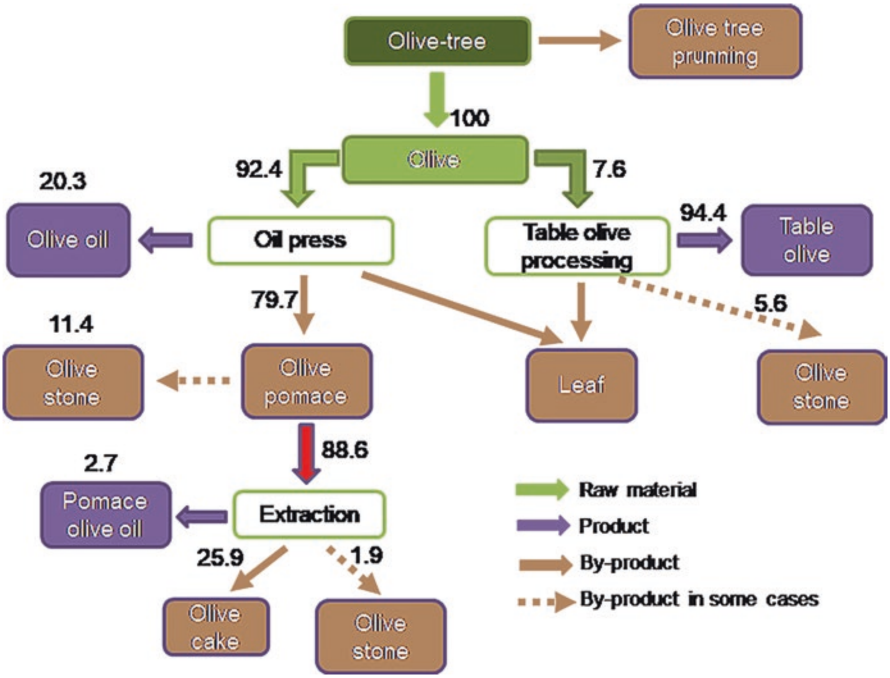

Fig. 2.1 Diagram of the olive processing. (Adapted to AGAPA 2015)

2.2 Olive Tree Pruning as Biosorbent of Heavy Metals from Aqueous Solutions

2.2.1 Characterization

Olive tree pruning is generated as a result of the agricultural labors during the olive tree cultivation. Currently, in the world, according to data of International Olive Council, approximately about 11 million of hectares are used for olive trees cultivation (International Olive Council 2015). This cultivation gets a biomass potential of pruning residue of about 1500 kg/ha (Romero-García et al. 2014).

This residual material has good properties to use directly as adsorbent as was reviewed in this work. Figure 2.2 shows a photograph of olive tree pruning as it was received in laboratory.

The main physical and chemical properties of raw olive tree pruning are collected in Table 2.2. Olive tree pruning, like other lignocellulosic solids, is a combination of three main components, cellulose, hemicellulose and lignin. According to published data, cellulose, hemicellulose, lignin and extractive contents are in the range of 17.90–27.19; 14.70–25.46; 14.00–19.76 and 21.48–39.26 (% w/w), respectively (Almendros et al. 2017; Delgado-Moreno et al. 2017; Martín-Lara et al. 2009; Mamaní et al. 2019a; Pérez et al. 2018; Toledano et al. 2013). The values are very different between published works; it can be mainly due to the heterogeneity of material since it can present a more or less amount of leaves or branch (Romero-García et al. 2014). Olive tree pruning has relatively low equilibrium moisture (between 3.80 and 7.80%) and ashes content (from 1.69% to 5.67%). Both parameters can vary depend on tree age, climate conditions and the collection method. With regards to elemental analysis, Olive tree pruning has not sulfur and low level

Fig. 2.2 Photograph of olive tree pruning

Table 2.2 Main physical and chemical properties of raw olive tree pruning (OTP)

Parameter		Value	Reference
Structural analysis	Cellulose	27.19 47.16 19.70 36.60	Martín-Lara et al. (2009) Mamaní et al. (2019a) Delgado-Moreno et al. (2017) Toledano et al. (2013)
	Hemicellulose	21.04 25.46 14.70 25.00	
	Lignin	19.76 15.37 14.00 18.40	
	Extractives (hot water)	39.26 21.48 18.00	Almendros et al. (2017) Pérez et al. (2018) Toledano et al. (2013)
Proximate analysis (wt, %)	Equilibrium moisture	6.57 6.65 5.36 5.36 7.80 3.80	Mamaní et al. (2019a) Mamaní et al. (2019b) Calero et al. (2013) Ronda et al. (2013) Martin-Lara et al. (2017a) Iáñez-Rodríguez et al. (2019)
	Fixed carbon	14.60 13.01 6.44 12.04 16.80 21.89	
	Volatile compounds	75.54 77.05 82.53 76.93 72.90 72.62	
	Ashes	3.29 3.29 5.67 5.67 2.50 1.69	

(continued)

Table 2.2 (continued)

Parameter		Value	Reference
Ultimate analysis (wt, %)	Carbon, C	51.27 48.52 45.69 51.16	Martín-Lara et al. (2009) Mamaní et al. (2019a, b) Martín-Lara et al. (2017a) Iáñez-Rodríguez et al. (2019)
	Nitrogen, N	0.70 0.24 0.10 1.12	
	Hydrogen, H	6.75 6.95 7.55 6.70	
	Sulfur, S	<0.10 0.06 0.01 0.00	
	Oxygen, O	41.23 44.23 46.66 39.33	
Physical analysis	Specific surface area (m^2/g)	0.631	Calero et al. (2013)
	Pore volumen (cm^3/g)	$1.54 \cdot 10^{-3}$	
	Pore diameter (Å)	97.44	
	Bulk density (g/cm^3)	0.272	Iáñez-Rodríguez et al. (2019)
	Real density (g/cm^3)	1.158	

of nitrogen. Its surface area and pore volume are very low, about 0.631 m^2/g and 1.5410^{-3} cm^3/g, respectively, especially low if it is compared to activated carbon.

2.2.2 *Biosorption Tests*

The use of olive tree pruning as biosorbent without any treatment (called raw olive tree pruning in this work) has been particularly studied in batch systems and for lead removal from aqueous solutions. Table 2.3 summarized the results found by various researchers.

Blázquez et al. (2011a) studied the equilibrium and kinetics of the lead biosorption onto raw OTP. They showed that the biosorption of lead(II) happened fast (few minutes) and reached total equilibrium in less than 90 min at all operating conditions studied. Kinetics was well-defined by a pseudo-second-order model and equilibrium by Sips isotherm model. The maximum lead biosorption capacity was 26.24 mg/g at a pH of 5 and 25 °C. They also evaluated the thermodynamics of lead biosorption and found that biosorption was spontaneous and exothermic. Finally,

Table 2.3 Main results of raw olive tree pruning as biosorbent material of heavy metals in batch systems

Heavy metal	Operational conditions			Maximum biosorption capacity (mg/g)	Reference
	pH	Time, min	Temperature, °C		
Lead	5	120	25	26.72	Blázquez et al. (2015)
Lead	5	120	25	86.40[a]	
Lead	5	120	25	72.78[b]	
Lead	5	120	25	123.80[c]	
Lead	5	120	25	26.24	Blázquez et al. (2011a)
Lead	5	120	40	33.39	
Lead	5	120	60	32.15	
Lead	5	120	25	8.13[d]	Hernáinz et al. (2009)
Chromium	5	120	25	3.90[d]	
Lead	5	120	25	22.79	Martín-Lara et al. (2009)
Lead	5	120	60	5.51[e]	Martin-Lara et al. (2011)
Nickel	NP	NP	Room	7.85[f]	Almendros et al. (2016)
Nickel	NP	1440	Room	5.47[g]	Iáñez-Rodríguez et al. (2019)

[a]Chemically-modified by nitric acid; [b]Chemically-modified by sulfuric acid; [c]Chemically-modified by sodium hydroxide; [d]Initial metal concentration = 110 mg/L; [e]Initial metal concentration = 70 mg/L; [f]Initial metal concentration = 200 mg/L; [g]Initial metal concentration = 100 mg/L; *NP* Not provided

the study confirmed participation of carboxylic groups of material in lead biosorption.

Firstly, the surface chemistry of olive tree pruning and its link with lead biosorption capacity was deeply evaluated by Martín-Lara et al. (2009). A great part of the work was dedicated to describe and estimate acidity/basicity of the surface of olive tree pruning using continuous potentiometric titrations. They found a positive link between lead removal and the concentration of acidic functional groups on solid.

Some other works carried out designs of experiments to statistically analyze the effect of important experimental conditions as biosorbent dosage, initial metal concentration, pH and temperature on lead biosorption (Martín-Lara et al. 2011). The results showed that initial lead concentration is the most important factor influencing biosorption behavior.

Other authors studied impact of chemical treatments of olive tree pruning on its biosorption properties. Calero et al. (2013) modified olive tree pruning with nitric acid, sulfuric acid and sodium hydroxide and studied the main characteristics of the resulting materials. Also, Blázquez et al. (2015) compared maximum biosorption capacities of raw and chemically treated samples. Data showed that chemical treatments increased biosorption capacity of the raw olive tree pruning. Concretely, the maximum biosorption capacities were 26.72, 86.40, 72.28 and 123.80 mg/g for raw, treated by nitric acid, treated by sulfuric acid and treated by sodium hydroxide samples, respectively. Similarly, Ronda et al. (2013) performed a complete kinetic study of these materials (raw and chemically treated OTP). Some important differences between materials were found with respect to initial rates of biosorption, external and internal mass transfer coefficients. In general, when raw olive tree pruning was treated with acids the mass transfer coefficients improved extraordinarily.

Regards the study of olive tree pruning as biosorbent in multimetal systems, Hernáinz et al. (2009) analyzed the binary biosorption of Cr(III) and Pb(II) onto olive tree pruning. The extended Sips-type isotherm model was found to fit well the experimental data. A greater affinity for lead ions was observed and the interaction between these two metal ions was antagonistic due to competition for adsorption sites.

Some other authors have investigated adsorption behavior of olive tree pruning in packed-bed columns. For example, Ronda et al. (2018) performed lead biosorption experiments in columns at two different scales (laboratory- and pilot-scales). Good performance of both columns was observed. Under optimal operating conditions and for a solution of 100 mg/L of lead, columns were able to adsorb about 21 mg/g.

Other pollutants were also removal by olive tree pruning. In the review of works Anastopoulos et al. (2015) about adsorption of dyes, heavy metals, pesticides, phenolic compounds and radionuclides by residues of the olive-oil production including olive tree pruning were examined. They concluded that residues of the olive-tree cultivation have potential to remove different pollutants from aqueous solutions, especially lead (the pollutant most studied). In other work, Delgado-Moreno et al. (2017) tested the potential of innovative biomixtures composed of olive tree pruning, between other materials, to remove five common pesticides. The novel biomixtures showed good adsorption capacities for pesticides (equal or better than traditional ones). Also, Anastopoulos et al. (2018) examined the effect of composting on adsorption properties of olive tree pruning for methylene blue from aqueous solutions. They obtained a greatly improve of biosorption behavior when composting was performed. Particularly, maximum adsorption capacities of 129.87 and 250 mg/g for raw olive tree pruning and composted olive tree pruning, respectively was found.

Finally, some authors prepared interesting activated sorbents from olive tree pruning following different activation routes. For example, Mamaní et al. (2019b) analyzed the chemical activations by potassium carbonate and potassium hydroxide on properties of the activated materials. They obtained adsorbents with very high areas (from 1477 m^2/g of olive tree pruning activated with potassium carbonate to 2662 m^2/g of olive tree pruning activated with potassium hydroxide) and very interesting maximum adsorption capacities (from 625 mg/g of olive tree pruning activated with potassium carbonate to 1000 mg/g of olive tree pruning activated with potassium hydroxide). In other work, Mamaní et al. (2019a) reported the optimum operating conditions using potassium hydroxide as chemical. The authors get carbon materials with surface areas of 3514 m^2/g when an impregnation ratio (potassium hydroxide-OTP) of 6.38, an activation time of 145 min and an activation temperature of 788.5 °C were used.

2.3 Olive Stone as Biosorbent of Heavy Metals from Aqueous Solutions

2.3.1 Characterization

A photograph of olive stone is showed in Fig. 2.3. Although currently the production of olive oil has implemented stages for recovering the olive stone and several valorization alternatives are essayed, a considerable amount of this biowaste, that presents a relatively high transportation cost as well as limited storage life, continue been a pending problem. There are already a number of alternatives for its valorization.

Olive stone has a relatively high heating power, a heat of combustion of 4.1 kcal/kg according to Matos et al. 2010 which allow finding applications on the electricity sector and thermal processes (i.e. calefaction in residential and commercial buildings). Furthermore, olive stone can be valorized by gasification and pyrolysis to generate feedstocks for the petrochemistry sector (Matos et al. 2010). Main organic components of olive stone, named lignin, hemicellulose and cellulose also drive an obvious integration in biorefinery process to produce chemicals and biofuels. Additionally, olive stone has shown promising results in the biosorption field, in both batch and flow conditions. A fine analysis of the application of olive stone,

Fig. 2.3 Photograph of olive stone

including its uses as bio-sorbent of heavy metals have been summarized by Rodríguez et al. (2008).

On the line of other biomass by-products and wastes, components, as well as chemical and morphological properties, are reported in a relatively wide range and depend to a large extent on several factors such as varieties, (Heredia-Moreno et al. 1987) region and industrial process. Table 2.4 presents the fractional composition of the olive stone. Olive stone obtained from the separation process of the olive cake with an industrial pitting machine (4 mm siev-separator) supplied by the olive cake oil extraction plant (Jaén, Spain) showed lignin, cellulose and hemicellulose of 403.80, 271.40 and 321.80 expressed in (g kg^{-1}), respectively. (Calero et al. 2009; Martín-Lara et al. 2009) Proximate analysis is also very frequently utilized to provide moisture, ash and volatile content, and fixed carbon of this by-products. Table 2.4 shows the obtained data for olive stone supplied by the same plant after air-dried at room temperature and a milling treatment to obtain particle size smaller than 1 mm.(Blázquez et al. 2014) Equilibrium moisture is usually reported below 6%, while fixed carbon, volatile compounds and ashes are commonly around data summarized in Table 2.4.(Moubarik and Grimi 2015; Ronda et al. 2015) Elemental analysis also shows relatively constant values as described in Table 2.4 for raw OS. Dominant carbonaceous species (more than 50%) are typically reported, being oxygen the second highest element. Such data have been mainly reported by

Table 2.4 Main physical and chemical properties of raw olive stone

Parameter		Value	Reference
Structural analysis	Cellulose	29.79–40.4	Calero et al. (2009, 2016), Martín-Lara et al. (2009, 2013), Moubarik and Grimi (2015), Nieto et al. (2010), and Trujillo et al. (2016)
	Hemicellulose	21.45–32.2	
	Lignin	20.63–27.2	
	Extractives (hot water)	12.16	Martín-Lara et al. (2013), Moubarik and Grimi (2015), Ronda et al. (2015), and Trujillo et al. (2016)
Proximate analysis	Equilibrium moisture (%)	5.43–6.97	Calero et al. (2016) and Martín-Lara et al. (2013)
	Fixed carbon (%)	19.54	
	Volatile compounds (%)	74.66	
	Ashes (%)	0.37	
Elemental analysis	Carbon, C (%)	51.78–52.34	Blázquez et al. (2011b, c), Calero et al. (2009, 2016), Martín-Lara et al. (2009, 2013), and Moubarik and Grimi (2015)
	Nitrogen, N (%)	0.03–0.04	
	Hydrogen, H (%)	6.33–7.11	
	Sulfur, S (%)	<0.10	
	Oxygen, O (%)	40.47	
Physical analysis	Specific surface area (m^2 g^{-1})	0.16–0.378	Calero et al. (2016), Moubarik and Grimi (2015), and Trujillo et al. (2016)
	Pore volume (cm^3 g^{-1})	1.84×10^{-3}-0.812	
	Pore diameter (Å)	127.0–453.0	

measurement of C–H–N–S (Blázquez et al. 2011b). Morphological properties are specially related to the adsorption capacity of the samples. Surface area and porosity parameters provide crucial information to interpret its sorption properties. Nitrogen adsorption, carbon dioxide adsorption and mercury porosimetry tests carried out using standard procedure have been used to provide volume and diameter of pore and describe a relatively low specific surface area (Table 2.4) (Calero et al. 2016; Moubarik and Grimi 2015; Trujillo et al. 2016) Morphological properties of olive stone have been also studied by microscopy. The micrograph commonly shows an irregular structure which could favour the biosorption process (Blázquez et al. 2014; Moubarik and Grimi 2015; Nieto et al. 2010). Fourier Transform Infrared Spectroscopy allows analyzing chemical groups of the bio-sorbent materials. Such technic has shown the presence of different oxygen groups, mainly alcohols, carbonyls, esters, ethers and phenols as is detailed described below (Aziz et al. 2009a; Blázquez et al. 2011b; Moubarik and Grimi 2015). In particular, a wide adsorption contribution situated at 3350–3330 cm^{-1} can be associated with O–H species. The signal at 2920 cm^{-1} corresponds to an aliphatic C–H bond and the contribution situated at 1630 cm^{-1} can be assigned to the carboxylic C=O double bond. The peaks detected at 1460–1420 cm^{-1} can be associated with the C–O bond of the carboxylic groups. Fourier Transform Infrared Spectroscopy usually shows several peaks at 1370–1320 cm^{-1} region which are difficult interpret but could be associated to O–C=O structures, C–N of amides or a distortion of C–H bonds. The peak situated at 1030 cm^{-1} has usually associated with the alcoholic C–O and C–N bonds (Blázquez et al. 2011b). Titration is also used to analyze the properties and surface concentrations of functional groups. Martín-Lara et al. (2009) have utilized this technic to provide evidence about the influence of the pH on the chemical properties of the surface of the solid. The titrations allowed the quantification of the total functional groups as well as their characterization associated with a couple of bands. A peak of carboxylic groups (in the pK range 3–5 position) and a second contribution preferably ascribed to various reactions of hydrolysis which generates a positive charge character to the solid.

2.3.2 Biosorption Tests

Raw or treated olive stone have been extensively essayed as heavy metals biosorption material of aqueous solutions. At batch condition, pH, contact time and temperature are the most studied operating condition as shown for representative examples the Table 2.5. Cr (VI) solutions are recognized as a very toxic effluent for what has become in a model experiment for heavy metals biosorption test. Cr (VI) tests are commonly analyzed in term of a well-defined two simultaneous processes occurring using olive stone materials. Adsorption of Cr (VI) and reduction of Cr (VI) to Cr (III) (Calero et al. 2008; Martín-Lara et al. 2014). Calero et al. (2008) reported an enhancement factor in the Cr (VI) maximum sorption capacity of 2.8 when the temperature of the process was increased from 25 to 80 °C. An increase of

Table 2.5 Main results of raw olive stone as biosorbent material of heavy metals in batch systems

Heavy metal	Operational conditions			Maximum biosorption capacity (mg/g)	Reference
	pH	Time, min	Temperature, °C		
Cr(III)	4	120	60	7.03	Hernáinz et al. (2008)
Cr(VI)	2	300	80	4.82	Calero et al. (2008)
Cd(II)	7	120	80	9.72	Blázquez et al. (2011c)
Cd(II)	7	120	60	6.00	Hernáinz et al. (2008)
Pb(II)	5	120	25	2.18	Ronda et al. (2014)
Pb(II)	5	120	25	6.39	Blázquez et al. (2010)
Pb(II)	5	120	25	6.33	Blázquez et al. (2015)
Pb(II)	5	120	25	6.57	Hernáinz et al. (2008)
Pb(II)	5	120	25	4.57	Blázquez et al. (2014)
Pb(II)[a]	5	120	25	14.11	
Pb(II)[b]	5	120	25	15.33	
Pb(II)[c]	5	120	25	16.25	
Cu (II)	5	120	25	1.97	Blázquez et al. (2011b)
Fe (II)	2.9	120	25	0.65	Nieto et al. (2010)

[a]Chemically-modified by sulfuric acid; [b]Chemically-modified by nitric acid; [c]Chemically-modified by sodium hydroxide

the temperature caused both; a clear Cr (VI) adsorption enhancement and higher amounts of Cr (III) as a result of the reduction. However, total Cr removal resulted less influenced by temperature with a relatively low incremental factor of 1.7. The phenomenon (sorption-reduction) is not simple and different trends as function of the temperature have also reported for Cr (III).

According to previously published data, the adsorptive quantity of Cr (III) slowly decreasing when temperature rising from 25 to 60 °C. Such behaviour was analyzed by authors in term of two main factors. Less efficiency of the active binding sites of the solid as well as a weakening of adsorptive forces between the solid and the target metal (Hernáinz et al. 2008). A fine analysis of the pH influence during the biosorption of Cr (III) and Cr (VI) by olive stone have been also carried out. Several biosorption experimental tests in combination with a complete Fourier Transform Infrared Spectroscopy study confirmed a remarkable dependence of the biosorption capacity to the pH solution. Values of removed percentages higher than 80% for pH lower than 2 and notably lower (around 15%) when the pH is increased have been reported. These results are in accordance with several contributions, which describe the optimization of the Cr (VI) biosorption using is acid conditions (pH lower than 2). In acid media, the active groups of the bio-sorbent are positively charged, which favour the attraction of negatively charged Cr (VI) species (Blázquez et al. 2009). The equilibrium biosorption time is also a very important parameter to evaluate the efficiency of metal biosorption. According to the data summarized in Table 2.5, the contact time is preferably fixed around 120–300 min (equilibrium) showing relatively high maximum biosorption capacity for several metals.

A similar situation has been described for both Cd (II) and Pb (II). In a comparative study, authors detected that at the beginning of the process (first 15 min), the biosorption of Cd (II) was lower than Cr (III) and Pd (II), but at equilibrium conditions, typically achieved at 120 min, Cd (II) is the most removed metal (Hernáinz et al. 2008). Maximum biosorption capacity, as well as used operation conditions are presented in Table 2.5. A modelling kinetic approach has been also usually accomplished, being a pseudo-second-order model one of the most appropriated for a wide range of tested metals (Blázquez et al. 2011b; Hernáinz et al. 2008; Moubarik and Grimi 2015; Trujillo et al. 2016). According to the obtained kinetic data,(Hernáinz et al. 2008) the initial sorption rate was increased for the three metals (Cd(II), Pb(II) and Cr(III) when the temperature was raised. However, no significative differences were detected for the maximum sorption capacity. The activation energy of sorption process was also determined by authors. The low activation energy values suggested that the forces involved in the binding have mainly physical character. The work also provided a quantitative evaluation of the maximum uptake capacity and affinity by the analysis of the Sips isotherm parameters (Hernáinz et al. 2008). As a conclusion, a sequence of affinities of olive stone for the metal as function of temperature was determined as Cd (II) > Pb (II) > Cr (III) and Pb (II) > Cd (II) > Cr (III) for 25 °C and 40 °C, respectively. This affinity trend and its relation to the enhancement of temperature was also explained in term of thermodynamic. For Cd(II), the process was exothermic, while Cr(III) and Pb(II) turned out to be endothermic.

Although, with much less attention, cations such as Ni (II), Cu (II) and Fe (II) have been also studied using olive stone as metal bio-sorbent (Table 2.5). In addition to Cd (II) and Pb (II), Fiol et al. (2006) have presented a comparison study using Ni (II) and Cu (II) as model metals. Authors described the two well-defined aforementioned steps and its significance for each metal. The first step involved a rapid metal uptake at relatively short times (20 min). Them the adsorption of the metal continues until the equilibrium, achieved at 60–80 min. The results confirmed that the Ni (II) sorption is dominated by an ion-exchange mechanism, while a mechanism which includes adsorption-complexation in addition to ion-exchange must be involved for Cu (II), Cd (II) and Pb (II) (Fiol et al. 2006). The work also highlights a clear pH-dependency. As the main conclusion, the manuscript showed that the solid has a preference to bind acidic ions and that speciation is more important if the ion-exchange is the dominant mechanism (Fiol et al. 2006).

Chemically treated olive stone have been also presented as an alternative biowaste-derived sorbent. In a representative report, Blázquez et al. (2014) compared the adsorption properties of Pb (II) using untreated olive stone and the olive stone treated with three different solutions (H_2SO_4, HNO_3, and NaOH) at 2 M. All treated samples significantly increase the biosorption capacity of the bio-sorbent (5 mg g^{-1} for untreated olive stone and more than 12 mg g^{-1} for chemically treated (Table 2.5). The enhancement of the sorption capacity was explained considering chemical and morphological modifications of the raw olive stone. The best results were obtained for the sample treated with NaOH which showed an enhancement of the surface area, pore volume and pore diameter as well as an improvement of the ion-exchange process (Blázquez et al. 2014). Olive stone treated with concentrated sulphuric acid without heating treatment has shown well properties as biosorbent for Cd (II) solution. In this case, the sorption process was found to be pH-independent (studied range: 4–6.8) (Aziz et al. 2009b).

Olive stone has been also studied using continuous-flow fixed-bed columns which presents clear advantages in term of practical operation and full-scale sorption processes. Using this configuration, in addition to pH and temperature, special attention must be put on the flow rate and bed depth parameters (Calero et al. 2018). Experiments under flow conditions for Cr (III) biosorption by olive stone have been analyzed as function of different operating conditions. When the flow rate was decreased an increase in the breakthrough and saturation time was observed. A similar effect was detected when the bed depth was increased. Furthermore, the breakthrough and saturation time was decreased as the inlet Cr (III) concentration increases (same bed depth and flow rate). Using optimized conditions, 0.08 mg/g (capacity) was accomplished, while the analysis of the breakthrough was carried out using the Dose–Response model (Calero et al. 2009). A very interesting example to improve the total removal of Cr (Cr (VI) and Cr (III) in a water solution has developed by Martín-Lara et al. (2010). As aforementioned, Cr (VI) removal includes two main effects: biosorption of chromium (both oxidation states) by olive stone and reduction of Cr (VI) to Cr (III). Olive stone resulted in a very advantageous material for two columns sorption system. In the first step (first column), the aim was the removal all Cr (VI) of the water, while in the second column the Cr (III) capturing is optimized (Martín-Lara et al. 2010).

Breakthrough and exhausting time were also different for samples treated with nitric acid, sodium hidroxide and sulphuric acid. The breakthrough curves indicated that the bio-sorbent with the best results was the olive stone samples treated with nitric acid (Ronda et al. 2015). The scale-up (pilot plant) of olive stone columns have been also performed. Cr (III) removal was higher at pilot-scale (59.3%) in comparison to lab-scale (32.6%), while the bio-sorption capacity showed an opposite effect. Value of 0.142 mg/g and 0.427 mg/g, were respectively reported for pilot-scale and lab-scale (Calero et al. 2016). The scale-up process for Cr (VI) sorption using olive stone has shown also similar data to the lab experiments and has provided evidence that Cr (VI)-Cr (III) reduction process is more affected in the pilot-scale process (Martín-Lara et al. 2017b) Obviously, the phenomenon is more complex when simultaneous biosorption is analyzed. Removal of binary metal mixtures (Cu/Cd, Cu/Ni, Cu/Pb, Ni/Cd, Ni/Pb and Cd/Pb) in equimolar concentrations have been investigated at pH 5.5, showing the extended Langmuir model as the most adequate approach to interpret the interaction with the solid. The analysis provided evidence that metals in binary mixture compete for binding sites which are not specific (Fiol et al. 2006). Finally could be highlighted a study in which the effect of the Cr (III)-Pb (II) interaction has been studied. The presence of chromium driven to a negative effect on the lead removal, which was understood as a consequence of a competition between the two metals for the binding sites (Hernáinz et al. 2009).

2.4 Olive Pomace and Olive-Cake as Biosorbents of Heavy Metals from Aqueous Solutions

2.4.1 Characterization

Olive pomace represents the main residue of the olive oil production by weight. In Spain olive pomace is further dried and processed in extracting industries with hexane to produce the “pomace oil”. The final solid residue is called “olive cake” and mainly is used as solid fuel for heat or power generation (Manzanares et al. 2020). According to data published by Quesada et al. (2018) olive cake has a moisture content between 9% and 12%, and a calorific value of 4200 kcal/kg on a dry basis. Figure 2.4 shows photograph of both olive pomace and olive cake as it are collected in industrial plants and as it was received in laboratory.

The main physical and chemical properties of these raw materials (olive pomace and olive cake) are collected in Tables 2.6 and 2.7. The olive pomace is typically composed of water (60–70%) and presents a residual olive oil (2.5–3.0%) and mineral solids (2.5%) (Coimbra et al. 2010). The content of cellulose (16–38%), hemicellulose (11–34%) and lignin (19–29%) contents are in the range of other lignocellulosic residues (Medouni-Haroune et al. 2018; Chiou et al. 2015; Manara et al. 2014). The differences can be attributed mainly to the heterogeneity of this material, depending on the place, type of crop and extraction technology. Olive pomace has relatively low equilibrium moisture (between 4.30 and 10.0%) and ashes content (from 2.56% to 9.30%). Both parameters may vary depending on the location of the crop, the climatic conditions and the method of extraction. With regards to elemental analysis, olive pomace has not sulfur and low level of nitrogen. The content of cellulose, hemicellulose, lignin and extractive content for the olive cake is very similar to that of olive pomace, although it has a much higher value for extractable compounds in hot water.

Fig. 2.4 Photographs of olive pomace (left) and olive cake (right) as they was collected in industrial plants and received in laboratory, respectively

Table 2.6 Main physical and chemical properties of olive pomace

Parameter		Value	Reference
Structural analysis	Cellulose	16.84 37.40* 37.70*	Medouni-Haroune et al. (2018) Chiou et al. (2015) Manara et al. (2014)
	Hemicellulose	11.49 33.90* 23.80*	
	Lignin	19.47 28.60* 29.10*	
	Extractives (hot water)	9.60	Manara et al. (2014)
Proximate analysis (wt, %)	Equilibrium moisture	4.30 7.51 6.00 6.01 6.53 – 7.31 10.00	Martín-Lara et al. (2017c) Bennini et al. (2019) Miranda et al. (2012) Abu-Qudais (1996) Atimtay and Topal (2004) Jauhiainen et al. (2004) Al-Widyan et al. (2006) Chouchene et al. (2010)
	Fixed carbon	21.20 20.20 17.92 44.34 15.64 33.70 9.94 23.40	
	Volatile compounds	65.10 74.20 77.77 43.15 68.82 58.70 80.19 66.60	
	Ashes	9.30 2.80 4.31 6.50 9.01 7.60 2.56 4.00	

(continued)

Table 2.6 (continued)

Parameter		Value	Reference
Ultimate analysis (wt, %)	Carbon, C	44.00 48.20 54.90 46.80 47.00 47.90 52.10	Martín-Lara et al. (2017c) Bennini et al. (2019) Miranda et al. (2012) Atimtay and Topal (2004) Jauhiainen et al. (2004) Al-Widyan et al. (2006) Chouchene et al. (2010)
	Nitrogen, N	1.70 1.40 2.20 0.70 1.10 1.50 1.40	
	Hydrogen, H	7.00 6.10 8.20 6.10 5.70 7.10 6.70	
	Sulfur, S	<0.10 0.00 <0.10 0.10 0.00 0.10 <0.30	
	Oxygen, O	38.00 44.30 34.40 36.70 46.20 33.60 41.20	
Physical analysis	Specific surface area (m^2/g)	79.30	Pagnanelli et al. (2008)
	Bulk density (g/cm^3)	0.400	Haddad et al. (2012)

Table 2.7 Main physical and chemical properties of olive cake

Parameter		Value	Reference
Structural analysis	Cellulose	48.16* 55.63–57.17* 14.30 12.70	Quesada et al. (2018) Pérez et al. (2018) Neifar et al. (2013) Delgado-Moreno et al. (2017)
	Hemicellulose	– – 14.10 13.70	
	Lignin	43.96* 42.83–44.37* 31.00 22.20	
	Extractives (hot water)	39.35 34.28–43.50	Quesada et al. (2018) Pérez et al. (2018)
Proximate analysis (wt, %)	Equilibrium moisture	6.65 6.60 4.59–6.54 12.80 6.90	Martín-Lara et al. (2019) Quesada et al. (2018) Pérez et al. (2018) Neifar et al. (2013) AlShwawra and Al Asfar (2018)
	Fixed carbon	22.15 22.20 – – 17.10	
	Volatile compounds	60.83 60.80 – – 71.5	
	Ashes	10.37 10.40 – 7.00 4.50	

(continued)

Table 2.7 (continued)

Parameter		Value	Reference
Ultimate analysis (wt, %)	Carbon, C	44.80 44.00 44.00 53.90	Martín-Lara et al. (2019) Quesada et al. (2018) Pérez et al. (2018) AlShwawra and Al Asfar (2018)
	Nitrogen, N	0.43 1.07 1.70 1.40	
	Hydrogen, H	7.10 7.03 7.03 6.10	
	Sulfur, S	– – <0.10 0.1	
	Oxygen, O	37.30 47.20 47.20 38.50	
Physical analysis	Specific surface area (m^2/g)	1020	Baccar et al. (2009)
	Bulk density (g/cm^3)	0.600 0.551	AlShwawra and Al Asfar (2018) Baccar et al. (2009)
	Real density (g/cm^3)	1.260	

2.4.2 *Biosorption Tests*

The use of olive pomace and olive cake as biosorbent without any treatment or with a soft chemical treatment has been particularly studied in batch systems and for the removal of different heavy metals from aqueous solutions. Table 2.8 summarized the results found by various researchers. For example, Martín-Lara et al. (2008) found a copper biosorption capacity of raw olive pomace of 11.44 mg/g. However, Pagnanelli et al. (2003) reported a lower value between 1.33 and 4.26 in function of pH of solution for the same metal a similar waste. The main difference was that Martín-Lara et al. (2008) worked with olive pomace derived from the two-phase olive-mill process and Pagnanelli et al. (2003) with olive pomace resulting from the three-phase olive mill process. Pagnanelli et al. (2003) found higher values (until 15.75 mg/g) of biosorption capacity when lead was used as adsorbate in their experimental study. If olive pomace and olive cake are compared, in general, higher values of biosorption capacities were found for olive cake. For example, Al-Anber and Matouq (2008) reported cadmium biosorption capacities of 44.44, 60.61 and 65.36 mg/g in function of temperature. Also, Fernández-González et al. (2018)

Table 2.8 Main results of raw olive pomace and olive cake as biosorbent material of heavy metals in batch systems

Material	Heavy metal	Operational conditions			Maximum biosorption capacity (mg/g)	Reference
		pH	Time, min	Temperature, °C		
Olive pomace	Copper	5	90	room	11.44	Martín-Lara et al. (2008)
	Copper	5	90	room	12.08[a]	
	Cadmium	5	90	room	3.37	
	Cadmium	5	90	room	11.24[b]	
	Copper	3	60	room	1.33	Pagnanelli et al. (2003)
	Copper	4	60	room	2.48	
	Copper	5	60	room	4.26	
	Cadmium	3	60	room	1.91	
	Cadmium	4	60	room	4.05	
	Cadmium	5	60	room	6.97	
	Lead	3	60	room	4.14	
	Lead	4	60	room	12.02	
	Lead	5	60	room	15.75	
Olive cake	Lead	5.6	1440	20	21.56	Gharaibeh et al. (1998)
	Zinc	5.7	1440	20	5.40	
	Chromium VI	2	120	30	33.44	Dakiky et al. (2002)
	Cadmium	6	1440	28	65.36	Al-Anber and Matouq (2008)
	Cadmium	6	1440	35	60.61	
	Cadmium	6	1440	45	44.44	
	Copper	6	120	25	30.03	Fernández-González et al. (2018)
	Chromium III	5	120	25	22.19	
	Manganese	6	120	25	3.57	
	Nickel	6	120	25	5.85	
	Lead	5	120	25	41.54	
	Zinc	6	120	25	12.69	
	Cadmium	4.5	30	30	10.56	Doyurum and Çelik (2006)
	Lead	6	30	30	19.53	

[a]Chemically-modified by hydrogen peroxide; [b]Chemically-modified by phosphoric acid

published chromium and lead biosorption capacities of 22.19 and 41.54 mg/g, respectively working at similar experimental conditions of previous cited works based on olive pomace (Martín-Lara et al. 2008; Pagnanelli et al. 2003).

Some other works, explored the use of olive cake as precursor for the preparation of activated carbon. For example, Baçaoui et al. (2001) using response surface methodology to optimize preparation of activated carbons from olive cake. Principally, authors prepared different carbon materials by physical activation with steam and studied the adsorption behavior in terms of iodine and methylene blue adsorption capacities. Baccar et al. (2009) also investigated the preparation of activated carbons by chemical activation with phosphoric acid and a modification using potassium permanganate. The researchers evaluated adsorption properties by means of a complete characterization of obtained activated carbons and adsorption of copper ions.

2.5 Other Valorization Opportunities for Olive-Oil Waste

In addition to its use as sorbent of heavy metals, the studies conducted with olive tree pruning has dedicated mostly to the production of bioethanol (Manzanares et al. 2011) and more recently to the production of a variety of high added-value products such as natural antioxidants, oligosaccharides and energy (electricity or heat) all of them of great interest to the food and pharmaceutical industries (Aranda-Barradas et al. 2010; Cara et al. 2012; Spizzirri et al. 2011; Vegas et al. 2005). In this sense, several biorefinery structures have been proposed for olive tree pruning (Requejo et al. 2012; Romero-García et al. 2016).

With regards to olive stone, the main use is as fuel to produce energy (mainly heat). However, the olive stone is a rich source of valuable components in addition to its combustion to produce heat (Rodríguez et al. 2008). Other uses such as production of activated carbon (Ubago-Pérez et al. 2006; Yakout and Sharaf El-Deen 2016), incorporation in cosmetics (Rodrigues et al. 2015), extraction of bioactive peptides, production of furfural (Montané et al. 2001), feed for animals or reinforcing agent or filler in polymeric composites (Siracusa et al. 2001) have been explored. Especially, pretreatment with a steam followed by chemical fractionation was recently investigated to obtain phenols, sugars or lignin materials (Fernández-Bolaños et al. 1998, 2001; Heredia-Moreno et al. 1987).

The olive pomace is one of the by-products obtained in the process of obtaining olive oil about researchers are put great interest. A future trend is the development of a strategy of integral use, which includes the extraction of pomace oil, manufacture of pellets for gasification or sale for electric power production (La Cal 2019).

Particularly, after extraction of pomace oil, olive cake presents great possibilities of energy recovery, to produce either thermal energy or electrical energy or both at the same time; however, it also has a series of problems that it is necessary to know when designing, operating and maintaining biomass plants that use this waste as fuel.

For the design of storage, seasonality, moisture content (hygroscopic material), explosiveness and self-combustion must be taken into account; and for the design of the process the composition, especially the chlorine content (it comes from the chlorophyll processes that occur in any vegetable) and potassium (one of the plant's foods). Therefore, the manufacture of the pellets should be studied, because at present the cake is not usually used for heating due to its high content of ashes and chlorine, or its strong odor.

Another aspect to study will be the design of the equipment. The union of chlorine and potassium produces potassium chloride, a compound with great insulating capacity, which, when dragged by the fly ash, can be deposited in the tubular beams of the boiler superheaters with the consequent fouling and loss of efficiency. Therefore, equipment must be designed to prevent the accumulation of potassium chloride, and avoid temperatures above 700 °C, which is the melting temperature of potassium.

For all this, the possibility of using mixtures of olive cake with other biomass, coals, even plastics, in the process of co-pyrolysis and co-gasification is being investigated.

Composting processes are also being studied. The compost is used for organic amendments of the highest quality, improving the structure of the soil and avoiding loss of it by phenomena such as erosion.

The company Bioland Energy S.L. is working on the appreciation of the olive cake by obtaining compost on an industrial scale. To prepare this type of compost has been used as raw materials, pomace and clean sheet; and as activators of the nitrogen composting process from an inorganic fertilizer and a strain of stabilized and controlled microorganisms that help and improve the degradation of the lignocellulosic part of the olive cake.

In summary, these future trends are included in a comprehensive, rational and balanced use of all by-products, with the consequent benefits for the sector such as new revenue from the sale of new products (pellets, biocarbon, electric power, ...), value added to the sector (better image, carbon footprint reduction, ...), as well as contributing to improve the competitiveness of the olive sector and to establish population in rural areas.

Other numerous studies have focused on the extraction of phenolic compounds from olive pomace or olive cake (Alu'datt et al. 2010; Cioffi et al. 2010; Chanioti and Tzia 2018; Lafka et al. 2011).

2.6 Conclusions

In Spain and many countries where olive-oil is produced, the by-products and wastes generated are a serious problem. Some solutions have been proposed for these solids and schemes of valorization are mainly based on the olive-oil by-products and wastes are rich in cellulose, hemicellulose and lignin. Particularly, in this review, investigations about their use as sorbents of heavy metals have been revised. Results showed that, from a technical point of view, olive-oil waste presented good properties for heavy metal removal from aqueous solutions and they could be used in industrial wastewater remediation. However, more research is needed to a large-scale operation and competition with existing technologies. Also, disposal of exhausted sorbents is still need to be addressed.

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Chapter 3
Metal Oxide Composites for Heavy Metal Ions Removal

Safoura Daneshfozoun, Anum Tahir, Zaman Tahir, Awais Ali Aslam, Muhammad Shahid Nazir, and Mohd Azmuddin Abdullah

Abstract Contamination of heavy metals is a major concern nowadays due to various environmental problems and hazardous effects on human, living organisms and eco-system. It is therefore of paramount importance to devise strategies for heavy metal ions removal which are workable and economical before discharging the wastewater such as industrial wastewater into the environment. The use of magnetic solid adsorbents for removing the metal ions is practical as the sorbents can be recovered and recycled for continued use. In this review, issues in heavy metal ion remediation are briefly explained and the different types of magnetic sorbents are highlighted. The focus is on ferrite magnetic nano-composite sorbent which is eco-friendly with good remediation efficiency. Case studies based on oil palm fibers, cellulose and *Ceiba pentandra* are illustrated as examples of recently developed metal-oxide composite based on the agro-wastes.

Keywords Heavy metal remediation · Adsorbents · Metal composites · Multi-walled carbon nanotubes · Magnetic nanoparticles · Eco-friendly sorbents · Functionalized nanoparticles · Industrial waste water treatment · Agricultural wastes

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Abbreviations

BET	Brunauer-Emmett-Teller
CDC	Center of Design Control
CNTs	Carbon Nanotubes
CS	Chitosan
CS/PAA-MCM	Chitosan/poly(acrylic acid) magnetic composite microspheres
EFB	Empty Fruit Bunch
EBCT	Empty Bed Contact Time
EDTA	Ethylenediaminetetraacetic acid
FTIR	Fourier Transform Infrared Spectroscopy
Fe_2O_3@CEL	Magnetic nano-sorbent of Cellulose
Fe_2O_3@EFB	Magnetic nano sorbent of Oil Palm Empty Fruit Bunch
Fe_2O_3@RKF	Magnetic nano sorbent of Raw Kapok Fibre
Fe_3O_4-Ag-TCM	Magnetite-layered thiourea-chitosan
Fe_3O_4-GS	Magnetic graphene substance
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
MCM	Magnetic Composite Microspheres
MNP	Magnetic nanoparticle
MPCVD	Micro plasma chemical vapour deposition
Fe_3O_4–NH_2/PEI	Amine-polyethyleneimine magnetite nanoparticle
OPEFB	Oil Palm Empty Fruit Bunch
PAA	Polyacrylic acid
PEI	Polyethyleneimine
PMPT	Organodisulfide polymer
RSM	Response surface methodology
RKF	Raw Kapok Fibre
TBBPA	Tetrabromobisphenol-A
TEM	Transmission Electron Microscopy
TGA	Thermo gravimetric analyzer
VSM	Vibrating Sample Magnetometer
XRD	X-ray Diffraction

3.1 Introduction

Magnetic nanomaterials have vast potentials, attributable to their characteristics, which are valuable for many applications. These materials are less than 1μm and can be controlled by an external magnetic field (Buzea et al. 2007). Magnetic materials can behave like super magnet (Karimi et al. 2013), but will lose their magnetic properties when the external magnetic field is eliminated. This has the benefit to develop tunable magnetic properties for the nanoparticles (Kolhatkar et al. 2013). Super paramagnetic nanoparticles, having modified shell and different surfaces, are synthesized from different advanced techniques (Horak et al. 2007; Reddy et al. 2012; Teja and Koh 2009; Xu and Sun 2013). Magnetic components which include cobalt, iron, nickel oxides, magnetite (Fe_3O_4), maghemite, cobalt ferrite and nickel ferrite have been used to synthesize magnetic nanoparticles (Indira & Lakshmi, 2009). Other components may include the coating with gold, platinum, aluminum, cobalt oxide, silica and activated carbon or organic layers such as polyethylene or surfactants and dextran (Karimi et al. 2013; Lu et al. 2007; Reddy et al. 2012). The aim is to stabilize against corrosion, spontaneous accumulation and oxidation, and to impart a functionalized surface and increase the physico-chemical stability.

Magnetic nano-composites posses superior characteristics for applications as coating, gas sensors, pigments, catalytic material in various data storage, imaging, and drug delivery systems (Jun et al. 2008; Shylesh et al. 2010; Xu et al. 2012; Xu and Sun 2013; Hasany et al. 2013). The chemically and physically improved magnetic nano-composites are applicable to solve ecological and environmental issues with higher efficiency and at lower cost (Ali 2012; Xu et al. 2012; Tang and Lo 2013; Saiz et al. 2014). Chemical stability, high surface tension and functionalization of properties facilitate in situ environmental remediation where the separation and recovery from complex multiphase system is made possible with the super paramagnetic character of the magnetic nanoparticles (Badruddoza et al. 2013). The sorption process of the magnetic nano-composites involves adsorption, magnetic recovery of adsorbent, and desorption of saturated adsorbent and the recovery of spent solution in which both can be controlled. The adsorbent recovery and material usability have their economic benefits. For effective utilization of the magnetic nano-composites, appropriate remediation mechanisms and the control of solid and liquid waste must be considered, together with the regeneration of the nano-materials for their eventual continued use for remediation work.

In this review, the issues of magnetic nano-composite application and the different types of magnetic biosorbent for environmental remediation are discussed. Case studies based on raw oil palm fibres, *Ceiba pentandra* and cellulose for remediation of heavy metal ions are highlighted.

3.2 Issues in Environmental Remediation

Magnetic nano-composites as nano-sorbents have been applied to remove heavy metals and dyes from water. The characteristics are comparable to conventional adsorbent with high active surface area, less particle diffusion, and high adsorption capacities. This makes their application in treating water favorable, with reduced cost and decreased water contamination (Nassar 2010; Tan et al. 2012). The current development in synthetic techniques could add many characteristic groups on the sorbent surface such as specific sites for adsorption. Refined metal nanoparticles and their alloy could act as very fine adsorbent. However, there are also many disadvantages such as the short-lasting performance and the lesser stability in the suspension medium. Particulate contamination removal can be improved by increasing the selectivity and the adsorption capacity and recovery by magnetic separators in

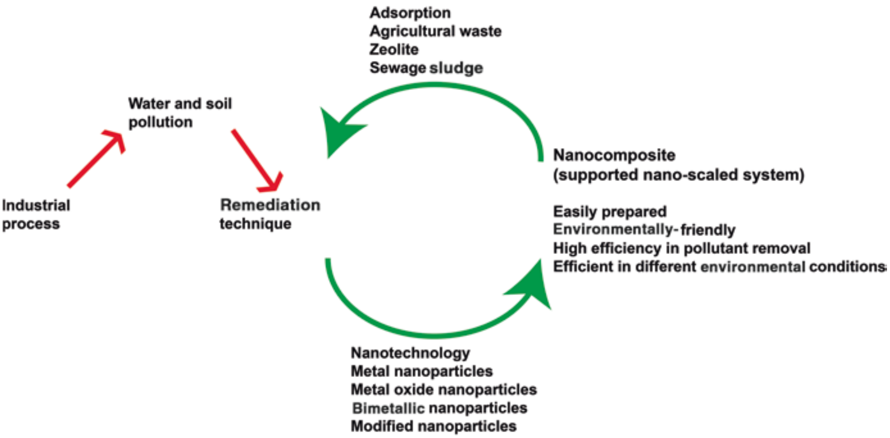

Fig. 3.1 Nanocomposites for remediation of water. Industrial pollution released into water and soil systems can be removed by different remediation techniques based on nanotechnology (Modified from Trujillo-Reyes et al. 2014)

the adsorption column. Functionalized and coated nanoparticles with inorganic and organic material are also effective (Fig. 3.1). These could prevent oxidation, corrosion, and spontaneous aggregation. Adsorption capacity could be increased by outer coating to remove specific pollutants with high surface functionalization. To control the magnetic properties, it is important to manipulate the ratio between the non-magnetic and magnetic components. Natural and organic material such as biopolymers which include chitosan, cyclodextrin, cellulose, kondagogue gum, Arabic gum, alginate and orange peel act as excellent additive material because of the different functional groups, which are highly selective and has high capacity for heavy metal ions and dyes (Gómez-Pastora et al. 2014).

3.3 Different Types of Magnetic Sorbents

3.3.1 Iron Oxide Modified Nanoparticle

Table 3.1 shows different types of magnetic sorbents for metal ion remediation. There are many ways to prepare the magnetic nanoparticles (Shen et al. 2009). Fe_2O_3 can be prepared with two separate methods: 1) coprecipitation process 2) Polyol process. The standard size 6 nm is used for the coprecipitaion process and 18 nm for the polyol process. Prepared Fe_2O_3 nanoparticle surface was modified with the layer of biocompatible polymer, hydrophilic layer and modified magnetic nanoparticles. These are then used for the purification of water. The adsorption capacity is influenced by particle size and can be enhanced by reducing the size or, enhancing surface area or by controlling the wastewater pH.

Table 3.1 Different magnetic sorbents for metal ion remediation

Adsorbent	Metal ions	Parameters	Removal (%)	Refs
Maghemite NTs (nanotubes)	Zinc Lead Copper	[Metal ions] = 100 mgL^{-1} pH = 6 T = 25 °C [Adsorbents] = 0.5gL^{-1}	95	Roy and Bhattacharya (2012)
Fe_3O_4	Chromium Nickel Copper	T = 20° [Metal ions] = 41.87–47.44 mgL^{-1} pH = 6 [Adsorbents] = 25 gL^{-1}	97.6 88.5 98	Shen et al. (2009)
Mixture of Fe_2O_3-Fe_3O_4	Chromium Lead	[Metal ions] = 2 mgL^{-1} pH = 7 Temperature = 25 °C [Adsorbents] = 0.4 gL^{-1}	>96	Ahmed et al. (2013)
Fe_3O_4@ chitosan	Lead Copper	[Metal ions] = 10 mgL^{-1} pH = 4 [Adsorbents] = 0.3 gL^{-1}	94.8 89.1	Liu et al. (2008a, b)
Fe_3O_4@ Carboxymethyl-bcyclodextrin	Lead Nickel Copper	[Metal ions] = 300 mgL^{-1} pH = 5.5 [Adsorbent] = 2.4 gL^{-1} T = 25 °C	99.9 29.6 63.4	Badruddoza et al. (2010)
Fe_3O_4@ $C_{187}H_{186}O_{89}N_9S_1$ (acid)	Copper Lead	[Metal ions] = 0.1 mgL^{-1} pH = 6 T = 20 °C [Adsorbents] = 0.1gL^{-1}	>90	Liu et al., (2008a, b)
Amine modified magnetite	Lead	[Metal ions] = 26.8–49.7 mgL^{-1} [Adsorbents] = 0.1 gL^{-1}	16.55	Tang et al. (2013)
Magnetite@SiO_2-mono,di,tri amine	Copper Lead	[Metal ions] = 10 mgL^{-1} T = 20 °C pH = 5.7–5.75 [Adsorbents] = 0.667 gL^{-1}	7–36 34–37	Chung et al. (2012)
Magnetite-SH-mSi (thiol-functionalized mesoporous silica)	Lead	[Metal ions] = 1–5 mgL^{-1} T = room temperature pH = 7.8–8.1 [Adsorbents] = 0.002–0.5 g/L	97	Li et al. (2011)
Magnetite@Gs	Chromium	[Metal ions] = 12.82 mgL^{-1} pH = 8 T = 30 °C Capacity = 17.29 mg g^{-1}	–	Guo et al. (2014)
Iron nanoscaled zero valency (nZVI)	Lead	[Metals ions] = 100 μgmL^{-1} T = room temperature [Adsorbents] = 1.86 $mgmL^{-1}$	> 80	Huang et al. (2013)

(continued)

Table 3.1 (continued)

Adsorbent	Metal ions	Parameters	Removal (%)	Refs
$SiO_2/Fe_3O_4/$ chitosan EDTA-modified	Lead Copper	Metal ions = 0.6 mM Temperature = 25° [Adsorbents] = 1 g/L pH = 5	> 90	Ren et al. (2013)
Hevea brasiliensis	Cadmium Sodium	pH = 6 T = 10.0–20.0 °C	> 80	Sebastian et al. (2019)
Magnetic chitin hydrogels	Copper	pH = 6	> 80	Liao and Huang (2019)
MeCM (mesoporous composite material)	Copper	pH = 7	> 90	Awual et al. (2019)

The Flame spray pyrolysis technique is used to prepare the superparamagnetic maghemite nanoparticles to eliminate the Cu^{2+} and Pb^{2+} from wastewater. The pH-dependency of adsorbent from the batch adsorption process suggests that electrostatic attraction is involved in taking up the metal ions (Shi et al. 2017). Porous Fe_2O_3 microcubes derived from metal organic frameworks have demonstrated outstanding adsorption capacity for the organic contaminants like methyl blue and humic acid and also for the heavy metal ions. Adsorption isotherm analysis with the microscopic study of prepared nano-adsorbent reveals ion exchange, electrostatic attraction and chemical mechanism involved in the adsorption of chromium and lead (Li et al. 2018). Many green processes make use of coprecipitation in nitrogen, glycine-nitrate, air, and citrate-nitrate atmosphere. Microwave-assisted citrate methods are used to prepare the mixed magnetite-hematite nanoparticles (Ahmed et al. 2013) with good adsorption achieved at pH 7 for the metal ion removal.

Modification and functionalization of the magnetic nano-composites should ensure that the adsorption efficiency and standard of the product must be maintained (Ge et al. 2011). Fe_3O_4 magnetic nanoparticles have been modified with acrylic acid copolymer, crotonic acid and 3-aminopropyltriethoxysilane and the sorption efficiency of maghamite@Ammonium persulfate for remediation of metals have been examined. While studying the pH, concentration, time and the effect of the background electrolytes, it is found that the adsorption capacity is decreased with an increase in the coexisting ion. An inverse spinel nanostructure of Fe_2O_3 functionalized magnetic nanoparticles has been attained with amine (ethylenediamine), carboxyl (succinic acid) and thiol to eliminate lead, cadmium, chromium, cobalt, nickel, arsenic and copper ions from wastewater. At pH 8, about 100% of all the ions are removed, excluding As^{3+}. The adsorption is very fast, attributable to the high reactive sites and the specific surface area. The nano-adsorbents can be recovered with the acidic treatment (Singh et al. 2011).

Other functionalized-amine magnetic iron oxide nanoparticles show rapid heavy metals adsorption processes depending on various conditions like complexation of amino surface and pH. The result of adsorption and desorption processes exhibit the strongest affinity in the order of lead, copper, zinc, cadmium, and nickel (Lin et al. 2017). Fe_2O_3 magnetic sulfonated nanoparticle adsorbent for cadmium and lead ions elimination in sludge has resulted in highest adsorption capacity of 80.9 and 108.93 mgg^{-1} for Pb^{2+} and Cd^2, at 25 °C, respectively (Chen et al. 2017). Magnetic solid–liquid extraction of Co^{2+}, Eu^{3+}, Ni^{2+} and La^{3+} has been carried out using maghemite nanoparticles. Sorbent with greater surface area (170 m^2g^{-1}), having more active sites, shows very fast adsorption and a maximum adsorption of about 0.5 mmol g^{-1} which fits well to the Langmuir model (Ngomsik et al. 2011). Magnetite functionalized nanoparticles with L-cysteine is also utilized for lead and chromium removal where maximum Cr^{6+} and Pb^{2+} removal take place at pH 2 and 6, respectively, with Langmuir adsorption capacities of 18.8 mgg^{-1} (Pb^{2+}) and 34.5mgg^{-1} (Cr^{6+}) at 45°C are reported (Bagbi et al. 2017). Co-precipitation technique is used to prepare the magnetic Fe_2O_3, and later modified with acryloyl chloride and triethoxysilane. For the elimination of heavy metal, the semispherical crystalline nanoparticles having mean size of 10 nm are used, resulting in high adsorption potential at lesser concentration, and the adsorbent is reproducible (Mahdavian and Mirrahimi 2010).

In the utilization of the magnetic nano-composites on metal ion adsorption, two important aspects are considered: 1) reusability of the nano-adsorbent; 2) cost of the process (Zhang et al. 2011). Immobilized ethylenediaminetetraacetic acid on amine-terminated Fe_2O_3 surface could act as a sorbent for heavy metals. Both Fe_3O_4-H_2/PEI-EDTA and Fe_3O_4-NH_2 magnetic nanoparticles having a mean size of 60 nm and great crystallinity can be used where the modified sorbent achieves 98.8% removal of Pb^{2+}, better than the unmodified one. The acid treatment technique exhibits the reusability potential of the sorbent material. Other application to decrease the cost for the industrial use is to treat the waste by recycling, and to regain $CuFe_2O_4$ from industrial waste using chemical exchange, ferrite process and acid leaching (Tu et al. 2012). This is used as adsorbent to eliminate cadmium from wastewater and water where the removal ability is enhanced from 88 to 99% from pH 2 to 6. The Langmuir isotherm and pseudo second order kinetics give better adsorption of Cd^{2+} whereas the thermodynamics analyses suggest spontaneous and endothermic adsorption process (Tu et al. 2012).

3.3.2 Zeolite

Zeolite could adsorb metals in raw, magnetic composite and modified form. The zeolite NaA prepared by hydrothermal method and later mixed with the Fe_3O_4 nanoparticles to form magnetic zeolite NaA, has been utilized in the removal of lead (II) and copper(II) from wastewater. The NaA loaded with Fe_3O_4 makes a good adsorbent having good stability and affinity. Although the loading has a lesser influence on the adsorbing rate, the efficiency of the sorbent material is 95% (Liu et al. 2013).

3.3.3 Silica

Silica-based nano-adsorbent as magnetic mesoporous silica functionalized by thiol prepared by the Stober method is efficient for the remediation of heavy metal ion (Li et al. 2011). It has been used to eliminate mercury (II) and lead (II) in water reservoir like lake, river, ground, and tap water. The materials are as stable in diverse aqueous solutions as in alkaline and acidic mixture. The maximum capacity of adsorption is at 260 and 91.5 mgg^{-1} for mercury and lead, respectively, and the intraparticle diffusion model has been proposed as the mechanism controlling the adsorption. Porous magnetic silica sphere having 400 nm diameter prepared by classical Stober technique in combination with hydrothermal treatments has been used to separate Ni(II) from aqueous mixture (Caparrós et al. 2012). The narrow size and homogeneous porous magnetic silica sphere synthesized by the calcination after the hydrothermal treatment exhibits a 15% increment in the sorption capacity, in comparison to similar material without any calcination after the hydrothermal treatment (Caparrós et al. 2012). The influence of steric elements on the ability to remove copper and lead by nano-magnetite with amine mesoporous grafting silica sorbents has been reported (Chung et al. 2012). The sorption rates and adsorption capacity are not linearly proportional to the quantity of amine group attached to a ligand. With greater pore size of the sorbent, functional groups like nano-magnetite and amines can be filled within the pores, but the removal ability is decreased with increasing loading molecules (Chung et al. 2012).

The monodispersed maghamite@silica core-shell has the capability in adsorbing lead and mercury ion in water (Hu et al. 2010). The contact time and pH show effect on adsorption capability and rate of adsorption process. Increased pH value enhances the adsorption capability as a result of polynuclear molecule formation with heavy metal ions in an aqueous medium. Another study with Fe_3O_4 microsphere has resulted in lesser efficiency than the $Fe_3O_4@SiO_2$. (Fig. 3.2) suggesting that the presence of silica on the Fe_3O_4 microsphere has improved the performance of the sorbent. With ultra-sonication, the sorption can be performed in a weakly acidic mixture with a reversible interaction between the heavy metals and silica group. Furthermore, the $Fe_3O_4@SiO_2$ microspheres can be recycled (Kharissova et al. 2015). Superparamagnetic nanoparticles in a silica matrix are used as magnetic carriers and seed particles with iron hydroxide to remove metal ions from the solution (Mandel et al. 2013). When superparamagnetic particles are present, a few amounts of Fe salt is added in heavy metal solution containing lead. The 4 to 8.95% increase in pH leads to the elimination occurring within 1–5 min, suggesting a good sorption.

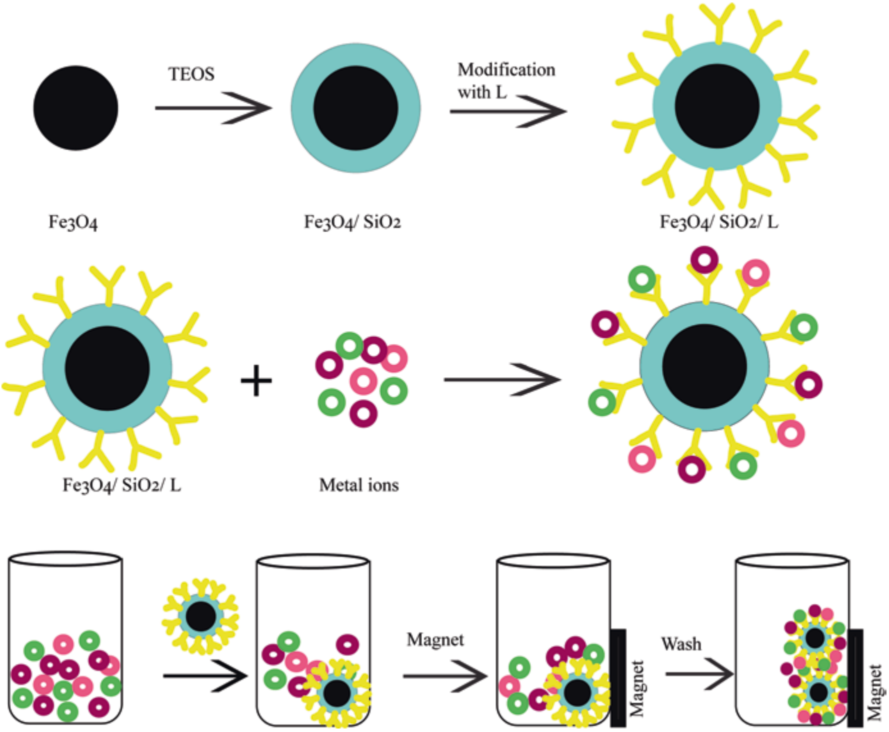

Fig. 3.2 Individual magnetic nano-composites stabilized and modified. Magnetite and Tetraethyl orthosilicate (TEOS) form Fe_3O_4 /SiO_2, which are modified with L to the new form, Fe_3O_4 /SiO_2/L, the metal ions are then sorbed, and the magnet is connected and later washed (Modified from Kharissova et al. 2015)

3.3.4 Polymer Functionalization

Fe_3O_4-NH_2 has been prepared by solvothermal method to synthesize maghemite-amine/PEI nanospheres (Zhang et al. 2011). The EDTA-functionalized magnetic iron oxide nanoparticles are later prepared to adsorb Pb^{2+} from the solution. The 60 nm diameter maghemite-amine/PEI-EDTA and maghemite-amine is characterized by the TEM image, and the adsorption of 98.8% Pb(II) is achieved at pH 5 (Zhang et al. 2011). The organodisulfide polymer (PTMT) is used for iron oxide modification of magnetic nanoparticles and the synthesized maghemite@PTMT magnetic microspheres composite is utilized for remediating metals ions from sludge. The MNP-PTMT demonstrates excellent ability for heavy metal adsorption even though the wastewater itself has the existing salts and inorganic contents. Both the maghemite and magnetite have more adsorption than the Fe-free metal sorbent (Huang et al. 2018). Fig. 3.3 shows that Iron and its oxide/poly-L-cysteine composites could remove metal ions or pollutants via mechanisms such as adsorption, reduction and co-precipitation.

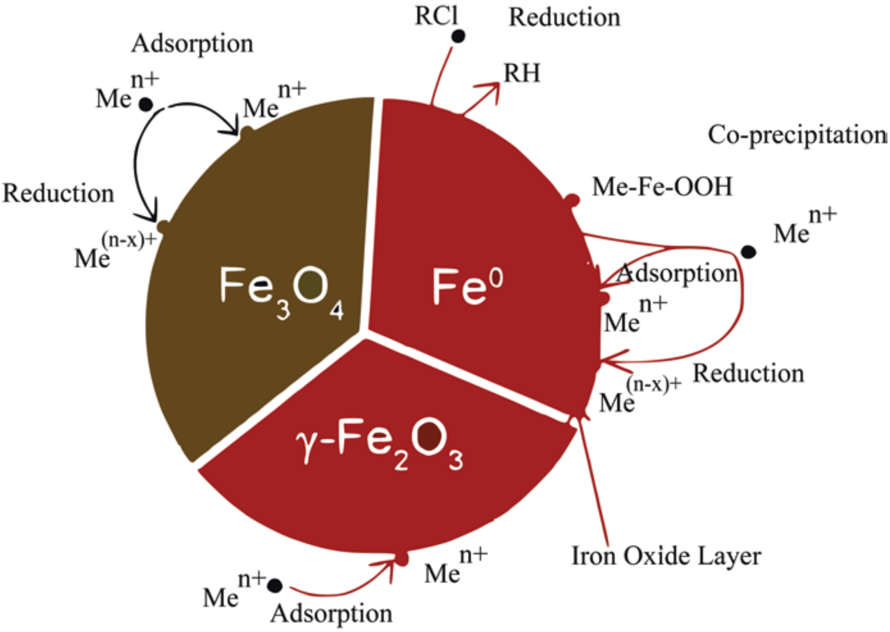

Fig. 3.3 Magnetic nano-composites on the micro-particles for metal ion/pollutant removal. Iron and its oxide/poly-L-cysteine composites in the form of magnetite and gamma magnetite remove or chelate metal ions and pollutants via different mechanisms (Modified from White et al. 2009; Namdeo 2017)

3.3.5 Chitosan and Alginate

Magnetic composite microsphere based on maghemite and polyacrylic acid have been developed with chitosan (CS/PAA-MCM) synthesized from precipitation process to remove Cu^{2+} from solution. Good adsorption capability of CS/PAA-MCM has been shown as compared to the CS-MCM, having maximum adsorption capacity of 108.0 and 63.0 mgg^{-1}, respectively. The attached PAA is vital for the sorption of the copper ion and the sorbent regeneration is achieved at a lower pH where the sorbent can be reused without any losses (Yan et al. 2012). The magnetite layered thiourea-chitosan (Fe_3O_4-Ag-TCM) has been synthesized to remove Ag^+ ion from water. In this method, the imprinted silver ions are used for the adsorption of silver. At pH 5, the maximum capacity is 4.93 $mmolg^{-1}$. The temperature of 30 °C is maintained for 50 minutes and the isotherm and kinetics study suggest a pseudo-second order sorption kinetics. However, the non-imprinted thiourea chitosan works better than the Ag(I) but the new sorbent has better reusability and stability with very quick recovery (Fan et al. 2011).

Magnetic maghemite/chitosan nanoparticles are more effective as metal ion sorbent when used in the continuous mode. The packed bed of magnetite/CS nanoparticles reach theoretical production value of 3.43 Kgh^{-1} having adsorption capacity of 36.42 mgg^{-1} and 79.24 mgg^{-1} for cadmium and lead, respectively, with faster and better sorption rates than the pure Fe_3O_4 sorbent (Fan et al. 2017). The surface graft copolymerization method has been carried out to prepare magnetic chitosan carboxylate rich multifunctional flocculants which is used for metal ion and cationic dye malachite green (MG) remediation from water. Optimal rate of 98.3% and 87.4% of nickel and MG flocculation, respectively, are achieved in rapid kinetic process (<60 min) and wide pH range (4.0–8.0 for Nickel (II), and 5–10 for magnetite) (Liu et al. 2018). Excellent sorbent material based on magnetic sodium alginate gel beads have been synthesized for removing Pb(II) ions in continuous system. The magnetic sodium alginate gel beads are proven to be very stable and sensitive magnetic material with good lead sorption capability of 333.33 mgg^{-1} which is fitted well to the Langmuir isotherm (Li et al. 2013).

3.3.6 Activated Carbon

The magnetic corn cob on activated carbon (MCCAC) is synthesized as adsorbent for chromium (VI) elimination from aqueous solution. The iron oxide nanoparticles of 50 nm size with saturation magnetization of 48.43 $emug^{-1}$ has resulted in effective adsorbents at pH 2 with a capacity of 57.37 mgg^{-1}. Sorption follows the pseudo-second order kinetics and Freundlich isotherm by external mass transfer and chemisorption process which is the rate-determining step (Nethaji et al. 2013). A facile co-precipitation method has been carried out to synthesize magnetic activated carbon particles (MACP) used for Cu(II) remediation in solution. The magnetic nanoparticles increase adsorption capability and regeneration ability of the activated carbon adsorbent (Gu et al. 2019).

3.3.7 Carbon Nanotubes (CNTs) and Graphene

The functionalized-thiol multi-walled CNTs/magnetite nano-sorbents have been applied to remediate Pb(II) and Hg(II) ions (Zhang et al. 2012). The 3-mercaptopropyltriethoxysilane transplantation on the surface of the CNT/magnetite is completely achieved where the functionalized thiol CNTs/Fe_3O_4 exhibits the super paramagnetic property. It has a greater surface area than the carbon nanotubes/magnetite nano-adsorbent. Higher pH affects removal efficiency and the sorption capacity of 65.4 and 65.52 mgg^{-1} for lead and mercury, respectively, is achieved, following the Langmuir model (Zhang et al. 2012). The CNTs/$CoFe_2O_4$, a magnetic hybrid coated on the multi-walled CNTs, and an amino-modified magnetic $CoFe_2O_4$ nanoparticles, and chitosan-modified composites have been prepared by polyol one-pot method. These functionalized chitosan multiwall carbon nanotubes/$CoFe_2O_4$-NH_2 sorbent is used for the remediation of tetrabromobisphenol-A

(TBBPA). The chitosan-modified composites exhibit better adsorption capacity with 140.1 mg/g and 42.48 mgg^{-1} for lead and TBBPA, respectively, than the non-modified bio sorbent. The pH at 6.3 is optimal for TBBPA removal, and pH 6 for lead. The chemisorption process is best described by pseudo-second order kinetics (Zhou et al. 2013).

Graphene has many applications in water purification. Three-dimensional graphene oxide/maghemite nano-sorbent has been fabricated via combining co-precipitation and micro-plasma chemical vapor deposition (MPCVD) technique for Cr(VI) removal. The chemical and morphological characterization suggest an adsorbent having layered graphene oxide sheets which are aligned and enclosed by 7 nm of magnetite nanoparticles, with 574.2 m^2g^{-1} surface area and greater saturation magnetization of 40.2 $emug^{-1}$. The sorption rates are high at 20 min achieving the maximum capacity at pH 2 of 258.6 mgg^{-1}. The sorbent is considered efficient for Cr(II) and Cr(VI) removal. Sorption process could be explained by ion exchange mechanism and Freundlich model (Lei et al. 2014).

Reduced-$CoFe_2O_4$ has been used to prepare graphene oxide as sorbent for mercury and lead removal from solution. The sorption capacity at pH 5.3 and 25 °C is 299.4 mgg^{-1} for lead(II), and pH 4.6 and 25 °C at 157.9 mgg^{-1} for mercury, both at the adsorbent time of 80 min. Pseudo-second order kinetics and Langmuir isotherm models appropriately describe the sorption mechanism (Zhou et al. 2013). The magnetic graphene oxide/chitosan has been utilized as Pb(II) sorbent where increase in surface area is due to the grafting by graphene oxide sheets. The sorption capacity of lead at pH 5 is 76.94 mgg^{-1} with the removal efficiency of 90.3% and the equilibrium time of 8 min (Fan et al. 2013). The magnetic graphene sheet (Fe_3O_4-GS) has been synthesized by Ferro ferric oxide and graphene sheets and the unique adsorbent is utilized in the elimination of cadmium, mercury, lead, chromium, and nickel from the media (Guo et al. 2014). The maximum adsorption of 23.03, 22.07, 27.95 and 27.83 at pH 6 to 7 for cadmium, nickel, lead, and mercury, respectively; and chromium of 17.29 mg g^{-1} at pH 1–3.5, are achieved at equilibrium time of 200 min. The Freundlich model and pseudo-second order kinetics are well fixed to the data. Metal ions sorption is attributable to the ion exchange or chelation mechanism, and it is thermodynamically spontaneous with endothermic adsorption process.

3.3.8 Agricultural Wastes

Low cost sorbents can be prepared by functionalization or modification of waste material. For example, the orange peel powder as farmed wastes and magnetite nanoparticles have been prepared as sorbent by precipitation technique for remediating cadmium from the solution (Gupta and Nayak 2012). Sorption process of orange peel powder, magnetic nano-composite, and orange peel powder-magnetic nano-composite have been optimized based on different parameters such as contact time, ionic strength, pH, temperature and adsorbent concentration. The physio-chemical characterization of the orange peel powder-magnetic nano-composite suggests the covalent binding of the carboxyl group of orange peel powder with the hydroxyl group of magnetic nano-composite which has contributed towards an active kinetics of cadmium removal, higher than the orange peel powder and magnetic nano-composite, separately. The kinetic data and the sorption processes are best described by pseudo-second order kinetics and Langmuir model. Industrial sludge is made free from the cadmium up to 82% and the sorbent can be reused. The orange peel powder–magnetic nano-composite has been suggested as an excellent sorbent having characteristics such as recovery and reusability, eco-friendly, economical and easily synthesized.

3.4 Case Studies

Magnetic nano-composites exhibit more affinity towards pollutants (both organic and inorganic) than any other conventional adsorbents, with higher adsorption kinetics but low adsorbent doses. In combination with advanced environmental technologies and surface modifications with specific functional groups, the utilization of magnetic nano-composites can be rationally designed and applied to attain high removal and sorbent recovery efficiency to remove a wide-range of pollutants. Magnetic nano-composites when tailored or coated with specific materials have exhibited high chemical and geometrical arrangements which can enhance the heavy metals and dyes removal efficiencies from the effluent streams. Agro-based magnetic biosorbents (ABMS) have been synthesized through a novel and economic route using the unprocessed oil palm empty fruit bunches (EFB), *Ceiba pentandra* (Raw kapok fibers) and cellulose obtained from the empty fruits bunches. These could be characterized to actively remove cationic ions in the liquid streams. Homogenous dispersion of synthesized sorbents have been exhibited where the Agro-based magnetic biosorbent based on raw kapok fibers achieves 99.4% Pb(II) removal with 49 mg g^{-1} maximum sorption capacity, as compared to 98.2% and 97.7%, respectively, for cellulose and empty fruits bunches. The removal efficiencies of agro-based magnetic biosorbents in general are 10% higher than the raw sorbents (Daneshfozoun et al. 2017). Fig. 3.4 shows the synthesized empty fruit bunch (EFB) ferrite magnetic nano-composite (Fe2O3@EFB).

3.4.1 Characterization

The X-ray Photoelectron Spectroscopy spectral areas of Fe C1s, O1s and 2p determined (Fig. 3.5) show the iron peak attributable to oxides of iron, most probably the Fe^{3+} – type species. The binding energies at around 710.0 and 711.2 eV are assigned to Fe^{3+} in the structure, around 530.0 eV to the O peaks for the transition metal oxides, and the energy centered at about 534.1 eV is assigned to O species

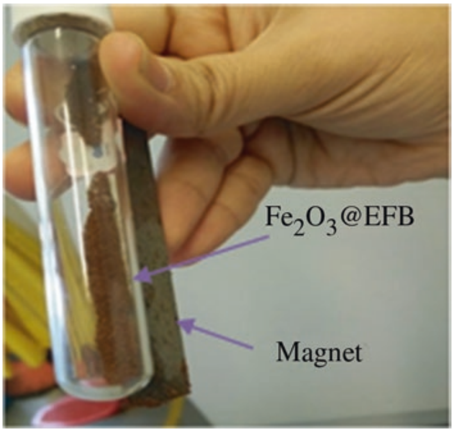

Fig. 3.4 Synthesized empty fruit bunch (EFB) ferrite magnetic nano composite (Fe_2O_3@EFB). The lab synthesized modified magnetite sample shows affinity for metal ions

in –$OHFe^{3+}$ structure. The X-ray Diffraction (XRD) diffractograms of the synthesized Agro-based magnetic biosorbents (Fig. 3.6) exhibit distinctive peaks at 2θ = 30.1°, 57.0°, 35.5°, 62.6° and 43.1° corresponding to (2 2 0), (5 1 1), (3 1 1), (4 4 0), (5 1 1) and (4 0 0) lattice parameters corresponding well to the Iron oxide nanoparticle database (PCPDFWIN v.2.02, PDF No. 85–1436). The similar diffraction points also indicate that compositions of the different biomass particles do not lead to change of phase of the magnetite nanoparticles.

3.4.2 *Factors Affecting Sorption Processes*

Figure 3.7 shows the schematic flow diagram of a magnetic biosorbent batch adsorption. The micro-sized sorbents and magnetic bio-sorbents at the sizes of 0.005–0.02 mm exhibit superior sorption efficiency as compared to the sizes of 1–2 cm and 0.2–1 mm tested. This proves that adsorptive capability of a sorbent can be improved by reducing the particle size as a result of an increase in active area (Hou et al. 2020). The adsorption capacity is further affected by the contact time for higher Pb^{2+}, Ni^{2+}, Mn^{2+}, $Cu^{2+}$and Zn^{2+} removal efficiency. At ppm 500 initial concentration, room temperature and pH 5.5, 1 gL^{-1} of Fe_2O_3@EFB adsorbs higher concentration of Pb(II) than the raw empty fruit bunch and the Pb^{2+} and Cu^{2+} sorption at 33–48 mgg^{-1} is greater than 20–34 mgg^{-1} for Zn^{2+}, Ni^{2+} and Mn^{2+}. The OH^- functional groups adsorb higher Pb(II) ions attributable to its large atomic radii and lower atomic weight but the same trend is not observed in the sorption behavior of Mn(II) which has higher atomic radii and smaller atomic weight. The higher removal efficiency of around 97–99% for Fe_2O_3@RKF and Fe_2O_3@CEL, in a lesser time period (Fig. 3.8a) too prove the importance of the availability of sorption sites with functional groups such as OH^- and esters for high affinity towards metal ions, but the lower sorption of Fe_2O_3@EFB could be due to steric hindrance. Hence, different factors could influence the sorption behavior such as the differences in ionic radius,

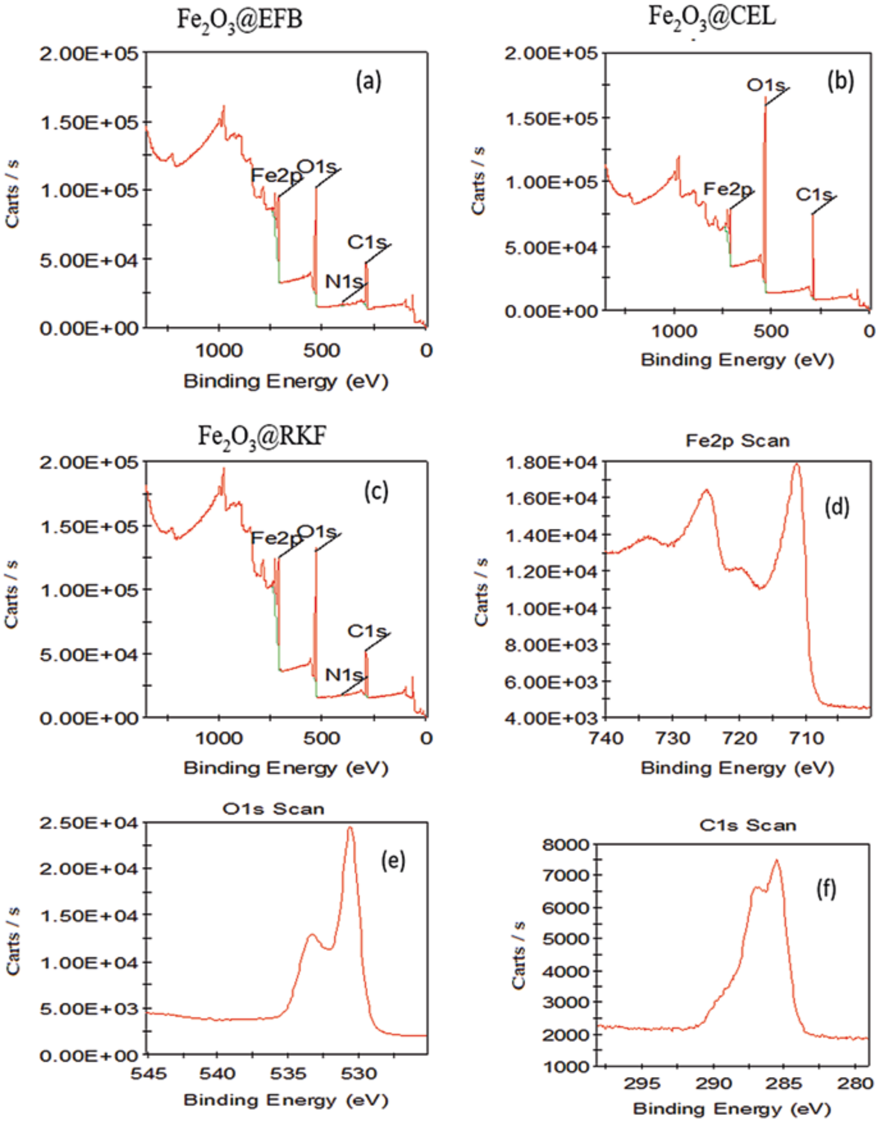

Fig. 3.5 XPS Spectrum of (**a**) Fe_2O_3@EFB, (**b**) Fe_2O_3@cellulose (**c**) Fe_2O_3@RKF; and the high-resolution scan of (**d**) Fe 2p, (**e**) O 1 s, (f) C 1 s. These XPS show binding energy for different modified magnetite

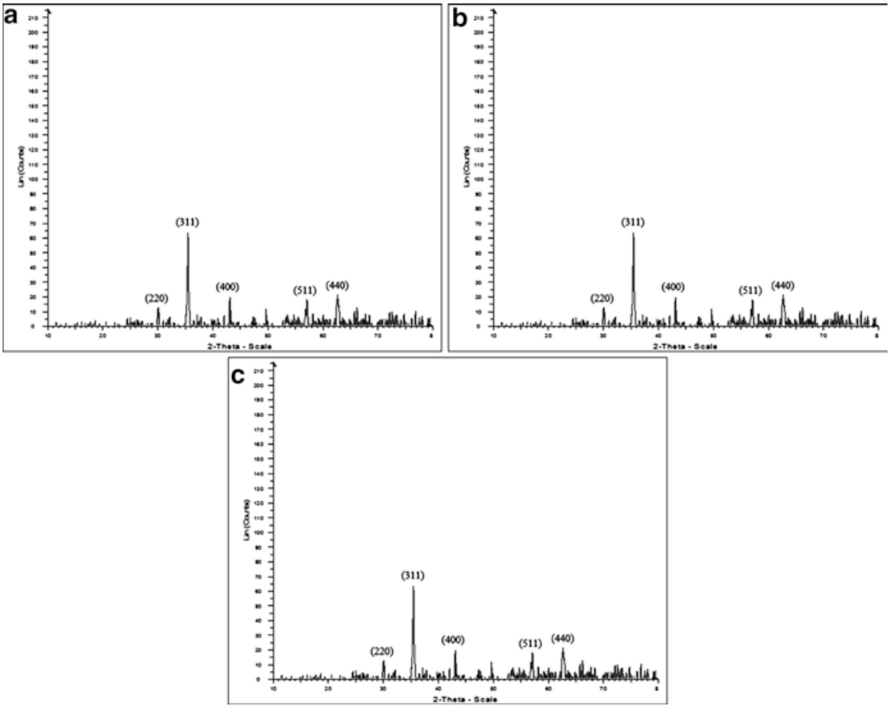

Fig. 3.6 XRD diffractogram of (**a**) Fe_2O_3@EFB (Daneshfozoun et al. 2017), (**b**) Fe_2O_3@CEL, (**c**) Fe_2O_3@RKF The results show distinctive peak at 2θ = 30.1°,57.0°, 35.5°,62.6° and 43.1° corresponding to (2 2 0), (5 1 1),(3 1 1), (4 4 0), (5 1 1) and (4 0 0) lattice properties. These are linked to the oxide of iron nanoparticles (PCPDFWIN v.2.02, PDF No. 85–1436). Point indicating deflection constituents in mass does not cause change in Fe_2O_3 nanoparticles. Similarly indicated are the XRD for Raw Kapok Fibers and cellulose composite

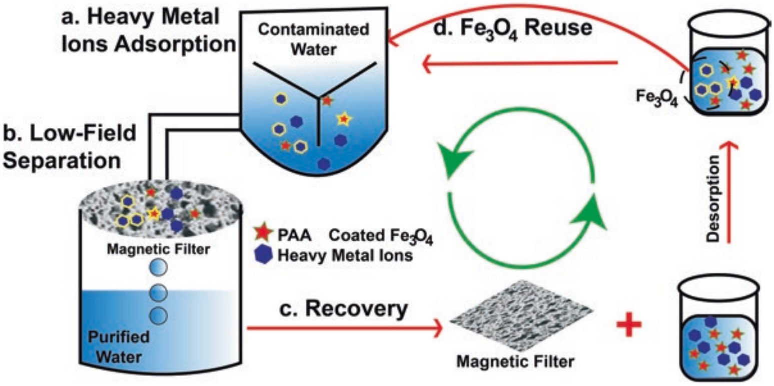

Fig. 3.7 Schematic flow diagram of a magnetic biosorbent batch adsorption which shows the separation of impurities from the contaminated water by magnetite and also the desorption of the impurities by magnetic filter, based on a soft magnetic material (Ni, Zn)Fe_2O_4) and poly(acrylic acid) (PAA)-coated quasi-superparamagnetic Fe_3O_4 nanoparticles (Modified from Wei et al. 2017)

atomic weight, the forces among the metal ions, the sorbent materials and the surface area available as sorption sites before attaining equilibrium (Daneshfozoun et al. 2017).

For the effects of pH in the range of 3–10, the Fe_2O_3@EFB sorbent performs optimally for all metal ion sorption at pH 5–7. Maximum sorption capacity for Pb^{2+}, Zn^{2+} and Ni^{2+} is at pH 7 at 48.4, 43.5 and 31.8 mgg^{-1}, respectively. For Mn^{2+} and Cu^{2+} at pH 6 at 39.9 and 45.6 mgg^{-1}, respectively. The Fe_2O_3@RKF shows wider optimal range at 4–7 for Pb^{2+} with capacity of 49 mg g^{-1} and 98% efficiency at pH 4, while Fe_2O_3@CEL at pH 5–7 with 48.7 mg g^{-1} Pb^{2+} (Fig. 3.8b) (Daneshfozoun et al. 2017). The zero potential charge pH (pH_{zpc}) is mostly at 4.5 for Fe_2O_3@EFB which explains the increment in electrostatic interaction between sorbent and metal ions at $pH > pH_{zpc}$. Furthermore, sorbent surface charges also become negative which attract the positively charged metal ions (Rao and Ikram 2011). The lower pH in contrast leads to competitive sorption of the higher concentrations of H^+ and H_3O^+ ions with the metal ions resulting in reduced removal efficiency. At higher pH, the affinity of divalent cations towards -OH or -COOH on the sorbent surface is enhanced due to hydrogen bonding, ion exchange as well as simultaneous sorption and diffusion mechanisms. Agro-based sorbents with carboxylic group have pKa values of 3–5 and the acid group of carboxylic acid starts integrating at pH more than 5 which could yield interaction between the negatively charged carboxylate ions with metal ions. Beyond optimum pH, the formation of metal hydroxides precipitate may reduce the availability of the free sorbent active sites.

The metal ions sorption is very much affected by the initial concentration and temperature. However, with increasing initial concentrations upto a threshold level, the competition for vacant active sites in Fe_2O_3@EFB (Fig. 3.9a) may lead to reduced removal efficiency. With increase in temperature, removal efficiency of all metal ions, excluding Ni^{2+}, are improved with Pb^{2+} ions achieving the highest removal at 91–98.5%. All ions, except Ni^{2+}, also exhibit high removal efficiency at the temperature range of 318-338 K with endothermic reactions, whilst Ni^{2+} exhibiting exothermic reactions. This could have caused a reduction in removal efficiency for Ni^{2+} with increasing temperature (Daneshfozoun et al. 2017). At 100 to 1000 mgL^{-1} initial concentrations and at optimum time and pH, the Fe_2O_3@CEL and Fe_2O_3@RKF show a more consistent efficiency (Fig. 3.9b & c) with only a slight reduction suggesting a higher availability of active sites. The elevated temperature from 298 to 338 K exhibit pronounced removal efficiency, proving the endothermic sorption nature of Pb^{2+} onto Fe_2O_3@RKF and Fe_2O_3@CEL. However, there is only a slight increase of 0.36% from 298 to 328 K as the removal efficiency at 97–98.2% is stably high for Fe_2O_3@CEL (Daneshfozoun et al. 2017). The high removal efficiency of around 90–99% for Pb^{2+} with increasing temperature is comparable to that reported for magnetic composites of cellulose, but the exothermic nature of sorption has been reported for cellulose/maghemite/activated carbon composite (Zhu et al. 2011).

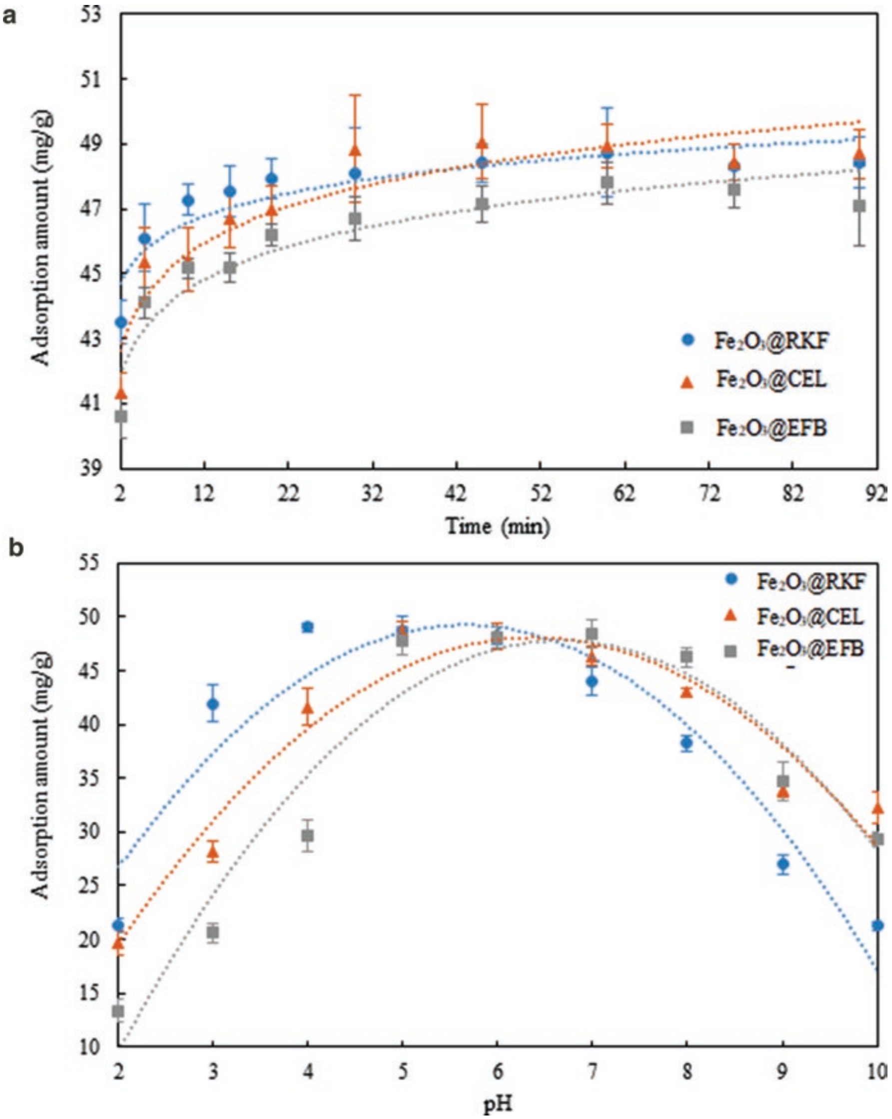

Fig. 3.8 Influence of (**a**) contact time on impurities sorption by differently altered magnetite, (**b**) solution pH, on lead adsorption by modified Fe_2O_3. (Reprinted with permission from [Preparation and characterization of magnetic biosorbent based on oil palm empty fruit bunch fibers, cellulose and *Ceiba pentandra* for heavy metal ions removal, Daneshfozoun et al. 2017, Elsevier])

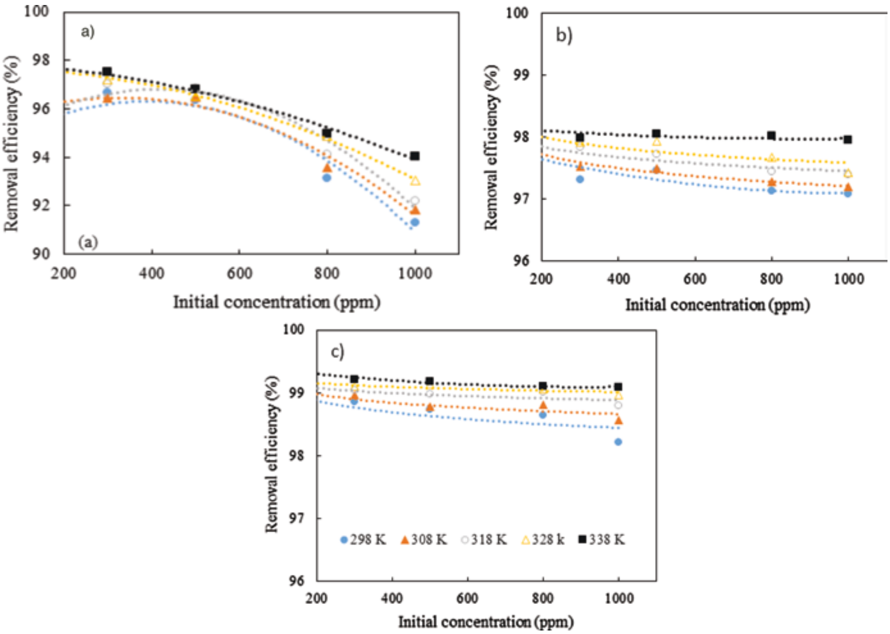

Fig. 3.9 Effects of temperature and concentration on the removal of lead showing that the differently modified sorbents had different effects on the heavy metals (**a**) Fe_2O_3@EFB, (**b**) Fe_2O_3@CEL, (**c**) Fe_2O_3@RKF (Reprinted with the permission from [Preparation and characterization of magnetic biosorbent based on oil palm empty fruit bunch fibers, cellulose and *Ceiba pentandra* for heavy metal ions removal, Daneshfozoun et al. 2017, Elsevier])

3.4.3 Agro-Based Magnetic Biosorbents Recovery and Reusability

Two important parameters for continued use of agro-based magnetic biosorbents are the reusability of the adsorbent and the ion sorption/desorption process. The major constraint is to recover the sorbed metal ions and regain maximum porosity/active sites. Mild acid such as 0.1 M HCl can be utilized in desorption procedure for the generation of active sites and metal ions removal. There is only 3–7% reduction in efficiency of the Agro-based magnetic biosorbents (Fe_2O_3@EFB, CEL, RKF) but all remain above 90% for the five-times sorption-desorption cycles (Daneshfozoun et al. 2017). Figure 3.10 shows the comparison with the raw sorbents for lead ion removal which clearly exhibit the superiority of the agro-based magnetic biosorbents with added advantages such as high adsorption capacity, enhanced separation and reusability for several cycles.

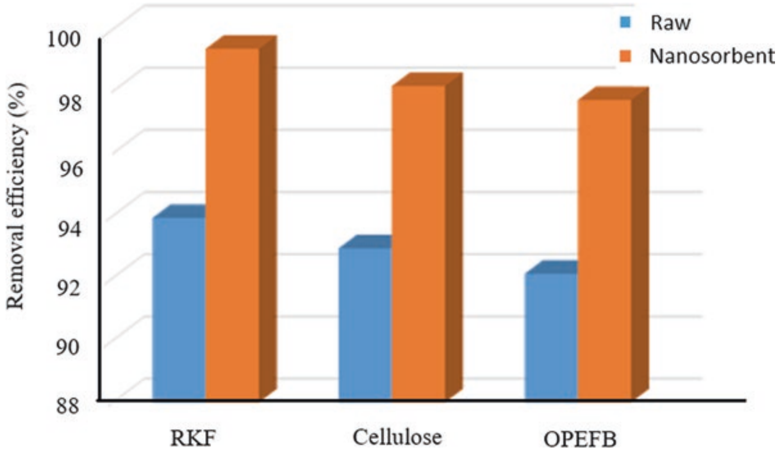

Fig. 3.10 Comparison of raw and nano-sorbents suggesting that the nano sorbents are much more efficient as compared to the raw sorbents in removing the metal ions. (Reprinted with the permission from [Preparation and characterization of magnetic biosorbent based on oil palm empty fruit bunch fibers, cellulose and *Ceiba pentandra* for heavy metal ions removal, Daneshfozoun et al. 2017, Elsevier])

3.5 Conclusion

The metal oxide composites can be synthesized from naturally available sources such as zeolite, silica, polymers, chitosan, alginate, carbon and lignocelluloses. There is an increasing interest to develop magnetic nanosorbents for environmental remediation such as for dyes and heavy metal ions removal from industrial waste water. The challenge is in developing economical and efficient sorbent, maintaining the intended reusability for continued use, high sorption capacity and versatility for wide-range of pollutants. The coating material and surface functionalization of the sorbent could remove specific pollutants and the magnetic features could be modified by optimizing the ratio between the non-magnetic and magnetic components. The magnetic nano-composites based on agro-wastes are especially attractive to be developed as excellent sorbent due to the vast availability of raw materials, eco-friendly, economical and ease of synthesis and recovery. Different factors such as sorbent particle sizes, types of wastes and mode of operation must be considered for large-scale application.

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Chapter 4

Two-Dimensional Materials for Heavy Metal Removal

Siyuan Luo and Hong Chen

Abstract Two-dimensional materials are referring to the materials which are confined in one dimension and growing in another two dimensions. Based on the chemical composition, two-dimensional materials can be further classified into single element layered two-dimensional material, such as graphene and phosphorene, and mixed elements two-dimensional materials, such as transition metal dichalcogenides, MXenes, clay minerals, layered double hydroxides and so on.

This chapter highlights the applications of two-dimensional materials on removing heavy metal ions from aquatic environment. The heavy metal ions removal mechanisms, including surface complexation, van der Waals force, and ion exchange were illustrated combining with typical examples of heavy metal ions removal by two-dimensional materials. Six recently extensively studied types of two-dimensional materials, graphene-based materials, dichalcogenides, MXenes, clay minerals, layered double hydroxides, and layered zeolites, have been discussed in details. Reference to the classification of two-dimensional materials, the most recent researches on developing two-dimensional materials for heavy metal removal, together with a perspective that could be instructive for future research in this topic has been addressed.

By employing different functionalities and techniques, the two-dimensional materials can be fabricated as adsorbents, membranes or electro-device to remove heavy metal from aqueous environment. In this chapter, most of the heavy metal removal by two-dimensional materials mentioned were based on adsorption techniques, because adsorption is one of the most intensive studied techniques for removing heavy metals, especially for novel two-dimensional materials. Besides, the heavy metal removal techniques other than adsorption were also introduced briefly in this chapter.

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Keywords Two-dimensional materials · Graphene-based materials · Dichalcogenides · MXenes · Electrostatic interactions · Surface complexation · Ion exchange · Heavy metals removal · Remediation technologies · Adsorbents · Membranes

4.1 Introduction

Two-dimensional materials are a broad class of materials, which are confined in one dimension and growing in another two dimensions. It is also named as layered materials. Based on the chemical composition composing in the materials, two-dimensional materials can be further divided into single element layered two-dimensional materials and mixed elements two-dimensional materials. The single-element layered materials involves a few typical examples, such as graphene and phosphorene; the mixed elements layered two-dimensional materials contains various types of classification, including transition metal dichalcogenides, MXenes, clay minerals, layered double hydroxides, and so on. The typical classes of two-dimensional materials have been summarized in Fig. 4.1.

Although the research on two-dimensional materials, such as layered clay materials, can be tracking back to 1970s or even earlier days, the intensive studies on two-dimensional materials actually boosted since 2004. One of the most famous two-dimensional materials, graphene, being isolated from graphite, has been defined by K. Novoselov (2004). The valence and conduction bands of this first reported isolated graphene were tiny overlapped, presenting a semimetal property. Thereafter, graphene analogous and other kinds of two-dimensional materials received attention from scientists and the two-dimensional material family kept continuously growing. For instance, another typical two-dimensional material, MXene, referring to the layered transition metal carbides, nitride or carbonitrides, was discovered in 2011 at Drexel University (Naguib et al. 2011a); later, the first post-graphene two-dimensional materials, silicene, was discovered in 2012 (Vogt et al. 2012).

When the thickness of the two-dimensional material decreasing down to a few nanometers size, because of the thickness dependent quantum confinement effect and other effects, two-dimensional materials exhibit significant different physical and chemical features. These unique properties induce various of interesting applications in a broad range of area, such as electronics, valleytronics, photodetectors, catalysis, biosensing, and environmental science (Bhimanapati et al. 2015).

In environmental science and engineering, two-dimensional materials have been extensively used as heavy metal removal materials. By employing different functionality, the two-dimensional materials can be fabricated as adsorbents, membranes or electro-device to remove heavy metal from aqueous environment. Relatively large surface area of the two-dimensional materials and specific surface interaction with heavy metal ions are the key to achieve the functionality.

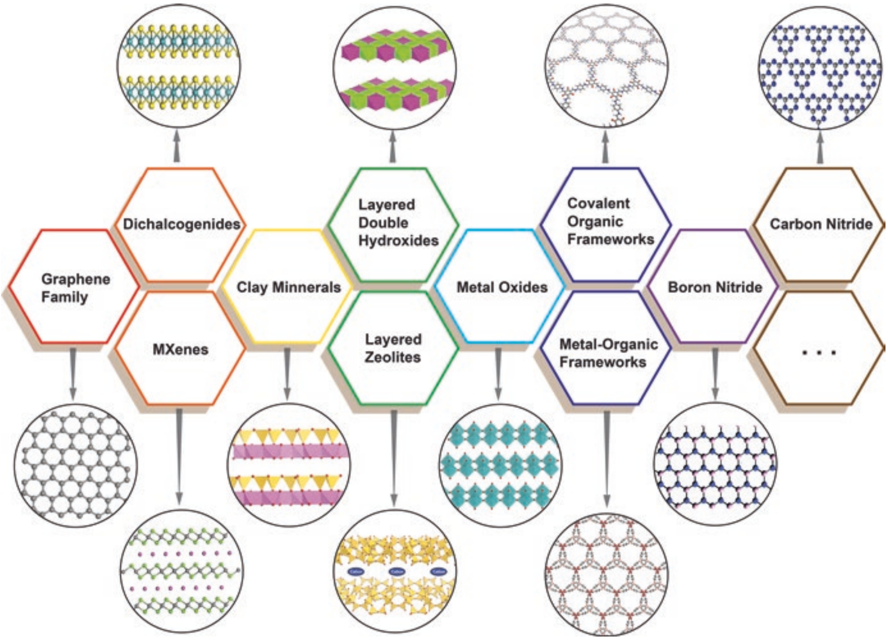

Fig. 4.1 Classification of two-dimensional materials, including graphene, transition metal dichalcogenides, MXenes, clay minerals, layered double hydroxides, layered zeolites, metal oxides, covalent organic frameworks, metal-organic frameworks

In this chapter, initializing from the typical heavy metal ions removal mechanisms, following by the introduction of different types two-dimensional materials, we give a detailed review on the applications of two-dimensional materials for heavy metal removal. Moreover, a summary together with a short perspective on future development on this area are given at the end.

4.2 Heavy Metal Ions Removal Mechanism

The interactions between the heavy metal ions and two-dimensional materials down to atomic scale is the intrinsic driving force for heavy metal removal from aquatic system. Understanding these interactions is crucial and of great significance, because mechanism could guide the effort on scientific designing or optimizing of novel two-dimensional materials. Due to the high anisotropy of two-dimensional materials, it is necessary to illustrate the mechanism underneath the application of two-dimensional materials for heavy metal removal.

The interaction between two-dimensional materials and heavy metal ions can be classified into several types: (1) surface complexation; (2) van der Waals force (electrostatic interactions); and (3) ion exchange. When heavy metal ions are trapped and removed by two-dimensional materials, one or multi-types of interactions mentioned above are involved. Herein, we firstly identified the interaction conception, respectively, then illustrated with examples to explain how different material structures correlating with different interactions, and eventually influencing the metal ion removal behavior.

4.2.1 Surface Complexation

Surface complexation is also classified as chemical adsorption, which is the driving force for the heavy metal ions to form covalent, coordination, or ionic bonding with the two-dimensional material surface. The surface bonding energy usually significantly larger than van der Waals interaction, therefore the formed bonding on the material surface is not easy to break.

Layered material with rich lone-pair electrons elements, such as sulfur, oxygen, nitrogen, on its surface and interlayer, typically shows enhanced the surface complexation capability. These elements can either come from functional dangling group incorporated on the material's surface, or come from two-dimensional material's own composition. Especially, the layered structures that largely expose sulfur or oxygen atoms to the environment, such as transition metal dichalcogenides and layered silicates, are capable to covalently or coordinatively bonding with heavy metal ions. Combining the advantages of abundant complexation sites and large surface area, the heavy metal capture capacity could be dramatically improved.

Except for the functional lone paired electron rich atoms within the two-dimensional materials, other functional groups, such as carboxylate acid group, amine group, thiol group, can be also incorporated into two-dimensional materials. These functional groups can be either decorated to the unit layer surface or intercalated into the interlayers. The resulted composites can bind with heavy metal ions through decorated functional group and be used for heavy metal removal. On the basis of hard-soft acids-bases theory, functional groups may have different affinities to different metal ions, which presents as the chemisorption selectivity. For instance, compounds functionalized by sulfur group can be considered as soft bases, which favor strong and selective binding with soft acids such as Hg^{2+}, Pd^{2+}, Pt^{2+}, Pt^{4+}, and Ag^{+}.

A "inner-sphere complexation" may exist when multilayer two-dimensional materials interact with metal ions (Brown et al. 1999; Giammar et al. 2006), which means the metal ions will not only interact with surface atom, but also the inner layer atoms. X. Guo et al. carried out computational experiments based on density functional theory to study the interaction between MXenes (Ti_3C_2, V_2C_1) and heavy metal ions (Pb^{2+}, Cu^{2+}) (Guo et al. 2016). The first-principles calculations indicated that the Pb^{2+} and Cu^{2+} interaction behavior on MXenes were different. When Pb^{2+} adsorbed onto Ti_3C_2, the Pb^{2+} obtained electrons were mainly from the external Ti atom layer; but for Cu^{2+}, the inner C atom layer also participated the interaction.

These different surface complexation pathways may contribute to the diversities on adsorption capacities and sorption selectivity of Pb^{2+} and Cu^{2+} on MXenes.

4.2.2 Van der Waals Interaction

Van der Waals interaction, or electrostatic interactions, is the attractive or repulsive interaction between objects those with electric charges. Van der Waals forces are additive and cannot be saturated. The adsorption caused by van der Waals force called physisorption, which is usually reversible. The energy of reversible interaction is very weak (~10–100 meV) with no directional characteristic. For two-dimensional materials, the monolayers attach with each other through van der Waals interaction; when the multilayers are exfoliated into thinner layers, the new exposed surface of the layer tend to interact with opposite electric charged species in the system.

The pH of the solution system may influence the physisorption. The Pb^{2+} adsorption behavior on TiO_2 surface is a typical example to demonstrate. When the pH of the solution is below the pH at point of zero charge, the TiO_2 surface is positively charged, forming $Ti–OH_2^+$ group, because of the excess of protons in aqueous system. As a result, the electrostatic repulsion between $Ti–OH_2^+$ and Pb^{2+} contribute an unsatisfactory removal efficiency. When rising the pH to 6.5, the TiO_2 surface is negatively charged in the form of $Ti–O^-$, resulting in effective electrostatic attraction between the TiO_2 surface and positively charged Pb species, i.e. Pb^{2+} and $Pb(OH)^+$. Therefore, with the pH increasing, the adsorption capacity of the materials is enhanced (Gu et al. 2019; Xie and Gao 2009).

Moreover, hydrations ions or defects within the materials or on the material surface can strongly influence the physisorption progress of two-dimensional materials. For instance, a thick layer of hydration ions on the material surface could significantly increase the interaction distance of the opposite charged substances and exhaust the heavy metal bind site, which weaken the adsorb efficiency (Jia et al. 2017; Shen et al. 2015).

4.2.3 Ion Exchange

Ion exchange is an exchange of ions involved in the two-dimensional materials with other substance in different phases. The free movable ions in the two-dimensional materials are replaced by other ions with the same type of electrical charge. These two-dimensional materials could be called as the “ion exchanger”. According to the exchanging charge type, ion exchangers can be classified into three groups: one group is cation exchangers, which exchange positively charged ions; one group is anion exchangers, which carry out negatively charged ions exchanging; the third group is amphoteric exchangers that are able to exchange both cations and anions simultaneously. Ion exchange is driven by chemical potential and it is a reversible process. By washing with excess of desirable ions, the ion exchanger can be regenerated. Upon removal of the divalent heavy metal ions, if the initial interlayer cation is mono charged, then two equivalent mono charged cations could exchange one equivalent divalent charged heavy metal ions such as Pb^{2+}, Hg^{2+}.

The alkaline cations such as sodium ions among the layered minerals can be exchanged with heavy metal ions. Because of the radius variety of the exchanging ion pairs, the interlayer spacing could be changed, resulting interlayer shrinking or expanding occurs after ion exchange. The decrease of the interlayer distance could be observed through X-ray diffraction pattern, where the characteristic crystallographic planes' diffraction peaks are shifted.

When applying two-dimensional materials to remove heavy metal species, multimetal removal mechanisms may be involved. Gu et al. used Ti_3AlC_2 powders, H_2O_2 and NaOH as raw materials to fabricate layered materials TAC@titanate composites by hydrothermal methods (Gu et al. 2019). The surface of the layer material Ti_3AlC_2 was partially converted into TiO_2 under the presence of H_2O_2. Thereafter, titanium oxycarbides underwent the alkalization treatment and finally formed sodium titanates. The Fourier-transform infrared spectroscopy spectra showed the shifts of –ONa/OK groups and the nuclear magnetic resonance showed the interlayer shrinking of these layered materials, indicating the ion exchange of Na^+ in –ONa with Pb^{2+}. Meanwhile, X-ray photoelectron spectroscopy reported the Ti–OH bonding energy shifted to a higher energy, which indicated the formation of Pb–O bonding. The formation of the Pb–O indicated the surface complexation occurred on the surface of the materials. A combination of various characterizations demonstrated that both ion exchange and surface complexation contributed to the material's excellent lead adsorbing ability.

4.3 Different Types of Two-Dimensional Material for Heavy Metal Removal

4.3.1 Graphene-Based Two-Dimensional Materials

4.3.1.1 Structure

Graphene family is an indispensable category when discussing two-dimensional materials. Its popularity can trace back to 2004, when monocrystalline graphene films were firstly prepared through mechanical exfoliation methods (Novoselov 2004). Since then, the graphene family came into researchers' sights and soon swept the whole world. The 2010 Nobel Prize in physics for graphene proved the rapid development and huge potential of this two-dimensional material (Dresselhaus and Araujo 2010).

Graphene is composed of three-coordinated carbon atoms arranged in a two-dimensional honeycomb lattice. The building unit is conjugated six-membered

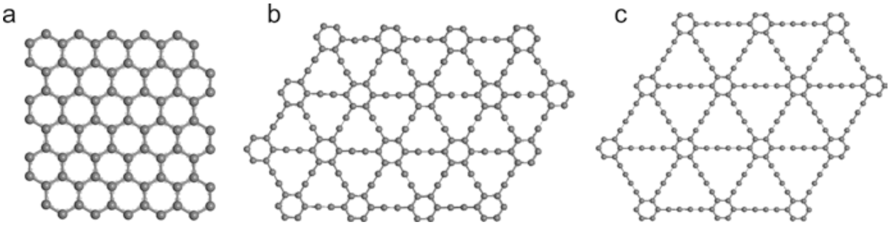

Fig. 4.2 Structures of typical graphene derivatives: (**a**) graphene, (**b**) graphyne, and (**c**) graphdiyne. The color scheme: grey ball: carbon

carbon ring. The average C–C bond length is 1.42 Å, and C–C–C bond angle is 120°. Each carbon atom bond with adjacent three carbon atoms in sp^2 hybrid structure; meanwhile, each carbon donates one p electron to form the huge conjugated π electron system. Due to the strong bonding among the C–C=C motif, it exhibits outstanding chemical stability, strong mechanical strength, and excellent electrical conductivity. Because of the π–π stacking effect of the extending layer, the monolayer trends to form a multilayer graphite structure.

The ideal perfect graphene is not really achievable in the lab. Most prepared graphene exists defects and non-carbon atoms are involved as functional groups. The fruitful defects and functional groups endow the two-dimensional matrix with new possibility in various applications. Besides, plenty of graphene derivatives such as hydrogenated graphene (graphane and graphone), graphene introduced by acetylenic chains (graphyne and graphdiyne), fluorinated graphene (fluorographene), and graphene derivatives involving group 1 or group 17 elements (graphXene), has been proposed and chemically synthesized (Fig. 4.2) (Inagaki and Kang 2014; Peng et al. 2014a). Nowadays, graphene family has been extended into a big category which includes few-layer-graphene, graphene oxide, reduced graphene oxide, ultrathin graphite, and graphene hybrids (Bianco et al. 2013).

4.3.1.2 Graphene-Based Materials for Heavy Metal Removal

Here we discuss the heavy metal removal applications of the graphene family materials by three classifications: graphene nanosheets, graphene oxides, and reduced graphene oxides. Graphene derivatives such as graphyne and graphdiyne, are rarely introduced in environment science and engineering application. The reason of their absence probably related to the complicate and expensive synthetic routes that involved.

Graphene nanosheets, have been applied as novel adsorbents for removing and preconcentrating various kinds of pollutions, such as toxic gases, organic dyes and hazardous metal ions (Yu et al. 2015). Benefited from the C–π electrons on the graphene, metal ions can be electrostatic adsorbed on single-layered graphene nanosheets. The heat treatment performed on graphene nanosheet could enhance the adsorption behavior, as the Lewis basicity and electrostatic attraction of the nanosheet may increase (Huang et al. 2011). Besides, graphene nanosheets–cargos composites with enhanced heavy metal adsorption capacity is an optimizing strategy. For example, mixed graphene with δ-MnO_2 to construct graphene nanosheet/δ-MnO_2 composites, the adsorption capacities for Ni^{2+} ions in aqueous solution of graphene nanosheet/δ-MnO_2 composites was 1.5 and 15 times higher than those of pure δ-MnO_2 and graphene nanosheets, respectively (Ren et al. 2012).

Graphene oxide, which hybrids the electron rich atom within the graphene, can bring us more possibilities to improve heavy metal removal performance. The graphene oxides surface generally contains various types of consecutive oxygen functional groups, such as –COOH, –C=O, and –OH. These functional groups result the negative charged graphene oxide layer surface, which enhance the electrostatic physisorption of cations. In addition, the functional oxygen group could bond with metal cations on graphene oxide surface, which is chemisorption progress. Cooperating with the nature of large surface area, graphene oxides are excellent adsorbents for heavy metal cations (Zhao et al. 2011).

The dispersibility of graphene oxides in water is different before and after adsorption experiments. Sitko et al. reported that the suspension of fresh graphene oxides nanosheets could keep in water solution without any aggregation in several months. However, after adsorption of heavy metals, the graphene oxides in water had the tendency to aggregate and precipitate (Sitko et al. 2013).

Except the pure oxygen hybrid graphene, other hybrid elements involved function group could also be incorporated in the graphene layer through the surface functionalization modification process starting from graphene oxide (Chandra and Kim 2011; Yuan et al. 2013). Typical inorganic nanomaterials, such as silicas (Sheet et al. 2014; Hao et al. 2012), metal sulfides (Jiang et al. 2015), magnetic nanoparticles (Gollavelli et al. 2013; Guo et al. 2014) have been decorated onto the graphene oxide two-dimensional material to enhance diversity of the heavy metal removal properties. For instance, mercapto group is one of the most popular functional groups that frequently be chosen, because of the $–S^-$ selectivity to soft Lewis base such as Pb^{2+}, Hg^{2+}. The introduction of the magnetic nanoparticles make contribution to easy recycling the heavy metal ions after adsorption.

Nevertheless, due to the strong electrostatic repulsion force between graphene oxide surface and anionic compounds, graphene oxide shows weak binding affinity for anionic species (Chowdhury and Balasubramanian 2014).

Starting with the graphene oxide composite, further reducing the graphene oxide in inert atmosphere, the reduced graphene oxides can be achieved. Undergoing similar modification routes, the materials can be decorated with inorganic particles, organic groups (Zhang et al. 2018), and magnetic cobalt ferrite (Zhang et al. 2014) to achieve different heavy metal removability.

Except for using the graphene family materials in two-dimensional nature for heavy metal removal, assembling of graphene into three-dimensional hierarchical construction has been learned as an efficient strategy to enhance heavy metal removal performance (Shen et al. 2015). The layered double hydroxide was reported to be grown in-situ on graphene, forming a hierarchical three-dimensional composite for U^{6+} removal (Tan et al. 2015). Wang et al. discovered a g-C_3N_4/graphene hydrogel system for Cr^{6+} removal via the stacking effect and the π–π conjugated at low temperature (Wang et al. 2017b). They combined two-dimensional nanosheets, making the matrix adsorb and reduce Cr^{6+} in a synergistic way. In this matrix, the graphene was responsible for fast speed adsorption and high adsorption capacity of Cr^{6+}; while the g-C_3N_4 nanosheets had outstanding photocatalytic activity to absorb and reduce Cr^{6+} in situ.

Very recently, Fu's group designed a Fe_3O_4-encapsulated $C_3N_3S_3$ polymer/reduced graphene oxide composite, in which Fe_3O_4 nanoparticles were wrapped between the rGO-poly($C_3N_3S_3$)matrix layers (Fu et al. 2019). The Fe_3O_4 nanoparticles not only prevent layer materials rGO-poly($C_3N_3S_3$) matrix aggregated, but also play a role in adsorbing heavy metal ions. The surface of Fe_3O_4 nanoparticles is positively charged, promoting the adsorption and in-situ polymerization of negatively charged $C_3N_3S_3^{3-}$ anions on reduced graphene oxides surface by electrostatic attraction. The poly($C_3N_3S_3$) molecules supported numerous sulfur and nitrogen functional groups, which are the bonding sites of heavy metal ions. The formation of metal–sulfur and metal–nitrogen coordination bond is demonstrated by Fourier-transform infrared spectroscopy spectra, indicating a chemisorption mechanism. The Hg cations, identified as soft acid, preferentially bound to sulfur functional groups. While Pb cations, identified as intermediate acid, tend to be interacted with nitrogen functional groups in poly($C_3N_3S_3$) matrix. This bonding priority is further confirmed by high-resolution X-ray photoelectron spectroscopy. Maximum metal-uptake capacities for Pb^{2+} and Hg^{2+} ions reach 270.3 and 400.0 mg/g, respectively.

4.3.2 Dichalcogenides

4.3.2.1 Structure

Transition metal dichalcogenides are a class of materials with a general formula of MX_2. Herein, M stands for group IV (Ti, Zr, or Hf), group V (V, Nb or Ta) or group VI (Mo or W) transition metal element, and X is a chalcogen (S, Se or Te) (Wang et al. 2012). Transition metal dichalcogenides typically shows layered structures form with atomic layers of X–M–X. Each transition metal atom M strongly covalent bonds with six adjacent chalcogen atoms X to form an octahedral geometry. The molecular layer X–M–X stacks with each other via the van der Waals forces along the vertical direction, forming the bulk materials. Such weak interlayer interaction and much stronger intralayer ionic interaction contribute to the high anisotropy of transition metal dichalcogenides. Due to the unique layered structure and high anisotropy, the electronic and catalytic properties of two-dimensional transition metal dichalcogenides could be tuned through different structural modification strategies such as intercalation, dimensions reducing, heterostructure, gating, alloying, pressure, and lighting (Fig. 4.3) (Wang et al. 2015a).

Many two-dimensional dichalcogenides have been found in nature and also been successfully synthesized in the lab, such as molybdenum disulfide (MoS_2), tungsten

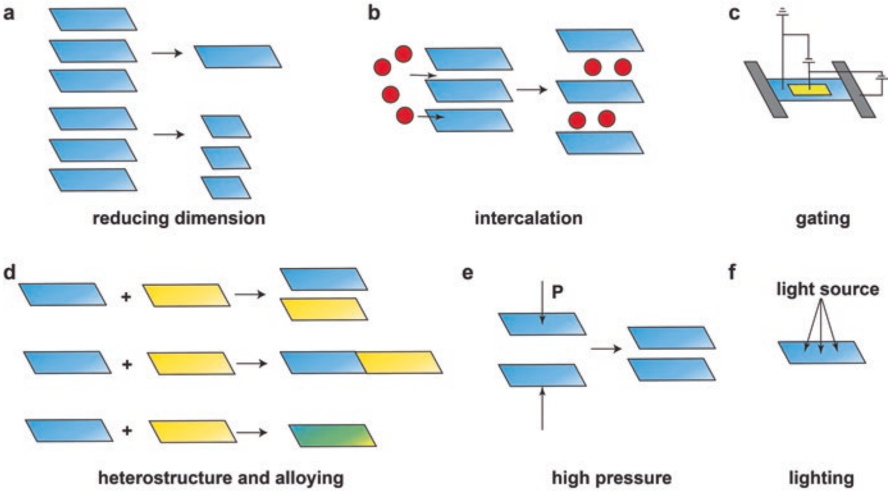

Fig. 4.3 Two-dimensional transition metal dichalcogenides structural modification. (**a**) dimension reducing, (**b**) guest ion intercalation, (**c**) heterostructures constructing and alloying, (**d**) gating, (**e**) high pressure applying, and (**f**) circularly-polarized light illuminating. (Modified after (Wang et al. 2015a))

disulfide (WS_2), and tungsten diselenide (WSe_2). MoS_2 is one of the most widely studied two-dimensional dichalcogenides, its crystal structure consists of a molybdenum atom layer sandwiched between two sulfur layers. The Mo–S bond length is 2.42 Å, which results a thickness of 6.5 Å MoS_2 monolayer (Yazyev and Kis 2015). Sandwich layers are coupled with each other by weak van der Waals interactions.

4.3.2.2 Molybdenum Disulfide for Heavy Metal Removal

Two-dimensional molybdenum disulfide has been extensively explored with various applications on designing semiconductors (Yazyev and Kis 2015), electronic devices (Lembke et al. 2015; Radisavljevic et al. 2011), and catalysts (Lukowski et al. 2013). Recently, the potential applications of molybdenum disulfide in environmental fields have been revealed (Wang and Mi 2017).

The interactions between MoS_2 and heavy metal ions are introduced in Fig. 4.4. The MoS_2 surfaces usually carry negative charges with H^+ or Li^+ as counterions due to the redox reaction or defect formation during the synthesis process. Therefore, metal ions get access into the interlayer by ion exchanges, following by a metal–S bonding, i.e. the inner layer metal–S complexation. The outer layer electrostatic attraction would happen afterwards in a multilayer style, which is generally considered as a minor interaction contribution (Wang and Mi 2017).

Because of the S–Mo–S sandwich structure nature of MoS_2 layer, a larger interlayer distance can help to expose more binding sites (sulfur atoms) to the environment, thus enhance the functionality. Ai et al. demonstrated the first experimental

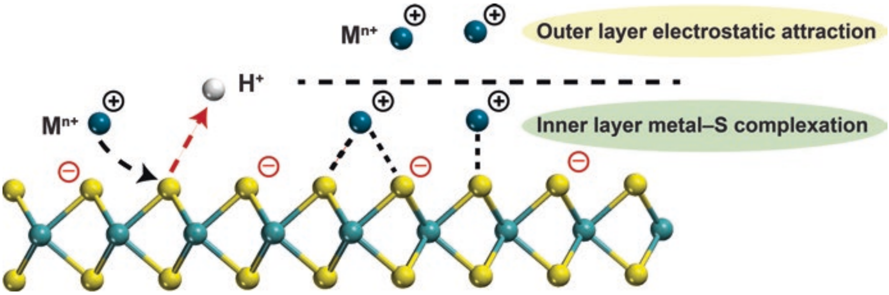

Fig. 4.4 MoS_2 surface interacts with heavy metal ions. Metal ions get access into the interlayer of MoS_2 by ion exchanges with H^+, following by a metal–S bonding, i.e. the inner layer metal–S complexation; outer layer electrostatic attraction would happen afterwards in a multilayer style. The color scheme: cyan ball: molybdenum; yellow ball: sulfur; green ball: aluminum

evidence that the mercury capture capacity of MoS_2 nanosheets could be enhanced by widening the interlayer spacing of the layer materials (Ai et al. 2016). Generally, the initial gallery height of 2.98 Å between two neighboring S–Mo–S layers is too narrow to host hydrated Hg^{2+} ion. The Hg^{2+} adsorb capacity of commercial MoS_2 powder was only 35.5 mg/g. The interlayer spacing of the obtained MoS_2 was greatly enlarged to 9.4 Å by one-step hydrothermal method, and the Hg^{2+} adsorb capacity of this modified MoS_2 reached 2562.8 mg/g (Ai et al. 2016). In addition, when using the 9.4 Å d-spacing MoS_2 to adsorb Hg^{2+}, the concentration of the heavy metal ions affected the surface bonding patterns. Extended X-ray absorption fine structure technique revealed that, with enough MoS_2 materials to adsorb Hg^{2+} at low Hg^{2+}/MoS_2 ratio, one equivalent Hg^{2+}ions exchanged for two equivalent H^+ ions. Under low Hg^{2+} concentration condition, each mercury atom probably interacted with two sulfur atoms through the following ion exchange and complexation process, as shown in Eq. (4.1):

$$H_xMoS_2 + nHgCl_2 \rightarrow Hg_nH_{(x-2y)}MoS_2 + 2nH^+ + 2nCl^- \tag{4.1}$$

When the Hg concentration increased, one equivalent Hg^{2+} ion only replaced one equivalent proton through ion exchange, and the coordination number of mercury ion gradually decreased from two to one. The dominant mechanism in high Hg concentration could represent as Eq. (4.2). Therefore, the complexation mode of MoS_2 to removal Hg^{2+} partly depended on the concentration of heavy metal ion.

$$H_xMoS_2 + nHgCl_2 \rightarrow \left[Hg_nH_{(x-y)}MoS_2\right]^{n+} + nH^+ + 2nCl^- \tag{4.2}$$

In 2017, Jia et al. studied the adsorption behavior of Hg^{2+} on natural and hydrous molybdenum disulfide surface through atomic force microscope (Jia et al. 2017). Under the help of atomic force microscope technique, authors clearly investigated how H_3O^+ influenced the adsorption process on the molybdenum disulfide surface and the layer thickness of Hg^{2+} adsorption. Atomic force microscope showed how

Hg^{2+} aggregated on the non-hydrous MoS_2 surface in 20 h. After 8 h exposure to moisture, the adsorbed Hg^{2+} ion layer almost covered the full MoS_2 surface. New adsorbed ion layers appeared afterwards and grew to maximum thickness of 20 nm in next 12 h. For the hydrous MoS_2, it observed a hydration layer with a thickness of 1.2 nm covered the surface at the very beginning, resulting a few Hg atoms aggregation was detected above hydration MoS_2 layer and a quicker adsorption saturation time in the next 20 h. From the microscopic investigation, it clearly showed that H_3O^+ cations occupy the adsorption active sites, resulting the low Hg^{2+} uptake ability of the hydrated materials. Besides, the molybdenum disulfide was thermodynamically unstable, which could be slightly oxidized into molybdenum oxides in presence of water vapor (Buck 1987). Therefore, the introduction of moisture on MoS_2 surface not only deceases the amount of active site, but also accelerates surface molybdenum disulfide degradation, greatly impeding the adsorption of Hg^{2+}.

4.3.3 MXenes

4.3.3.1 Structure

MXenes are a class of two-dimensional inorganic compounds which consist of few-atoms-thick layers of transition metal carbides, nitrides, or carbonitrides. These two-dimensional materials are called 'MXenes' because they are fabricated by etching 'A' layer from MAX phases (M stands for a transition metal, A stands for mainly a group 13 or 14 element, and X stands for carbon and nitrogen). Adding the suffix 'ene' to emphasize their similarity to graphene (Naguib et al. 2014). These materials have been receiving numerous scholarly attentions since from the discovery of Ti_3C_2 by Y. Gogotsi group in 2011(Naguib et al. 2011a). The general chemical formula of MAX phase is $M_{n+1}AX_n$ ($n = 1, 2$ or 3) and Fig. 4.5 represents three typical structures of MAX phases and their corresponding MXenes. In the MAX phase, the X layers are packed in order, and transition metal atoms fill the octahedral center, forming $M_{n+1}X_n$ multilayers. The A atom layers are intercalated between the $M_{n+1}X_n$ layers. Because of the bonding energy difference between M–A bonds and M–X bonds, the A layers, i.e. the group 13 or 14 elements, can be selectively etched though different physical or chemical processes, such as heating in molten salts (Naguib et al. 2011b) or molten metal (El-Raghy et al. 2001), and corrosion with hydrofluoric acid (Naguib et al. 2011a). When the layers of A atom were removed, two-dimensional MXenes sheets (M_2X, M_3X_2, and M_4X_3) could be generated (Fig. 4.5).

4.3.3.2 MXenes for Heavy Metal Removal

Typical types of MXenes materials, such as Ti_2C, Nb_2C, V_2C, Ti_3C_2, and Ta_4C_3, have been explored with many practical applications other than heavy metal removal (Boota et al. 2016; Sun et al. 2018; Wang et al. 2015b).

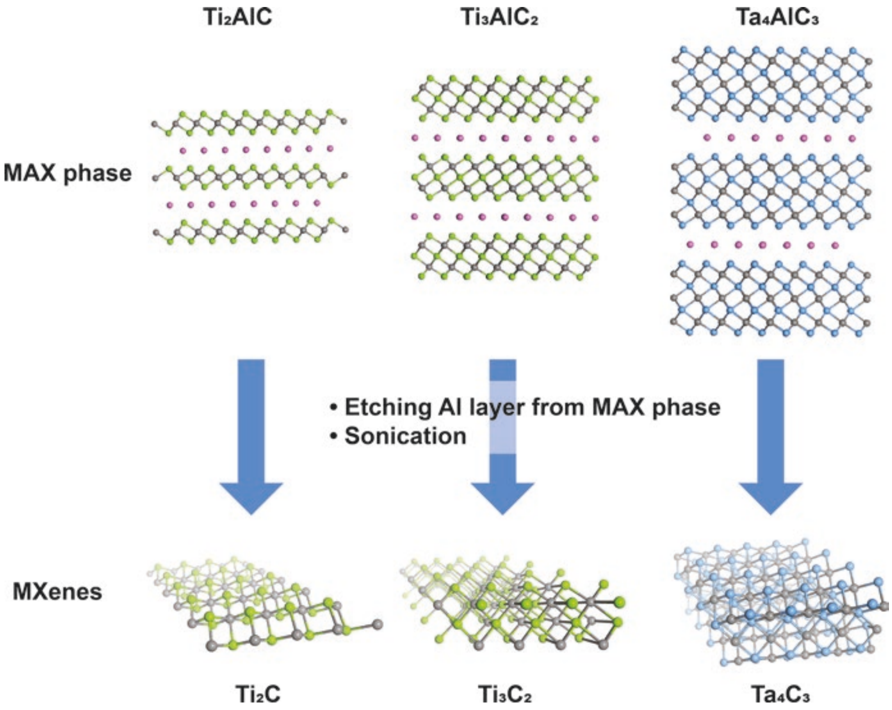

Fig. 4.5 Crystal structures of typical MAX phases (Ti_2AlC, Ti_3AlC_2, and Ta_4AlC_3) and the corresponding achieved MXenes through etching method (Ti_2C, Ti_3C_2, and Ta_4C_3). The color scheme: pink ball: aluminum; black ball: carbon atom; green ball: titanium atom; blue ball: tantalum atom

In recent years, many MXene materials containing Ti were found to be good for absorbents for removing heavy metals, such as two-dimensional alk-MXene ($Ti_3C_2(OH/ONa)_xF_{2-x}$)(Peng et al. 2014b), $Ti_3C_2T_x$ MXenes (Wang et al. 2017a), layered titanates ($Na_2Ti_3O_7{\cdot}nH_2O$)(Li et al. 2012). On one hand, titanium atom generally shows high sorption affinity toward heavy metal ions such as Cu^{2+}, Cd^{2+}, and Pb^{2+} (Peng et al. 2014b). On the other hand, when fabricating MXenes from the MAX phases by HF acid assisted exfoliation, the exposed titanium surfaces are terminated by OH^- or F^- group. The terminal hydroxyl groups are potential cation ion exchange sites, which might enhance the capture of target metal ions.

For instance, the two-dimensional $Ti_3C_2T_x$ nanosheet, it not only achieved reducing toxic Cr^{6+} to Cr^{3+} rapidly and effectively from aqueous solution, but also adsorbed the reduced Cr^{3+} simultaneously (Ying et al. 2015). Moreover, MXenes and their derivatives, e.g. alkalization-intercalated MXene or MXene composites, have been demonstrated with good capabilities on removing Pb^{2+} (Gu et al. 2019), Cr^{6+} (Ying et al. 2015), Ba^{2+} (Fard et al. 2017) and Cu^{2+} (Shahzad et al. 2017). Therefore, MXenes family is a promising and emerging material category for heavy metal removal and need to be extensively explored in the future.

4.3.4 Clay Minerals

4.3.4.1 Structure

Clay minerals are phyllo-aluminosilicates, which individual layer units compose of tetrahedral oxide sheets (T sheets) and octahedral oxide sheets (O sheets) in a 2:1 or 1:1 proportion (Zhu et al. 2016).

Montmorillonite is a typical 2:1 type clay mineral with one layer of O sheets being sandwiched between two layers of T sheets (Fig. 4.6a). Other typical clay minerals with T:O layer proportion of 2:1 include rectorite, bentonite, talc, and vermiculite. The general formula for montmorillonite is $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$. The theoretical composition without the interlayer material is SiO_2, 66.7%, Al_2O_3, 28.3%, H_2O, 5% (Bhattacharyya and Gupta 2008). Because of the isomorphous substitution of $Al^{3+}$by Mg^{2+} in O sheet, montmorillonite carries negative layer charge density around 0.2 to 0.6 per half unit cell. To balance the negative charges, cationic counter ions are usually required to be hosted in the interlayer space. Therefore, montmorillonite has been used as a good cation exchanger (Brigatti et al. 2013).

Kaolinite, is another silicate with the tetrahedral hydroxide sheet and the octahedral silicate sheet ratio of 1:1 (Fig. 4.6b). If water molecular layer occupies among interlayers, there forms another type of mineral called halloysite with nanotube-like morphology. The general formula of kaolinite is $Al_2Si_2O_5(OH)_4$. The theoretical composition is SiO_2 46.54%, Al_2O_3 39.50%, H_2O 13.96% expressed in terms of the oxides (Bhattacharyya and Gupta 2008). Compared to montmorillonite, the net layer charge of kaolinite is zero, thus there is no permanent negative charge present on the layers. However, the natural kaolinite shows a small net negative charge due to the defects of mineral crystalline structure.

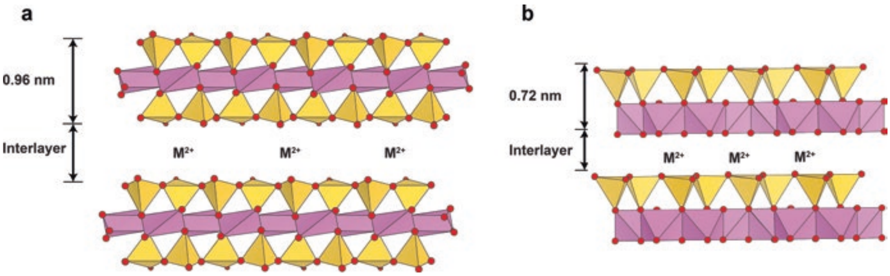

Fig. 4.6 Crystal structure of montmorillonite (**a**) and kaolinite (**b**). Montmorillonite is a typical 2:1 type clay mineral with one layer of octahedral silicate sheets being sandwiched between two layers of tetrahedral oxide sheets. Kaolinite is a typical clay mineral with the tetrahedral hydroxide sheet and the octahedral silicate sheet ratio of 1:1. Color scheme: yellow: Al–O tetrahedra; pink: Si–O octahedra. M^{2+} represents metal cation

4.3.4.2 Clay Mineral for Heavy Metal Removal

The research on clay minerals for environmental remediation has been launched since 1970s (Abd-Elfattah and Wada 1981; Farrah and Pickering 1978). In general, raw clays are attractive natural adsorbents because of their low cost, relative high surface area, chemical and mechanical stability, ion exchange capacity, and hydrophilicity nature. Ion exchange and physisorption are the main driving forces to capture heavy metal cations in nature clay mineral materials. For certain mineral materials, their capacity of exchanging cations is close to a constant which we define as cation exchange capacity.

Apart from raw montmorillonite, montmorillonite derivatives such as acid-activated montmorillonite (Ma et al. 2011; Wu et al. 2011), thermal-treated montmorillonite (Qin et al. 2010), inorganic modified montmorillonite (Sani et al. 2017), and organic modified montmorillonite (Addy et al. 2012; Tsai et al. 2016), their heavy metal sorption behaviors have been studied in either single metal ion solution or metal ions mixture. The adsorption mechanism behind different modified montmorillonite-based adsorbents are diverse: acid-activated montmorillonite and thermal-treated montmorillonite uptake heavy metal cations mainly through cation exchange process; organic modified montmorillonite uptakes heavy metal through chemisorption, physisorption, and anion exchange; inorganic modified montmorillonite uptakes heavy metal through physisorption, cation/anion exchange, and surface precipitation (Zhu et al. 2016). Most of the modifications aimed to introduce chemical interactions into the adsorb progress, which could help clay materials overcome their nature of low selectivity and weak affinity, as well as the relatively low adsorption capacity.

Similar with montmorillonite, natural kaolinite has been used for heavy metal removal, although it has a low cation exchange capacity (3–15 meq/100 g of clay) and smaller surface area ranged from 10 to 20 m^2/g (Jiang et al. 2010). Modification by pillaring and acid activation can influence the layer charges and interlayer distance, which help enhance their heavy metal ion adsorption capacities. Nevertheless, the reverse trends, i.e. heavy metal ion leaching, are more likely to be observed.

4.3.5 Layered Double Hydroxides

4.3.5.1 Structure

Layered double hydroxide family consists of hydrotalcites and hydrotalcite-like compounds. Layered double hydroxides are available as naturally occurring minerals and as-synthesized materials which belong to the member of metal hydroxides. There were first prepared in the laboratory in 1942 and the layer feature has been elucidated in late 1960s (Newman and Jones 1998). The typical formula of layered double hydroxide can be represented as: $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]A^{n-}{}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively; A is an anion of valence n; x is equal to the ratio $M^{3+}/(M^{2+} + M^{3+})$. On the brucite-like layers of the layered double hydroxide, divalent cations partially substitute to trivalent cations, leading to an excess of positive charge on every single layer (Pérez et al. 2006) (Fig. 4.7). The primary positive charges are balanced through the counter anions on the interlayer, or called hydroxide layers. The charge density on the interlayer of the layered double hydroxide will depend upon the M^{2+}/M^{3+} ratio.

In general, the anions A^{n-} on the interlayer regions of layered double hydroxides can be replaced easily through ion exchange progress. Various different kinds of anions A^{n-} including simple inorganic anions, organic anions, and complex biomolecules can be incorporated. This property has led to intense interests on using layered double hydroxide intercalates for different applications. Different with the layered clay minerals, the layered double hydroxide layer is positive charged in principle, which concludes the interlayer species present negative charge. Besides, montmorillonites are capable of swelling to accommodate many layers of H_2O molecules; while layered double hydroxides can be swelled to only one or two layers. (Carrado et al. 1988).

4.3.5.2 Layered Double Hydroxides for Heavy Metal Removal

Due to the excellent intercalation and anion exchange properties, layered double hydroxides has been employed for versatile applications, such as catalysts, two-dimensional nanoreactors, and scavengers (Wang and O'Hare 2012). As a typical two-dimensional material with high surface area, layered double hydroxide's single layer electronic density and adsorption site alkaline intensity can be tuned easily, which achieves layered double hydroxide a potential class of adsorbents with high adsorption capacity. As an anion-exchanger, layered double hydroxide can be used for removing anion clusters such as SeO_4^{2-}, SeO_3^{2-}, AsO_4^{-}, CrO_4^{-}, TcO_4^{-}, and ReO_4^{-} from aqueous solution. Meanwhiles, as a hydroxide, layered double

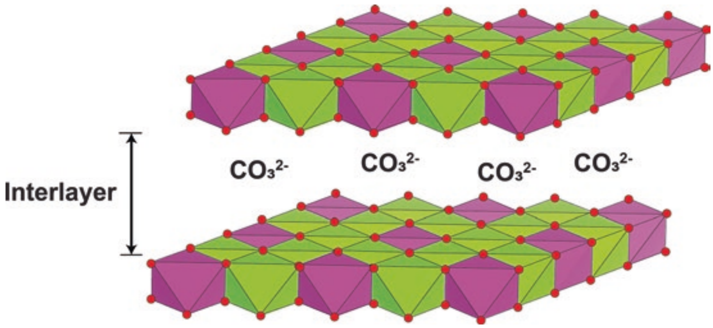

Fig. 4.7 Crystal structure of layered double hydroxides. Color scheme: Green: M^{3+}–O octahedra; Pink: M^{3+}–O octahedra. Divalent cations partially substitute to trivalent cations result the layers carry positive charge. Interlayer contains negative charged species (e.g. carbonate ions) to balance charges

hydroxide can behave as a precipitation reagent for heavy metal cations such as Cu^{2+}, Pb^{2+}, and Zn^{2+} via hydroxide formation (Kameda et al. 2008).

Intercalating functional groups is one of the most popular strategies to improve the heavy metal uptake capability. Recently, $(MoS_4)^{2-}$ intercalated layered double hydroxides material, a stoichiometric composition of $Mg_{0.66}Al_{0.34}(OH)_2(MoS_4)_{0.17}\cdot 0.8H_2O$, was reported to remove heavy metal ions (Ma et al. 2016). The intercalated $(MoS_4)^{2-}$ firstly interacted with the layered double hydroxides layer through Mo–S···HO hydrogen bonding, and then formed different compositions depending on the target metal cation concentration. When the materials reacted with stoichiometric metal nitrate salts, $(MoS_4)^{2-}$ reacted with heavy metal ions to form $[M(MoS_4)_2{}^{2-}]$ species, with a slightly decrease of basal spacing from 1.07 nm to 0.96 nm. To balance the interlayer charges, a new composition of NO_3–layered double hydroxides with basal spacing d = 0.89 nm was formed. Under the condition of adding the excess of metal ions, neutral amorphous salts $MMoS_4$ were observed. In this case, layered double hydroxides not only adsorbed metal ion as an ion-exchanger, but also prevent the aggregation of $(MoS_4)_2{}^{2-}$ in bulk solution, therefore largely increased the adsorption efficiency. As a result, this intercalated layered double hydroxides showed enormous adsorption capacities, for Hg^{2+} was~500 mg/g and for Ag^+ was 450 mg/g, respectively. Such a high adsorption capacities with a high distribution coefficients (K_d) of ~10^7 mL/g, place this MoS_4–layered double hydroxide materials at the top of absorbents known for Hg^{2+} and Ag^+ removal.

4.3.6 *Layered Zeolites*

4.3.6.1 Structure

Zeolites are crystalline microporous materials that formed by covalently bonded corner-sharing $[SiO_4]$ and $[AlO_4]$ tetrahedra in three-dimension. Layered zeolites are a special kind of zeolites, because their crystal growth is constrained in the third direction (Xu and Wu 2016). It can be also named as a "precursor" for the traditional three-dimensional zeolite frameworks, as some of the three-dimensional zeolites can be obtained by calcinating the layered zeolites, which is called topotactic condensation reaction. Up to date, there have been 238 unique zeolite framework structures collected by the International Zeolite Association and 14 types of them were investigated to have corresponding layered precursors (Xu and Wu 2016). Figure 4.8 represents the crystal structure of layered silicate RUB-51 with interlayer distance of 8.4 Å discovered by Li et al. (2008). RUB-51 was synthesized using benzyl trimethylammonium hydroxide as the structure-directing agent from hydrothermal method. The silicate layers carried negative charges; these negative charges are balanced by the benzyl trimethylammonium cations that intercalated between neighboring silicate layers.

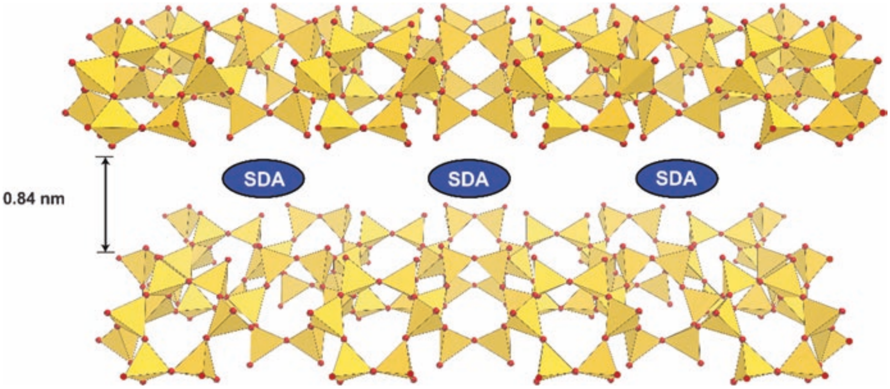

Fig. 4.8 Crystal structure of layered zeolite RUB-51. Color scheme: Yellow: Si–O tetrahedra; red: O atom; SDA (structure-directing agents): benzyl trimethylammonium hydroxide

4.3.6.2 Layered Zeolites for Heavy Metal Removal

Although there are various types of layered zeolites (Xu and Wu 2016), the research reported on exploring their adsorption ability for heavy metal ions is limited to a few cases, such as AM-4 (Lopes et al. 2007), RUB-15 (Chen et al. 2017), AMH-3 (Kim and Kwak 2017).

Two-dimensional layered silicate RUB-15 was firstly fabricated in 1996 (Oberhagemann et al. 1996) and then applied in water remediation for the first time in 2017 (Chen et al. 2017). RUB-15 composed of three-connected [SiO_3O^-] and four-connected [SiO_4] tetrahedral units, forming six-membered rings and four-membered rings of silicate layer. Tetramethylammonium cations located at inter-space between silicate layers to balance negative charges on silicate layers. The adsorption of heavy metal cations on RUB-15 was relatively reversible, indicating ion exchange was the dominate adsorption mechanism. Maximum adsorption capacities for UO_2^{2+}, Pb^{2+} and Cd^{2+} of RUB-15 were 152, 338, and 190 mg/g, respectively. Apart from the high adsorption capacities for heavy metal ions, RUB-15 dispersed well in water with low-cost and efficient regeneration capability. Although some surface breaking and irreversible adsorption happened, the adsorbents could be recycled for further adsorption.

Layered zeolite AMH-3, the unit cell formula is $Na_8Sr_8Si_{32}O_{76}\cdot 16H_2O$, had characteristics of both zeolite and layered silicate without hydroxyl group on its surface (Jeong et al. 2003). The silicate layers are built of tetrahedral SiO_4 units, forming eight membered ring pores; meanwhile, alkali cations and water molecules occupy in the interlayer spaces. Kim et al. applied AMH-3 to do competitive heavy metal cation sorption experiment (Kim and Kwak 2017). The selectivity sorption capacity of AMH-3 was in the order Pb^{2+}(167.5 mg/g) > Cu^{2+}(84 mg/g) > Zn^{2+}(7.7 mg/g) > Cd^{2+}(1.9 mg/g), indicating AMH-3 might be an excellent sorbent for selectively removing heavy metals from mixed metal ions aqueous solutions. However, the mechanism of selective heavy metal removal was unclear. The potential mechanism contributed to the high selectivity of sorption might be the synergetic effects of ion exchange in interlayers together with the extra ion exchange or electrostatic interactions sorption point contributed by the eight membered ring channels.

4.3.7 Other Two-Dimensional Materials

Except the aforementioned two-dimensional materials, there are also other types of two-dimensional materials such as: transition metal oxides (Kalantar-Zadeh et al. 2016), graphitic carbon nitride (g-C_3N_4) (Hu et al. 2015;Lan et al. 2019), boron nitride-based materials (Yu et al. 2018), van der Waals heterostructures (Geim and Grigorieva 2013; Novoselov et al. 2016), cationic inorganic networks(Yang and Fei 2017), metal-organic frameworks nanosheets (Zhao et al. 2018), and two-dimensional covalent organic frameworks (Sun et al. 2017). Transition metal oxides includes h-MoO_3, h-WO_3, MoO_2, and MnO_2, the layered structure feature is quite similar to the transition metal dichalcogenides. Graphitic carbon nitride and boron nitride-based materials, are graphene-like two-dimensional monolayer materials. With nitrogen atoms replacing part of the carbon atoms, it can introduce some defective carbon position within the layer. Van der Waals heterostructure is a multiple layered structure that integrating different monolayer material with each other through van der Walls force. Ultrathin two-dimensional MOF nanosheets are highly crystalline hybrid porous materials, their pores orient perpendicular to molecular plane, forming abundant inside channels. The inside channels support two-dimensional MOF materials accessible chemical bonding sites. Two-dimensional covalent organic frameworks as a new type of porous materials, has been introduced into the research pertinent to energy and environmental sustainability. Due to the structure tunability nature, two-dimensional covalent organic frameworks show great potential as excellent sorbents for heavy metal removal. Ma's group post synthesized a thiol-functionalized covalent organic framework with two-dimensional structure and well-defined mesopores, which can serve as ideal adsorbents for Hg^{2+} and Hg^0 in solution (Sun et al. 2017). Each covalent organic framework layer attached with through π–π stacking interaction with the interlayer distance 3.6 Å. The stacked layers formed one-dimensional meso-channel, where numerous adsorptive active sites, i.e. sulfur species, located in order. The adsorbent exhibits exceedingly high Hg^{2+} and Hg^0 uptake capacities of 1350 mg/g and 863 mg/g, respectively. The flexible sulfur chelating sites in the framework would contribute this impressive result.

4.4 Heavy Metal Removal Other than Adsorption

For all aforementioned heavy metal removal, we mainly addressed the adsorption techniques. Multiple advantages such as the facility of operation with relatively low cost, practical accessibility, and the simple adsorbents regeneration procedures, support adsorption become one of the most common and effective techniques for removing metal ions (Wang et al. 2018). Except the adsorption, there are many other different techniques can be implemented for heavy metal removal, including but not limited to ion electrodialysis, chemical precipitation, membrane filtration, reduction, reverse osmosis, and photocatalysis. In this section, we will briefly introduce the heavy metal removal other than adsorption, i.e. membrane engineering and electrodeposition techniques.

Membrane separation technique has been widely used in water pollution treatment. Muti-advantages, such as low operation temperature, low energy consumption, and pore-size controllability, making the membrane engineering popular for several decades. Two-dimensional materials have emerged as nano-building blocks to develop high-efficient separation membranes because of their unique nanochannels in interlayers or among the layers (Liu et al. 2016). Zhang et al. reported a stable and highly charged framework membrane with the graphene oxide selective layer thickness of 70 nm for effective heavy metal removal via nanofiltration (Zhang et al. 2015). Authors carried out a dual-modification strategy to fabricate the graphene oxide framework membranes: Firstly, they cross-linked two-dimensional graphene oxide nanosheets by ethylenediamine to form the graphene oxide framework; then they modified the frameworks surface with hyperbranched polyethylenimine (Fig. 4.9). On one hand, the introduction of ethylenediamine cross-linking reconstructed two-dimensional structure into three dimensional ones, which enhanced structural stability. On the other hand, the cross-linking enlarged the nanochannels among the laminated graphene oxide nanosheets for higher water permeability. Hyperbranched polyethylenimine supported the membranes a higher surface charge, which guaranteed the high rejections toward heavy metal cation ions. The

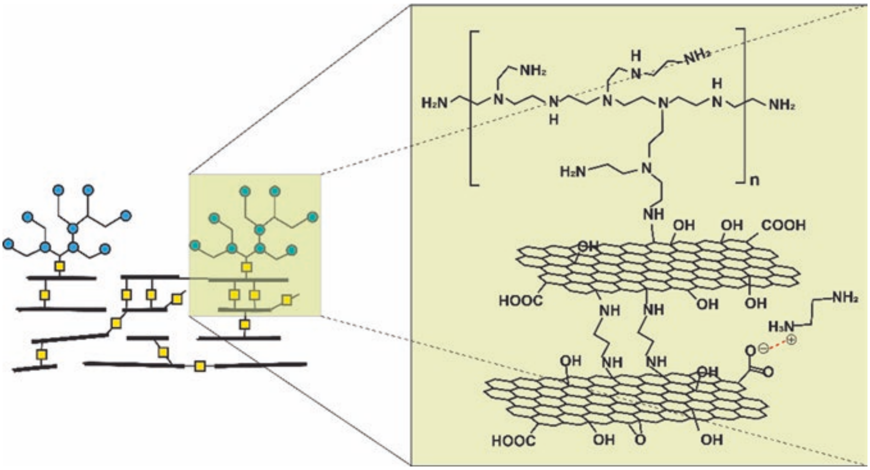

Fig. 4.9 Nanoporous graphene oxide framework membranes. Two-dimensional graphene oxide nanosheets was cross-linked by ethylenediamine to form a graphene oxide framework; then frameworks surface was decorated with hyperbranched polyethylenimine. (Modified after (Zhang et al. 2015))

two-dimensional graphene oxide nanosheet can work as the additives to be mixed into membrane as well. On the addition of graphene oxide, mixed matrix membrane became highly permeable, hydrophilic and charged (Mukherjee et al. 2016; Zhang et al. 2016).

Exfoliated dichalcogenides has been used to fabricate membranes for organic molecules and gas separation. Especially, MoS_2 not only can be synthesized through various facile and scalable procedure, but also has many excellent properties, such as high mechanical and thermal stability, photocatalytic and antibacterial properties, supporting it become a promising two-dimensional building blocks to fabricate novel membranes (Sun et al. 2013; Wang and Mi 2017). Very recently, Wang et al. investigated the Ag^+ removal behavior of the layer-stacked MoS_2 membrane (Wang et al. 2018). Two mechanisms were involved in Ag^+ removal from solution: one is physisorption, the other one is redox reaction through which the Ag^+ has been reduced into Ag^0 on the surface of the semiconducting MoS_2 under the light radiation. For the membrane performance, under continuous filtration mode, MoS_2 membrane effectively removed Ag^+ from the low concentration (2 ppm) feed solution. However, for high concentration (20 ppm) feed solution, after filtrate volume was beyond 50 ml, the removal efficiency showed a decreasing trend which caused by oxidative degradation of the membrane. Due to the redox reaction between the Ag^+–MoS_2 pair, Ag^+ reduced into Ag^0 and MoS_2 surface oxidized, which shortened the contacting time between Ag^+ and MoS_2 membrane. The increased water flux and detected soluble Mo species (MoO_4^{2-}) are additional evidences of the membrane oxidative degradation.

Two-dimensional materials can also be used to fabricate the electrode for employing the electrodeposition technique to remove heavy metal ions. Very recently, Liu's group developed the direct current or alternating current electrodeposition method to remove and recover heavy metals from aqueous solution with graphene oxide electrodes (Liu et al. 2019). By utilizing the numerous defects and functional groups on the graphene oxide electrode, i.e. C−O and C=O groups, metal ions migrated towards to the working electrode under certain bias voltage, forming an electrical double layer (Fig. 4.10). The metal ions then reduced to metal nanoparticles and attached onto the graphene oxide electrode surface. This electrochemical method showed two-orders of magnitude higher sorption capacity (>29 g/g) for Cu^{2+}, Cd^{2+}, and Pb^{2+} than the traditional adsorption method.

4.5 Conclusions and Perspectives

In this chapter, we drew a panoramic image of two-dimensional materials for heavy metal removal. The interaction mechanism between two-dimensional material and metal ion has been discussed at the beginning, then structural feature of each material and typical examples for heavy metal removal are summarized. These examples covered multi-subject fields, including the discovery of novel two-dimensional

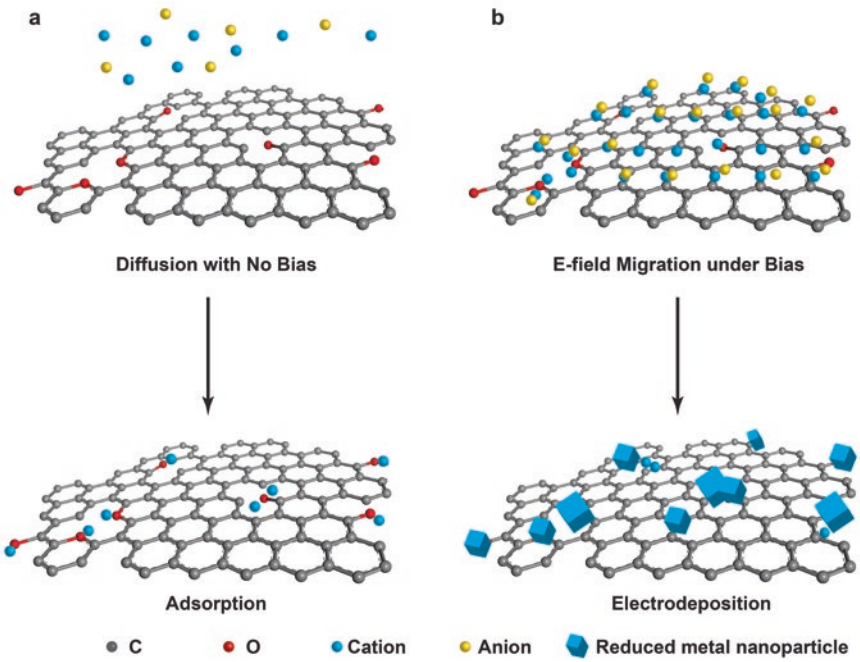

Fig. 4.10 Schematics showing the difference between (**a**) adsorption progress and (**b**) electrochemical deposition progress on the graphene oxide. Under Bias, the metal ions migrated towards to the working electrode, forming an electrical double layer in the first place. (Modified after (Liu et al. 2019))

structure, surface modification, mechanism study, fabrication optimization, and removal technique evolution.

In order to promote future research, several challenges need to be took into account and overcome. Firstly, the fate and potential ecotoxicological effects of most two-dimensional materials are currently unclear. It partially due to the limited analytical methods for nanomaterials measurements (Goodwin et al. 2018; Suárez-Iglesias et al. 2017). Whether such large amount of two-dimensional nano-absorbents would transfer into secondary pollutants need receive more attentions.

Selectivity for heavy metal removal is another challenge. Physisorption have no selectively to heavy metal ions; although chemisorption may support separating soft and hard metal ions, the divalent transition metal ions with similar electronic structure and ionic radius are still difficult to be selectively separated. In the future, using steric effect or pH adjustment may assist the materials to improve their selectivity.

The removal mechanism studies are of great importance. Only through the understanding of interaction mechanism, novel two-dimensional materials for heavy metal removal can be guided to design and synthesized.

Although two-dimensional materials are a huge family, a few types of two-dimensional materials such as MoS_2, graphene oxide, Ti_3C_2, Mxene, clay minerals received intensive studies on heavy metal removal. Many promising two-dimensional materials such as MOF, covalent organic framework, and the transition metal dichalcogenides other than MoS_2, are facing obstruction on large scale reproducing technology, which might directly restrict their applications.

Finally, the application of two-dimensional materials for heavy metal removal can be various, besides the extensive studies on adsorbents application. Currently, several attempts have been devoted to fabricate two-dimensional material-based membrane and electrodes for environmental application, but these technology promotions are insufficient.

The summary of this chapter and the perspectives for heavy metal removal by two-dimensional materials can be concluded as shown in Fig. 4.11. Aiming to explore the possibility of two-dimensional materials for commercial heavy metal removal, lots of effort need to be devoted in the future, which relate to material structures, techniques, and mechanisms: (1) developing promising novel structured two-dimensional materials and their derivates, which is suitable for heavy metal removal (non-ecotoxicological, large-scale production and selectivity); (2) more attempts should be explored based on different techniques and chemo-physical driving forces, nowadays only the adsorption capability of two-dimensional materials has been extensively studied; (3) more in-depth fundamental understandings of the interaction mechanism between heavy metal ions and material surface need to be addressed. In all, two-dimensional materials are a class of promising materials to be employed for heavy metal removal, although it is still an emerging topic that need environmental scientists, physicists, chemists, materials scientists work together in interdisciplinary field.

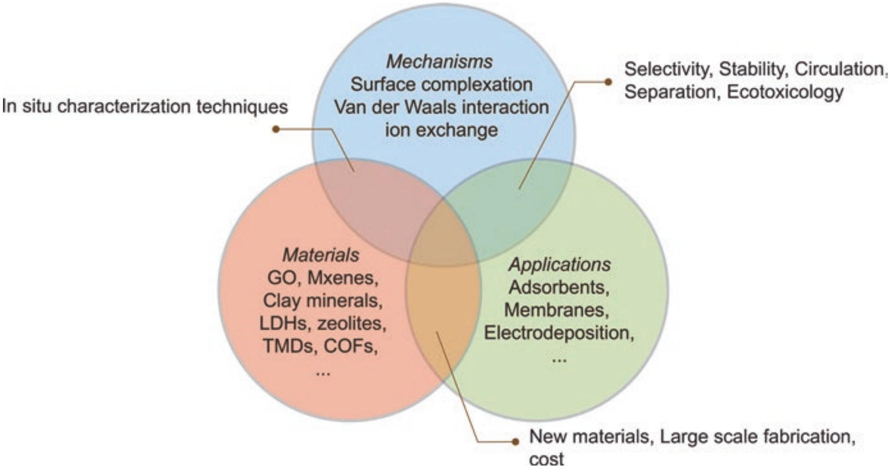

Fig. 4.11 Summary and perspectives of this chapter

Appendix: List of Two-Dimensional Materials that Mentioned in this Chapter for Heavy Metal Removal and their Removal Capacities

Two-dimensional Materials	Metal Ion	Removal capacity (mg/g)	References
GNS500	Pb^{2+}	35.2	Huang et al. (2011)
GNS/MnO_2	Cu^{2+} Pb^{2+}	102 161	Ren et al. (2012)
Few-layered GO nanosheets	Cd^{2+} Co^{2+}	106.3 68.2	Zhao et al. (2011)
GO powder	Cu^{2+} Zn^{2+} Cd^{2+} Pb^{2+}	294 345 530 1119	Sitko et al. (2013)
GO/CdS(en) composite	Cu^{2+}	137.2	Jiang et al. (2015)
Amino functionalized Fe_3O_4-GS	Cr^{6+} Pb^{2+} Hg^{2+} Cd^{2+} Ni^{2+}	17.3 27.9 23.0 27.8 22.1	Guo et al. (2014)
RGOS (rGO grafted by 4-sulfophenylazo groups)	Pb^{2+} Cu^{2+} Ni^{2+} Cd^{2+} Cr^{3+}	689 59 66 267 191	Zhang et al. (2018)
$CoFe_2O_4$-rGO composite	Pb^{2+} Hg^{2+}	299.4 157.9	Zhang et al. (2014)
g-C_3N_4/rGH	Cr^{6+}	49.7	Wang et al. (2017b)
rGO/LDH	U^{6+}	277.8	Tan et al. (2015)
rGO-poly($C_3N_3S_3$) matrix	Pb^{2+} Hg^{2+}	270 400	Fu et al. (2019)
Commercial MoS_2 (2.98 Å d-spacing)	Hg^{2+}	35.5	Ai et al. (2016)
Interlayer widen MoS_2 (9.4 Å d-spacing)	Hg^{2+}	2562.8	Ai et al. (2016)
Ce-MoS_2	Ag^{2+}	980	Wang et al. (2018)
Alk-MXenes	Pb^{2+}	140	Peng et al. (2014b)
Layered titanates	Ag^{+} Cu^{2+} Pb^{2+} Eu^{3+}	546.5 202.3 563.0 264.0	Li et al. (2012)

(continued)

Two-dimensional Materials	Metal Ion	Removal capacity (mg/g)	References
$Ti_3C_2T_x$ MXenes	U^{6+} Pb^{2+} Cr^{6+} Ba^{2+} Cu^{2+}	214 328.9 250 9.3 78.5	Wang et al. (2017a) Gu et al. (2019) Ying et al. (2015) Fard et al. (2017) Shahzad et al. (2017)
Kaolinite	Cd^{2+} Cr^{6+}	9.9 11.6	Bhattacharyya and Gupta (2008)
Acid-activated kaolinite	Cd^{2+} Cr^{6+}	11.4 13.9	Bhattacharyya and Gupta (2008)
Montmorillonite	Cd^{2+}	32.7	Bhattacharyya and Gupta (2008)
Acid-activated montmorillonite	Cd^{2+}	33.2	Bhattacharyya and Gupta (2008)
Bentonite	Cd^{2+}	9.3	Bhattacharyya and Gupta (2008)
LS-LDH	Cu^{2+}	75	Ma et al. (2016)
EDTA-LDH	Cu^{2+}	71	Ma et al. (2016)
MoS_4-LDH	Cu^{2+} Hg^{2+} Ag^{+}	181 500 450	Ma et al. (2016)
RUB-15	UO_2^{2+} Pb^{2+} Cd^{2+}	152 338 190	Chen et al. (2017)
AMH-3	Pb^{2+} Cu^{2+} Cd^{2+} Zn^{2+}	238.5 180.3 64.3 26.6	Kim and Kwak (2017)
COF-S-SH	Hg^{2+} Hg^{0}	1350 863	Sun et al. (2017)

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Chapter 5
Membranes for Heavy Metals Removal

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Abstract The contamination of the water bodies from industrial activities is a well-known problem faced by countries around the world, demanding its effluents management. In this context, membrane separation processes, as electrodialysis, play an important role, since they allow removing, recovery and/or producing essential products from metals processing wastes. It is unthinkable to see the present world without metals, and membrane separation processes are a key technology to solve the environmental problems associated with their processing. This chapter focuses the electrodialysis membrane-based process centered on the metal electroplating and mining and mineral activities. Research results showing the possibility of recovering nickel, copper, zinc and chromium salts to be reused on electroplating processes, as well as the recovery of copper and zinc from mining processing solutions, are discussed.

Keywords Ion-exchange membrane · Electrodialysis · Electro-electrodialysis · Zinc · Nickel · Copper · Chromium · Electroplating · Mining · Wastewater

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Abbreviations

ce	current efficiency
dr	demineralization rate
ec	energy consumption
pe	percent extraction

List of Symbols

C	ion concentration in solution (g/L)
F	Faraday's constant (96,485 A s/mol)
I	applied current (A)
M	molar mass of the ion (g/mol)
N	number of membrane pairs
t	time (s)
Δt	time interval (s)
U	electrodialysis module voltage (V)
V	volume of solution (L)
z	valence of the ion

Greek Letter

δ	solution conductivity (mS/cm)

Subscripts and Superscripts

i	initial
t	time

5.1 Introduction

In recent decades, membranes have been developed and applied in a wide range of activities as in the medical field (Faria et al. 2018), in the chemical (Nunes and Peinemann 2006; Venzke et al. 2018; Castro-Muñoz et al. 2018), biotechnology (Giacobbo et al. 2017b; Hoffmann et al. 2019), food (Giacobbo et al. 2017a), pharmaceutical (de Souza et al. 2018), mining (Buzzi et al. 2013; Martí-Calatayud et al.

2014) and metallurgical (Korzenowski et al. 2008; Benvenuti et al. 2014; Bittencourt et al. 2017) industries as well as in water (Bernardes and Rodrigues 2014; Bacher et al. 2017) and wastewater (da Trindade et al. 2015; Albornoz et al. 2019) treatment.

This wide field of applications has provided to the membrane technologies a broad acknowledge as efficient and viable cleaner technologies. In addition, due to their intrinsic characteristics, namely mild operating conditions, less energy consumption, small footprint requirement, separation efficiency, no chemical additives, and easy control and scaling up, they have gained an edge over classical separation processes (Strathmann et al. 2006; Giacobbo et al. 2015; Nath and Patel 2019).

Membrane technologies are unit operations of physical nature, which, through a perm-selective barrier, the membrane is able to restricts the transport of one or more components present in the phases (Fane et al. 2011). In order to occur this separation, the existence of a driving force, such as gradients of pressure, temperature, concentration or of electric potential, is necessary (Baker 2012).

Despite the growing use of membrane technologies driven by gradients of concentration and of temperature, e.g. membrane distillation, for the treatment of water and wastewater, the ones driven by gradients of pressure like microfiltration, ultrafiltration, nanofiltration and reverse osmosis, and of electric potential, as electrodialysis, still predominate in large-scale treatment plants. This can be attributed to the fact that these five technologies are well established and several experienced companies serve the global market (Baker 2012).

In fact, the listed membrane processes present certain advantages and disadvantages when used for the removal of a specific contaminant. The ones driven by pressure are mainly categorized on the basis of their membrane pore size, with microfiltration having the maximum pore size range (10,000–100 nm), followed by ultrafiltration (100–10 nm) and nanofiltration (0.5–5 nm) (Purkait and Singh 2018), while reverse osmosis have membranes so dense whose pores do not exist on the membrane surface and the transport take places through statistically distributed free volume areas in the polymeric matrix (Baker 2012). Thus, microfiltration is used to retain suspended solids, large colloids and bacteria; ultrafiltration for removal of macromolecules, proteins and virus; nanofiltration for separation of micropollutants and multivalent ions; while reverse osmosis additionally remove monovalent ions (Fane et al. 2011; Purkait and Singh 2018). On the other hand, electrodialysis is fundamentally addressed to remove ions from a feed stream. This technology is grounded on the selective transport of ions across ion-selective membranes (Bernardes et al. 2014).

Indeed, if not adequately designed and operated, membrane technologies can present severe problems of loss of selectivity and productivity, mainly attributed to the phenomena of concentration polarization and membrane fouling (Giacobbo et al. 2018). Notwithstanding, as a membrane separation process, electrodialysis has significant potentialities such as high water recovery rates, limited consumption of chemicals, possibility of selective ions separation even with similar charge and (or) valence applying complexing agents (Frioui et al. 2017; Babilas and Dydo 2018) or mono-selective membranes (Chen et al. 2009), in addition to fouling minimization, possible by the periodical polarity reversion of the electrodes, typically many times per hour, reducing, thus, the cleaning procedures (Bernardes et al. 2014). Therefore, regarding the decontamination of water and wastewater containing toxic heavy metals by membrane technologies, the main issue addressed in this chapter, electrodialysis is a promising technology.

5.2 Electrodialysis

5.2.1 Electrodialysis Applied to Metal Removal

The application of electrodialysis for metals removal has increased in scientific research. The recovery of transition metals has been extensively studied. According to the search in the database *Scopus*, membrane processes for metals removal from water and wastewater has been reported since 1956. The terms “membrane”, “metal” and “removal” were seeking simultaneously in *title*, *abstract* and *keywords* fields, totaling 4143 occurrences. For the last 15 years membrane processes for metal removal has been enlarged, registering more than 100 publications per year.

When the term “membrane” is changed by “electrodialysis”, 270 documents are listed in the *Scopus* Platform, mainly in the past 10 years. Firsts reports that brings metal separation by electrodialysis were published in Russian studies by separating platinum in solutions containing metal chlorides like iron, copper and nickel (Ezerskaya and Solovykh 1969). Additionally, the search was narrowed for specific publications related to the main metals applied in coating and surface treatment, thus the search criteria “metal” can be specified.

Using the search terms “electrodialysis”, “copper” and “removal”, 112 documents were listed, while 51 report “nickel” studies, 77 talk about “chromium” and 63 present “zinc”. Once wastewater may contain a mix of metals, the same study could report results about more than one metal. Other important application of electrodialysis is in mining processes. The terms “electrodialysis” and “mining” were searched in *title*, *abstract* and *keywords* fields from documents in *Scopus* database, showing 75 occurrences. Dating back to 1973, the biggest number of publications in mining applications has been verified in the last 5 years.

5.2.2 Principle

As introduced earlier, electrodialysis is a separation technique based on ion-selective membranes and an electrical field as driving force. The applied membranes, of cationic and anionic nature, allow the selective separation of existing ions in a solution. The cation-exchange membrane presents negative fixed ions, attached to the membrane structure, and allows the transport of positively charged ions, that is, the cations. The anion-exchange membrane, on other side, contains positive fixed ions, attached to its structure, and allows the transport of negatively charged ions, the anions. If a feed solution is pumped through chambers formed by a switched arrangement of cation- and anion-exchange membranes, disposed between electrodes, a cathode and an anode, as illustrated in Fig. 5.1, under the application of an electric field, two new solutions can be obtained, one more diluted than the original (feed) one, and another one more concentrated (Genders and Weinberg 1992; Noble and Stern 1995; Rowe and Abdel-Magid 1995; Scott 1995; Boucher et al. 1997; Strathmann 2010; Campione et al. 2018). Additionally, the electrodialysis module is usually designed forming independent electrode chambers through which solutions of sodium sulfate are commonly pumped, avoiding the contact with the working solutions. In these compartments, the following electrochemical reactions can occur (Applegate 1984; Sequeira 1994):

(i) on the cathode

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{5.1}$$

$$M^{n+} + ne^- \rightarrow M \tag{5.2}$$

(ii) on the anode

$$H_2O \rightarrow ½O_2 + 2H^+ + 2e^- \tag{5.3}$$

$$M^{m+} \rightarrow M^{n+} + (n-m)e^-, \tag{5.4}$$

where M means metal.

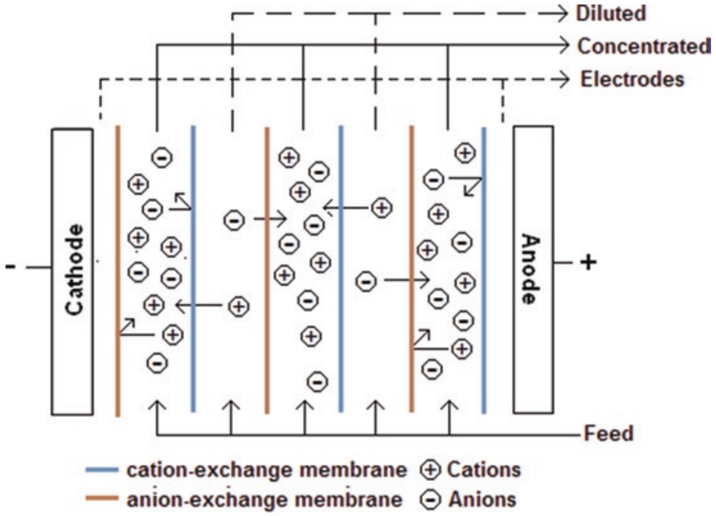

Fig. 5.1 Electrodialysis principle. Cations and anions from a feed solution are selectively transferred through alternated cation- and anion-exchange membranes producing diluted and concentrated solutions. Modified after Marder et al. (2003)

When the electrochemical reactions at the electrodes take part on the formation of the products of interest, the technique is named electro-electrodialysis or reactive electrodialysis (Cifuentes et al. 2015).

5.2.3 Evaluation and Control Parameters

The applied current density or potential are critical points that must be taken into account to ensure high operational performance of the technique. The selective ions transport, across the ion-exchange membranes, lead up to appearance of concentration gradients in membrane-solution interfaces and, depending on the applied current density, the ions concentration, in the dilute side of the membranes, can be reached to values close to zero, characterizing a limiting current density state or value. The trespass of this limiting state leads to different overlimiting mechanisms, as water splitting and electroconvection (Taky et al. 1992b; Taky et al. 1992a; Noble and Stern 1995; Krol et al. 1999; Tanaka 2010; Nikonenko et al. 2014).

In a general way, the applied current density respects the limiting state in 60–80% of the so-called limiting current density value (Chandramowleeswaran and Palanivelu 2006), which can be obtained from current density-voltage curves (Rubinstein et al. 1988; Taky et al. 1992b; Taky et al. 1992a; Kang et al. 2004; Chamoulaud and Bélanger 2005; Belashova et al. 2017), to avoid or minimize the water splitting manifestation in the membrane-solution interfaces. Water splitting can result in energy loss, due to the unproductive transport of proton and hydroxyl ions and, in the case of metal containing solutions, the precipitation of insoluble species on the membrane surface (Noble and Stern 1995). When the electrodialysis runs in reactive mode, it is interesting to define the applied current density or potential based on the electrode potential, that is, the favorable electrode potential to precede the desired electrochemical reaction, which can be drawn also from current density-voltage curves (Cifuentes et al. 2014).

Other basic electrodialysis control parameters include the electrical conductivity, the pH and the concentration of the electrodialysis device solutions. It is also suggested the evaluation of parameters such as demineralization rate (Wang et al. 2016), percent extraction (Marder et al. 2003; Moura et al. 2012), current efficiency (Tzanetakis et al. 2003; Marder et al. 2004) and energy consumption (Yan et al. 2015).

The demineralization rate, *dr*, indicates the total amount of ions removed from the feed solution and is obtained from conductivity data (Wang et al. 2016), using Eq. 5.5.

$$dr(\%) = \left(\frac{\delta_i - \delta_t}{\delta_i} \right) \times 100 \tag{5.5}$$

where δ_i is the initial solution conductivity (mS/cm) and δ_t is the solution conductivity at time t (mS/cm).

The percent extraction, *pe*, expresses the amount removed from a given ion of the solution, and is obtained using ion concentration data (Moura et al. 2012), using the Eq. 5.6.

$$pe(\%) = \left(\frac{C_i - C_t}{C_i} \right) \times 100 \tag{5.6}$$

where C_i and C_t are the initial ion concentration in solution and the ion concentration in solution at time t, in g/L, respectively.

The current efficiency, *ce*, determines the portion of the applied current density which is used to transfer ions from the feed solution, that is, the amount of current density that is really used to extract the ions of interest (Tzanetakis et al. 2003), and is obtained by Eq. 5.7.

$$ce(\%) = \left(\frac{zF\left(V_i C_i - V_t C_t\right)}{N I \Delta t M} \right) \times 100 \tag{5.7}$$

where F is the Faraday's constant (96,485 A s/mol), z the valence of the ion, N the number of membrane pairs, I the applied current (A), M the molar mass of the ion (g/mol), Δt the time interval (s), V_i the volume of solution before the treatment (L) and V_t the volume of solution at time t (L).

Energy consumption, *ec*, can be related to the quantity of energy needed to extract a mass unit of ions achieved from current, potential and ion concentration data (Yan et al. 2015), according the Eq. 5.8.

$$ec(kWh / kg) = \left(\frac{U_t I t}{3{,}600\left(V_i C_i - V_t C_t\right)} \right) \tag{5.8}$$

where U_t is the electrodialysis module voltage at time t (V) and t, the time (s).

5.2.4 Use in Electroplating Industry

Electroplating is one of the most working procedures to obtain metal coatings on metal surfaces (Schlesinger and Paunovic 2000) and one of the most important fields of activity of the electrodialysis technique when dealing with heavy metals (Nagarale et al. 2006). In electroplating, the metal used as a coating is deposited on the base metal by the passage of a continuous electric current through an electrolytic solution, commonly called a bath, which contains ions of the metal to be deposited. Different solutions with different compositions may be employed, from single acid solutions, prepared from sulfate and chloride salts, to those containing complexing or chelating agents (Schlesinger and Paunovic 2000). Depending on the type and the amount of steps employed, a large amount of pollutants, that must be eliminated from the effluent before being disposed of in the environment, can be generated. The effluents come mainly from the rinsewaters or electroplating baths whose efficiency has already been exhausted, requiring the exchange to new solutions (Hartinger 1994).

Because electrodialysis is a separation process capable of transforming a solution into two others, one more diluted and another more concentrated than the original one, it presents great application with regard to the treatment of effluents from electroplating processes. A flow chart illustrating the application of electrodialysis in the electroplating process to recover metals, salts and water is presented in Fig. 5.2. The diluted solution can be used as rinsewater of the process, and the concentrated, as a supply of chemical products for the electroplating bath, once this stream is enriched in metals (Itoi 1979; Audinos 1983; Chiapello and Gal 1992). These aims has stimulated several works along the years, producing important data to the removal and recovery of the main metals used in electroplating processes. In researches applying electrodialysis for separation of metals from electroplating baths and rinsewater, it was verified that zinc, chromium, nickel and copper appear as the most common targets (Korzenowski et al. 2008; Benvenuti et al. 2017; Barros et al. 2018; Babilas and Dydo 2018; Scarazzato et al. 2018).

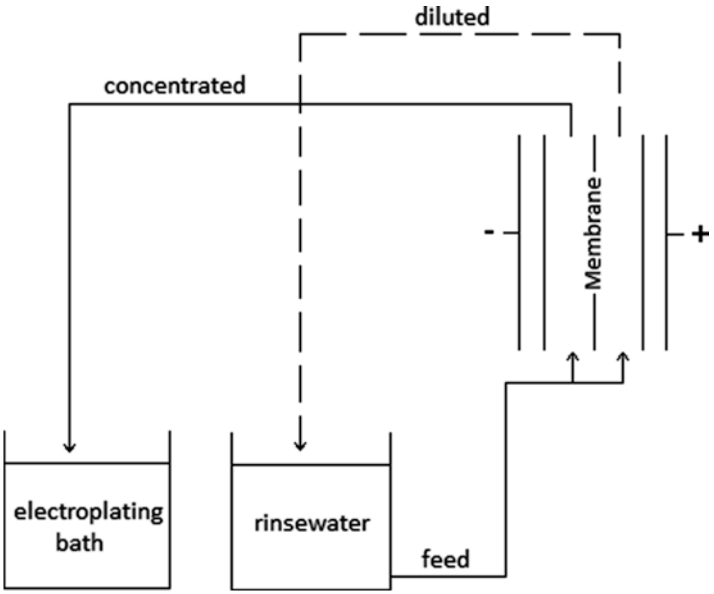

Fig. 5.2 Flow chart illustrating the application of electrodialysis in the galvanic process. Exhausted rinsewater is diluted and concentrated by an electrodialyzer allowing the recovery of chemicals and water in the process. Modified after Chiapello and Gal (1992)

5.2.4.1 Zinc

Zinc is need as a micronutrient; however, due to its increasing world production this metal is disseminated in the environment as a contaminant. It is found in several wastewaters, in concentrations ranging from lower than 1 mg/L to higher than 48 g/L (Babilas and Dydo 2018). Once this metal is one of the most hazardous metals, whose high concentrations cause significant environmental and human health problems, there are limits for discharge and ingestion (Caprarescu et al. 2017). The United States Environmental Protection Agency has reported that, because of taste, drinking water should contain no more than 5 mg Zn/L (ATSDR 2005). Additionally, for wastewater discharge, Brazilian guidelines, for instance, limit to the same concentration (CONAMA 2011). In order to reach the limiting value for discharge and aiming zinc recovery, electrodialysis has been successfully investigated.

Herraiz-Cardona et al. (2010) evaluated the zinc transport properties across a cation-exchange membrane, 67-HMR-412 (Ionics, USA), for a treatment of the rinsewater from the $ZnSO_4$ plating baths by electrodialysis. The study provided very significant data regarding to operate an electrodialysis system at overlimiting membrane current density condition, where phenomena as electroconvection and water splitting may occur. The authors appointed that at this condition, changes in pH on the solution/membrane diffusion boundary layer should occur for 0.125 M $ZnSO_4$ + 0.125–0.375 H_3BO_3 solutions, causing the precipitation of $Zn(BO_2)_2$ on the diluted side of the cation-exchange membrane. The obtained data revealed also that the greater the boric acid concentration, the greater the $Zn(BO_2)_2$ precipitated.

Bittencourt et al. (2017), evaluating the electrodialysis at under and overlimiting membrane current density conditions, with a model zinc electroplating effluent (0.5 g/L $ZnCl_2$ + 2.0 g/L KCl + 0.25 g/L H_3BO_3) and heterogeneous Chinese origin membranes, observed that more than 98% of chloride, zinc and potassium ions were removed from the effluent, and independent of the current density applied none precipitation of insoluble species onto the membrane surfaces was verified. The study also showed that operating at overlimiting mode a 42% time saved is achieved, enabling a material cost economy with reduced membrane area needed, however at the expense of increase energy consumption than at underlimiting mode.

Babilas and Dydo (2018) evaluated the selective zinc recovery from galvanic rinsewater by electrodialysis improved by complex formation. The study, did with model zinc electroplating solutions having 0.748 M $ZnSO_4 \cdot 7H_2O$ (48.9 g Zn/L) + 0.0089 M $Fe_2(SO_4)_3 \cdot xH_2O$ (1 g Fe/L) + specific chelating agent (lactic, malic or citric acids), with a membrane current density of 25 mA/cm^2 and heterogeneous, Ralex AM(H)-CM(H) (Mega, Czech Republic), and homogeneous, Neosepta AMX–CMX (Astom, Japan), Selemion AMV–CMV (Asahi Glass, Japan) membranes, showed that, among the investigated membranes and complexing agents, the heterogeneous Ralex CM(H)-AM(H) membranes using citric acid as complexing agent achieved the highest zinc removal selectivity. Zinc recovery higher than 86%, with a current efficiency of 85% and 92% for ferric retention coefficient was achieved.

Caprarescu et al. (2015), studying the removal of Zn^{2+} from 1.5–6 g Zn/L simulating electroplating acid wastewaters using adsorbents/ion-exchangers-polyvinyl alcohol blended membranes, described that the removal ratio of the metal ion growths with the concentration, as well as with the flow rate. Under a constant voltage of 5 V, with a flow rate of 6.6 mL/min and a solution concentration of 6 g Zn/L, the authors achieved a zinc removal ratio of 77.5% with an energy consumption of 242.7 kWh/m^3.

5.2.4.2 Chromium

Chromium species are considered as a major environmental concern in metallurgical and rinsewater from electroplating processes (Hosseini et al. 2019). United States Environmental Protection Agency has a drinking water standard of 0.1 mg/L for total chromium. This considers all forms of chromium, including the most toxic, Cr(VI). The current standard is due to potential adverse dermatological effects over many years, such as allergic dermatitis (skin reactions) (US EPA 2019). For wastewater discharge, limit values of 1 mg/L for Cr(III) and 0.1 mg/L for Cr(VI), as defined in Brazilian law (CONAMA 2011), or most restrictive standards, need to be reached.

Moura et al. (2012) evaluated the removal of chromium ions from a 60 mg/L Cr(III) metal-finishing effluent with synthetized blended high impact polystyrene/polyaniline cation-exchange membranes and with a commercial Nafion 450 cation-exchange membrane. The authors reported better chromium removal results with the commercial membrane and associated this fact to the lower electrical resistance of the commercial membrane if compared to the synthetized ones. Using the commercial membrane and applying a current density of 10 mA/cm^2, a percent extraction of 37.9% of chromium ions, from a 0.2 L feed solution, was achieved with 3 hours of electrodialysis and a membrane area of 16 cm^2.

Chen et al. (2009) studied the purification and concentration of chromate ions from a 418 mg/L Cr(VI), 7.4 mg/L Ca^{2+}, 2.3 mg/L Mg^{2+}, 19.8 mg/L SO_4^{2-}, 164 mg/L Na^+, 90 mg/L Cl^-, 4.2 mg/L total organic carbon and pH 2.2 electroplating plant rinsewater using a two-stage electrodialysis process designed with Selemion AST (Asahi Glass, Japan) mono-selective anion-exchange membranes and Selemion CMV (Asahi Glass, Japan) non-selective cation-exchange membranes. The proposed electrodialysis process, conducted at a membrane current density of 30 mA/cm^2, and based on the ability of mono-selective membranes to separate monovalent and divalent ions, provided the removal and concentration up to 191% of $HCrO_4^-$ (stable chromate form at pH 2.2) in the first stage and, by adjusting the pH of the first stage concentrated stream to 8.5, the separation of 45% of the equally concentrated chloride ions from CrO_4^{2-} (stable chromate form at pH 8.5), in the second stage.

Chang et al. (2015), studying the recovery of chromate ions from a plating wastewater concentrated by a micellar-enhanced ultrafiltration process, using an Ionac MA-3475 (Sybron Chemicals Inc., USA) anion-exchange membrane, identified a chromate recovery of 85.3% with 6 hours of electrodialysis using a current density of 20 mA/cm^2.

Marder et al. (2016) examined the use of electrodialysis applied to a chromate-free coating process. The study, accomplished with 0.005 M Na_2MoO_4 solutions and Chinese origin ion-exchange membranes, allowed defining suitable solution pH and current density conditions to remove molybdate ions (MoO_4^{2-}). Operating at a solution pH of 6.5, the authors reported that the limiting current density should be respected, since at overlimiting current density conditions, an undesirable fixation of polynuclear anions ($HMo_7O_{24}^{5-}$, $H_2Mo_7O_{24}^{4-}$, $H_3Mo_7O_{24}^{3-}$), resulted from water splitting, occurred on the anion-exchange membrane structure. With a solution pH of 4.8, a non-practicable condition is reported, independently of the applied current density, since the polynuclear anions are the dominant molybdate species in solution. At a solution pH of 12.0, a favorable condition was achieved, since no evidence of polynuclear anions was observed to a wide range of current density values. However, to properly operate an electrodialysis system at this pH condition of 12.0, the authors caution against the need of using alkali resistance anion-exchange membranes. The stability of the ion-exchange membranes is also something appointed to be taken in account with chromium containing solutions (Frenzel et al. 2005a, b; Korzenowski et al. 2008). In this case, the necessity of using oxidative resistance ion-exchange membranes is stated.

5.2.4.3 Copper

Copper is one of the most valuable and predominant metals used in the industrial sector, with a myriad of applications, such as metal finishing, electroplating, etching, and plastics (Mohammadi et al. 2004; Caprarescu et al. 2014; Scarazzato et al. 2017). Consequently, it is frequently found at high concentrations in wastewaters. Nevertheless, the United States Environmental Protection Agency fixed its permissible limit in industrial wastewaters at 1.3 mg/L, while the World Health Organization reports that in drinking water it should not overtake 2 mg/L (WHO 2004).

For copper, a first electrodialysis treatment was reported in 1978. Copper-mine brackish waters with a salinity between 3 and 8000 mg/L were desalted in the electrodialysis process involving a system of cation-exchange and neutral membranes (Winnicki and Manczak 1978). Huang et al. (1983) studied the transport of copper ions across ion-exchange membranes in a 3 compartment electrodialysis cell with effective membrane area of 4 × 5 cm^2. The effects of thickness of electrodialyzer and viscosity of electrodialysate solution to the ionic mass transfer rate were evaluated, since copper is found in many different industrial wastewaters. The authors developed a math equation for describe the ions transport.

There were studies evaluating commercial and laboratory membranes, ions transport and different electrodialysis systems and configurations. A variation of electrodialysis, the electrodeionization, where ion-exchange resins is included inside the diluted compartments of an electrodialysis system, was efficient on the removal of nickel and copper from industrial wastewater, achieving removal rates as high as 84% for copper (Dermentzis et al. 2009).

Caprarescu et al. (2014) studied the copper removal from synthetic wastewater solutions. In batch mode and operating at a constant potential value of 9 V, a circular electrodialysis cell with three compartments was used. These compartments was separated by different polymer ion-exchanging membranes based on the copolymer acrylonitrile-vinyl acetate-α methyl styrene and containing small quantities of cation- (Puropack PPC100) or anion-exchange resins (Purolite A500). The results showed ion removal rates increasing with the solution flow rate and the percent extraction of copper ions increased over 88%, when initial copper ions concentration was high (4000 mg/L).

Recently, studies evaluated the feasibility of the wastewater treatment from new developments in copper plating baths, once cyanide based baths have been replaced by agents as 1-hidroxietane-1,1-diphosphonic acid in order to reduce the toxicity and risks related to the process. The treatment of synthetic wastewaters from the 1-hidroxietane-1,1-diphosphonic acid-Cu bath by applying electrodialysis (Scarazzato et al. 2015) showed up to 99% of ions removal and no membrane clogging was detected.

These initial results motivated a detailed investigation aiming to close the loop in the electrodialysis usage for the evaluated bath. Thus, the research group (Scarazzato et al. 2018) treated a 1-hidroxietane-1,1-diphosphonic acid-Cu bath with initial copper concentration of 45 mg/L and electric conductivity of 1.72 mS/cm in lab scale. The demineralization rate and ions removal achieved up to 90% and 80%, respectively. In bench scale, a 5-cycle of rinsewater treatment and concentration test resulted in a concentrated solution containing 259 mg Cu/L. The concentrated solution was applied as bath reinforcement and the diluted one was used as rinsewater in electrodeposition tests. In addition to the high rates of copper recovery from electroplating wastewater, with simultaneous water reclamation, the tests confirmed the quality of the obtained solutions in the reuse test.

5.2.4.4 Nickel

Nickel is mainly employed in the production of nickel alloys and stainless steel. It is also extensively applied in coating processes once increases the corrosion resistance as well as gives decorative characteristics (Schario 2007; Benvenuti et al. 2017). Nickel is also a toxic metal even at low concentrations. The limit for nickel in industrial wastewaters was reported by United States Environmental Protection Agency as 2 mg/L, on the other hand, the World Health Organization stated that nickel content in drinking water should not overtake 0.02 mg/L (WHO 2004).

Primary studies that successfully applied electrodialysis for treating electroplating baths and rinsewater containing nickel were reported in 1972 (Trivedi and Prober 1972) and promoted the industrial application, directly into a plating bath (Tison and Mikhail 1982). They assessed electrodialysis employing a low electric current to recycle and recover nickel (salts) from diluted wastewater. The electrodialysis cell used nickel metallic plates as electrodes and two membranes, one cation-exchange before the cathode and one anion-exchange before the anode, forming a three compartment electrodialysis cell. It was used to treat a diluted solution from a Watts nickel process having 4000 mg Ni/L, which, in turn, fed the central compartment while the others contained the concentrated nickel bath. Their findings indicated that nickel in typical rinsewater concentrations can be transported electrically through commercial ion-selective membranes, to a concentrated Watt's nickel plating bath containing 72,000 mg/L. Current efficiency near 90% was reached with current densities as low as 3.0 mA/cm^2. The lowest current densities indicated loss of efficiency, on the nickel diffusion across the membranes. The study verified that without current application, there was a diffusive transport of nickel through the cation-exchange membrane at a rate of 7.1 x 10^{-5} g/(h cm^2). During the evaluation, nickel and water co-transported were recycled as a concentrated solution which did not cause a bath dilution.

With the same motivation, Benvenuti et al. (2014) performed the treatment of synthetic nickel plating rinsewater in bench scale and the produced solutions, diluted and concentrated, were evaluated for reuse as rinsewater and bath reinforcement in laboratorial tests, respectively. The electrodialysis treatment achieved a percent extraction for nickel around 97%. The diluted solution with an electric conductivity of 130μS/cm was able to be reused as rinsewater. The concentrated solution, produced in concentration mode, reached 53,000 mg Ni/L, near to the operational range for nickel plating bath. This solution can feed the bath and help the recovery of volumes lost by dragging out and evaporation during the nickel-plating process. The reuse tests were successful, indicating that the solutions recovered by electrodialysis do not cause any damage to the quality of plated pieces, either in appearance or in corrosion resistance.

New bench-scale electrodialysis tests were performed by Benvenuti et al. (2017), who treated a synthetic solution simulating a nickel plating rinsewater. The solution contained nickel sulfate, nickel chloride and boric acid of analytical grade and commercial organic additives, featuring 1300 mg Ni/L, conductivity of 3 mS/cm, 27 mg/L total organic carbon (organic matter) and pH close to 4. Based on the bench scale results, an electrodialysis plant was inserted in an industrial nickel plating process, and the reuse of treated rinsewater and concentrated solution was included as operational routine in the production line (Benvenuti et al. 2016, 2017). Nickel plating rinsewater was pumped to electrodialysis system continuously and directly from the process line during the work time, 18 h/day, and monitored for 40 days. The electrodialysis operated in reversal mode allowed an effective nickel removal and demineralization, both over 95%. Considering that the rinsewater treated by electrodialysis presented sufficient quality to be reused in the nickel plating process, during the test, the rinsewater was continuously treated by electrodialysis and recycled back into the process, avoiding thus the use of clean water, saving 96 m^3/year in this step. Additional gains are related to the increase in ion-exchange resins lifetime, in use in the industrial plant, and the reuse of concentration solution, that achieved an average concentration of 20,000 mg Ni/L. The recovery of nickel, other salts and also organic additives, reduced the costs with chemicals and maintained the quality of the nickel plating bath without harm the produced pieces.

The behavior of nickel transport through Nafion 117 cation-exchange membranes was studied for plating solutions containing also chromium (Martí-Calatayud et al. 2011). Chronopotentiometric analysis revealed the competition between Ni^{2+} and H^+, indicating that, in acidic media, the transport number for nickel through the membrane can be low, reducing the current efficiency for nickel. Among the results obtained, this study indicated the need of consider the pH during electrodialysis treatment for nickel removal.

Among the variations of electrodialysis system, the electrodeionization reversal, working with a polarity reversal time of 4 h, displayed a good separation performance, in such a way that 97.0% of Ni^{2+} was removed from the initial solution and simultaneously recovered into a highly concentrated stream (3961 mg Ni/L), which represents a concentration factor of 79.2. In this study, Lu et al. (2014) achieved a current efficiency of 32.6% and energy consumption of 1.02 kWh/m^3. Thus, electrodeionization reversal is able to promote the recovery and reuse of metal ions from metal plating rinsewater.

Electrodeionization and complexing agents were associated for the selective separation of nickel and cobalt ions from diluted solutions (Taghdirian et al. 2010). The separation of Ni^{2+} and Co^{2+} ions was performed applying electrodialysis by adding ethylenediamine tetraacetic acid, since the highest stability of the ethylenediamine tetraacetic acid complex with nickel. Using a three-chamber electrodialysis cell, where the central chamber was separated from the others by two cation-exchange membranes (CR67 MKIII, Ionics, USA). Strongly acid cation-exchange resins (Purolite, C100E), in the H^+ form, was used to fill the central chamber. A platinum-coated titanium mesh was used as anode while stainless steel was used as cathode. A 0.05 M sulfuric acid solution filled the electrodes chambers. The nickel in solution as a negatively charged complex due to the Donnan exclusion effect did not allow the transport of this complex into the gel phase of the membrane and resins.

5.2.5 Use in Mining and Mineral Processing Industry

The interest in recovering valuable metals increased with the threat of depletion of non-renewable resources. The amount of copper in ores, for instance, decreased from 4% to less than 1% in the last century and it is possible that copper demand will surpass its production through the next years (Veit 2005; Scarazzato et al. 2017). Nickel sulfide ores represent the minority of the sources of nickel production, but they usually present an easier beneficiation route. On the other hand, laterite ores account for 60% of nickel sources and usually contain higher concentration of nickel. Due to the easier extraction and beneficiation, sulfide ores will deplete sooner than laterite ores. If nickel mining starts to be performed mostly from lateritic ores, the price per ton may be greatly affected (Mudd 2010).

The reported scenarios motivated the development of secondary beneficiation routes for recovering valuable compounds using hydrometallurgy processing (Bernardes et al. 2004; Provazi et al. 2011; Yamane et al. 2011; Silvas et al. 2015). Electrodialysis allied with those hydrometallurgical routes may allow the recovery of metals and chemicals of economic interest (Cifuentes et al. 2009; Song and Zhao 2018).

Studies conducted by Cifuentes et al. (2009, 2014) have demonstrated that the electrodialysis operating in reactive mode is a promising technology to be used in the copper and zinc electrowinning stage of the copper and zinc metals production. The proposed reactive electrodialysis method consists in a two-chamber reactive electrodialysis module type, separated by an anion-exchange membrane and, with the copper or zinc solution from the leaching and purification metal production stage, basically $CuSO_4$ or $ZnSO_4$ dissolved in sulfuric acid, placed in contact with a cathode, as represented in Fig. 5.3. With this arrangement and, under the effect of an electric field, the copper or zinc metal ions are reduced on the cathode, promoting its recovery from the solution. In the anode chamber, the authors suggested the use of a solution with ferrous sulfate ($FeSO_4$) and sulfuric acid, once the Fe^{2+} is quickly oxidized to Fe^{3+} on the anode, resulting in low energy consumption and forming a ferric sulfate (Fe_3SO_4) solution, which is appointed as a suitable product to further uses.

Studying the process performance with 190 g/L of H_2SO_4 + 1 M Fe^{2+} (as $FeSO_4·7H_2O$), 190 g/L of H_2SO_4 + 30 g/L of Cu^{2+} (as $CuSO_4·5H_2O$), copper sheet as

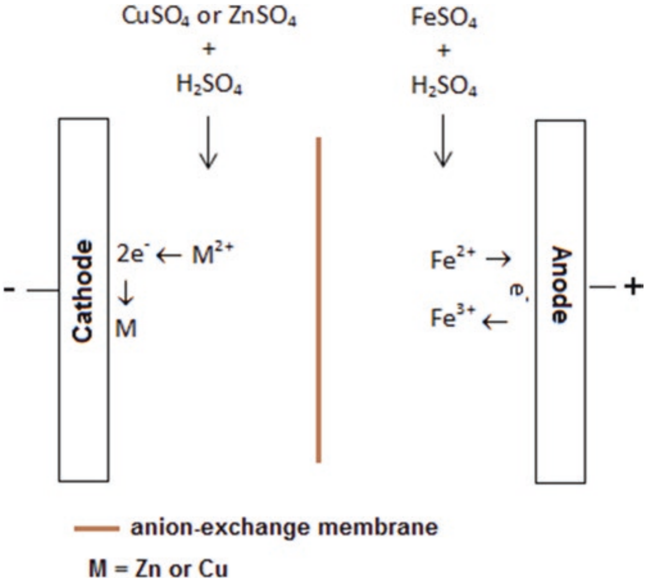

Fig. 5.3 Two-chamber reactive electrodialysis principle on Zn or Cu electrowinning. Zn or Cu metal ions are reduced in the cathode, allowing its removal and recovery from metal sulfate acid solutions, while Fe^{2+} is oxidized in the anode. Modified after Cifuentes et al. (2004)

cathode, platinum as anode, Ionac 3475 (Sybron, USA) as anion-exchange membrane, cathode current density of 30, 45 and 60 mA/cm^2, flow rates of 700, 800, 900 and 1200 cm^3/min and working solution temperatures of 40, 50 and 60 °C, Cifuentes et al. (2009) reported an average cathode current efficiency of 98.7% for all the conditions tested and specific energy consumption varying between 0.51 and 2.05 kWh/kg-Cu. The lowest specific energy consumption was achieved with the highest cathode current density, flow rate and temperature conditions (60 mA/cm^2, 1200 cm^3/min and 60 °C).

Studies conducted by Martí-Calatayud et al. (2014) and Cifuentes et al. (2015) have also demonstrated that the reactive electrodialysis can be employed in the recovery of acids from mining and mineral processing activities with simultaneous metal ions removal. In this case, it is proposed the use of a three-chamber reactive electrodialysis module type, separated by a cation- and an anion-exchange membrane, with the working solution filling the middle module chamber. With this arrangement and, under the influence of an electric field, metal cations are transferred to the cathode chamber, crossing the cation-exchange membrane and, acid anions to the anode chamber, crossing the anion-exchange membrane. Furthermore, protons are generated at the anode from the oxidation of water. Consequently, the acid concentration increases in the anode chamber allowing its recovery.

Studying the process performance to recover hydrochloric acid contaminated with antimony and bismuth metal ions, resulted from ion-exchange resins regeneration in copper electrorefining practice, and conducted with a 6 M HCl solution, stainless steel plate as cathode, graphite block as anode, Chinese origin ion-exchange membranes, anode current density of 30, 40 and 50 mA/cm^2, flow rates of 1 and 0.5 L/min and working temperatures of 20, 30 and 40 °C, Cifuentes et al. (2015) reported an enhanced process performance operating at lower current density and higher temperature and flow rate. Applying an anode current density of 30 mA/cm^2, with a flow rate of 1 L/min and a temperature of 40 °C, the authors obtained a specific energy consumption of 3.4 kWh/kg-Cl.

Martí-Calatayud et al. (2014), studying the recovery of sulfuric acid from a model acid mine drainage solution (0.02 M $Fe_2(SO_4)_3$ + 0.01 M Na_2SO_4, pH 1.68) and conducted with an AISI 304 stainless steel plate as cathode, a RuO_2/IrO_2:0.70/0.30 coated sheet of titanium as anode and Chinese origin ion-exchange membranes, reported that the acid recovery decreases and an $Fe(OH)_3$ precipitated is formed on the cation-exchange membrane if the applied current density trespass the membranes limiting current density values. Therefore, to assure a good operational performance, the authors appointed that the $Fe(OH)_3$ precipitation should be prevented, since it increases the reactive electrodialysis module voltage, rising the energy consumption for the process.

5.2.6 Final Considerations

Studies and applications of electrodialysis and its variations as treatment in order to extract metals from water and wastewater, highlighting metallurgical area, in plating processes and mining, reported the effectiveness of the technology not only for the production of clean water or water recovery from wastewater, but mainly as an alternative treatment for the recovery of metals as reusable solutions in plating processes or as pure metals or metal alloys in mining processes, for many different applications. In this sense, the development of new membranes and studies about operational parameters and different solutions composition, including the presence of organic compounds as binders or metal complexing agents tends to improve the already obtained results and enlarge the application of electrodialysis process for metals removal and recovery.

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Chapter 6
Metal Oxides for Removal of Heavy Metal Ions

Trishamoni Kashyap and Biswajit Choudhury

Abstract "Heavy metals" are elements of high atomic weight with a density much higher than that of water. Presence and the use of these heavy metals are found in agriculture, medicine, electronics, paints, and many others. These heavy metals are non-biodegradable and are toxic to human and animal health if found above the permissible limit. These metals enter the human body via food, drinking water, and air. These heavy metal ions inside the biological system are not easily disposed-off. These ions start damaging different tissues and organs.

Herein, we discuss heavy metal ion contamination in water and their subsequent removal by adsorption based technique using metal oxide nanostructures. Metal oxides are particularly useful for water decontamination because of its chemical stability and durability, low-cost fabrication, and availability. Metal oxides of various shapes and morphology have different sorption capacity for heavy metal ions. A few examples of metal oxides are titanium dioxide, manganese oxide, iron oxide, zinc oxide, silica, aluminum oxide and their binary hybrids. We have discussed the removal of arsenic, lead, cadmium, mercury, chromium, which possess potential health hazard. The health effects of copper, and zinc are also briefly discussed. Freundlich and Langmuir isotherm models are considered to measure the adsorption of heavy metals. We have addressed the mechanism of heavy metal ion adsorption in different systems of metal oxide surface. We have discussed the impact of pH, contact time, the initial dose of metal ions and adsorbent on the overall efficiency of the adsorption process.

Keywords Adsorption · Heavy metals · Isotherm · Surface area · Porosity · Morphology · Nanostructures · Metal oxide · Toxicity · Hazard

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6.1 Introduction

Industrial wastes including battery wastes, electronic wastes, nuclear plants wastes, mining wastes contain a large number of heavy metal ions. These metals are arsenic, lead, mercury, cadmium, chromium, zinc, nickel, and uranium (Gautam et al. 2015). The wastes disposed at landfill sites, and water bodies can contaminate agricultural soils and drinking water. The metals are non-biodegradable. A high dose of these ions inside a human or animal body cause health hazards. For example, the presence of lead in human can cause kidney problem, nervous system problem, problems in the reproductive organs. Exposure to cadmium creates damage in bone, liver, and blood.

Copper is an essential element for metabolic functioning. However, a large amount of copper can cause gastrointestinal problems, liver, kidney, renal, and cardiac problems (National Research Council (US) Committee on Copper in Drinking Water. Copper in Drinking Water. Washington (DC): National Academies Press (US); 2000. 5). Similar to copper, another essential element is zinc. Toxic effects of zinc on human health is rare; however, a high dosage can cause brain problem (Plum et al. 2010).

A major heavy metal ion contamination in water is arsenic. Its predominant forms are arsenic (+5) and arsenic (+3). Arsenic has a strong carcinogenic effect and might cause skin cancer, lung cancer, bladder cancer, liver cancer, prostate cancer, and leukemia (Hong et al. 2014). Drinking of mercury-contaminated water results in damage to the kidney, lung, nervous system (Song et al. 2013). Various environmental agencies in the world have set a maximum permissible limit for heavy metal ions in water (Kumar and Puri 2012). In India, the permissible amount of arsenic, chromium, copper, lead, mercury, and zinc are 0.05 mg/L, 0.05 mg/L, 0.05 mg/L, 0.1 mg/L, 0.001 mg/L, and 5 mg/L, respectively (Kumar and Puri 2012).

The different techniques available for cleaning wastewater are precipitation, reverse-osmosis, ion-exchange, sedimentation, photocatalysis, and adsorption (Gautam et al. 2015). In this chapter, we will discuss the adsorption method for cleaning wastewater. Adsorption method for the uptake of heavy metal ions is a simple process with smooth operation. Hence, this chapter will be dedicated to the use of metal oxides for the removal of heavy metal ions from water.

6.2 Adsorption Methods

We will consider batch operation for measuring the amount of heavy metal ions captured by the metal oxides. In a batch adsorption process, a measured amount of sorbent is mixed with a specific volume of the adsorbate. Several factors are considered in the sorption technique, including pH, contact time, temperature, adsorbent, and adsorbate amount (Al-Anber 2011). Suppose C_0 (mg/L) is the initial concentration of any heavy metal ion, C_t (mg/L) is the concentration measured after a contact time t, C_e (mg/L) is the equilibrium concentration (Zha et al. 2014). Thus, removal efficiency R (%) is expressed as-

$$\%R = \frac{C_0 - C_t}{C} \times 100 \tag{6.1}$$

Suppose, q_t (mg/g) is the amount of any heavy metal ion adsorbed at any time t, and q_e (mg/g) is the adsorbed amount at equilibrium.

$$q_t = \left(C_0 - C_t\right)\frac{V}{m} \tag{6.2}$$

$$q_e = \left(C_0 - C_e\right)\frac{V}{m} \tag{6.3}$$

where V is the solution volume (L) and m is the mass of adsorbent (g).

Adsorption techniques for heavy metal ions removal mostly consider two adsorption isotherms: (1) Freundlich and (2) Langmuir. Although other adsorption techniques are also adopted, we will discuss these two models to determine the uptake amount of heavy metal ions by the metal oxides.

Freundlich Isotherm The Freundlich Isotherm is described with the following equation-.

$$\begin{aligned} q_e &= k_f C_e^{1/n} \\ \ln q_e &= \ln k_f + \frac{1}{n} C_e \end{aligned} \tag{6.4}$$

The Freundlich model assumes multilayer heterogeneous surface adsorption (Zha et al. 2014; Xiao et al. 2009; Le and Van Phuc 2015). In this equation, q_e (mg/g) is the amount of metal ions adsorbed at equilibrium, C_e (mg/L) is equilibrium metal ion concentration, k_f is Freundlich constant (mg/g) measuring the sorption ability of adsorbent, n is the heterogeneity factor and measures the adsorption capacity of the adsorbent.

Langmuir Isotherm It involves a monolayer adsorption process on a homogenous surface. It does not consider any interaction between adsorbate and adsorbent. The general expression of Langmuir adsorption isotherm is-

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \tag{6.5}$$

The terms C_e, q_e are already defined in Eq. 6.1. $k_L$is Langmuir constant (L/mg), q_m is the maximum adsorption capacity of the adsorbent (Zha et al. 2014; Mishra et al. 2018b).

6.3 Metal Oxides for the Removal of Heavy Metal Ions from Water

In this section, we will discuss the various types of metal oxides which are used for the sorption of heavy metal ions from water. These heavy metals are present in their ionic states in various oxidation states, such as +2, +3, +4, +5, +6.

6.3.1 Titanium Dioxide

Titanium dioxide nanowires, nanoflowers, and nanospheres show excellent results in the removal of heavy metal ions from water. In a column elution technique, titanium dioxide nanowires are loaded onto a glass column containing cotton. Water containing zinc (+2), copper (+2), cadmium (+2), lead (+2) passes through the column (Youssef and Malhat 2014). The sample collected is tested for the metal ion concentration with atomic absorption spectroscopy. The percentage removal of various metal ions at pH 7 follows an order of lead (+2) > iron (+3) > copper (+2) > cadmium (+2) > zinc (+2). It indicates a better adsorption affinity and removal capacity of titanium dioxide nanowire for lead (+2) than zinc (+2).

The extent of lead (+2) adsorption varies over a surface-modified titanium dioxide (Seidlerová et al. 2016). For example, magnetically modified titanium dioxide nanoparticles show a better affinity for lead (+2) adsorption than that of unmodified one. The maximum amount of lead (+2) per unit mass of adsorbent (mg/g) is calculated using linear and non-linear regression using Langmuir isotherms. Lead (+2) forms monolayer adsorption over titanium dioxide surface. The amount of lead (+2) adsorption over magnetic titanium dioxide is 162 mg/g, while over non-magnetic titanium dioxide it is 127 mg/g. Similarly, the calculated value of Freundlich constant for magnetic titanium dioxide is comparatively higher than nonmagnetic titanium dioxide. The surface heterogeneity of magnetically modified titanium dioxide is the reason for the enhanced sorption ability over unmodified titanium dioxide (Seidlerová et al. 2016).

One study considers the influence of different parameters on the extent of lead (+2) adsorption over titanium dioxide. These parameters include the presence of functional groups on titanium dioxide, sorbent content, pH (Jin et al. 2015). The presence of surface hydroxyl groups provides anchoring sites for lead (+2) adsorption. For a fixed initial lead (+2) concentration, an increase in titanium dioxide dosage (g/L) leads to enhanced lead (+2) ions adsorption. Adsorption steadily decreases at a high titanium dioxide dose because of the titanium dioxide aggregation. The adsorption process is pH-dependent because the interaction between heavy metal ions and adsorbent is electrostatic. A pH variation on lead (+2) adsorption shows that 90% adsorption occurs at a pH 6.0. Electrostatic stabilization between cationic lead and negatively charged metal oxides stabilizes the adsorption process. At a pH lower than 5.5, cation exchange reactions dominate the adsorption process. However, at pH 6–11, the adsorption decreases because of the precipitation of different hydroxide species of lead and an increased electrostatic repulsion between negatively charged ions and titanium dioxide surface.

Co-adsorption of neutral arsenic (+3) and cadmium (+2) from aqueous solution occurs via a surface complexation modelling (Hu et al. 2015). The coexistence of arsenic (+3) and cadmium (+2) in solution forms a ternary surface complex cadmium-arsenic-titanium dioxide. Titanium dioxide surface has limited available sites for cadmium adsorption. The adsorption on the vacant surface sites is 13.4 μmol/m^2. In the presence of arsenic (+3), cadmium (+2) adsorption elevates, thus increasing the cadmium adsorption to 25.2 μmol/m^2. Surface complexation is the dominant way for enhanced cadmium and arsenic adsorption and their subsequent removal. Similarly, arsenic adsorption increases from 1.6 μmol/m^2 in arsenic-titanium dioxide to 4.6 μmol/m^2 in cadmium-arsenic-titanium dioxide.

Titanium dioxide microspheres display useful properties for the strong adsorption of heavy metal ions. Some of the properties are high surface area with mesoporous structure, wrinkled surface with high external surface area for ion accumulation, and presence of surface abundant hydroxyl groups (Yu et al. 2018b). An acidified titanium dioxide microsphere reduce chromium (+6) to chromium (+3). At a low pH, the dominant chromium (+6) species, such as chromate ion interact actively with protonated titanium dioxide surface. However, at pH 10, chromate ion and the deprotonated negative surface of titanium dioxide repel each other leading to weak chromium (+6) adsorption. The initial chromium (+6) concentration is 10 ppm, and sorbent dose is 1 g/L. There is a rapid uptake of 3 mg/g of chromium (+6) in the first 5 min. The adsorption increases to 5.5 mg/g after 5 h. Titanium (+3) on the lattice site acts as reducing sites for chromium (+6) to chromium (+3) conversion (Yu et al. 2018b).

Titanium dioxide dandelion and flowers show different attributes in cadmium removal from waste water (Zha et al. 2014). Dandelion with a surface area of 226 m^2/g adsorbs 396 mg/g of cadmium, whereas flowers with a surface area of 172 m^2/g remove 282 mg/g of cadmium from wastewater. Cadmium forms a preferential attachment with the hydroxyl moieties on titanium dioxide. Antimony pollution is an another aquatic hazard. Both antimony (+3) and antimony (+5) are active heavy metal pollutants, which can be effectively removed using titanium dioxide nanotubes (Zhao et al. 2019). The activity is tested with tap water, natural surface water, and wastewater. The adsorbed amount of antimony (+3) and antimony (+5) on titanium dioxide nanotube is 250 mg/g and 56.3 mg/g, respectively. The higher adsorption of antimony (+3) than antimony (+5) is because of the strong attraction on the hydroxylated {101} and {001} titanium dioxide facets (Zhao et al.). In comparison to titanium dioxide nanoparticles, layered sodium titanate shows the excellent result in adsorption and removal of strontium (2+), barium (2+), and lead (+2) via an ion exchange method between adsorbed heavy metal ions with a high concentration of interlayer sodium ions (Yang et al. 2008).

6.3.2 Manganese Dioxide

The different crystallographic forms of manganese dioxide are α, β, γ, δ, and λ. These different forms or structures have different sorption ability for heavy metal ions. The sorption ability follows an order δ> α>λ >γ > β. δ-manganese dioxide is capable of adsorbing 242.6 mg/g of lead (+2). α-manganese dioxide adsorbs 84.4 mg/g, β-58.9 mg/g, γ-62.1 mg/g, and λ-61.9 mg/g (Zhang et al. 2017b). The surface area of δ-manganese dioxide is 270.8 m^2/g, α has 97.5 m^2/g, β-14.2 m^2/g, γ-71.4 m^2/g, and λ-36.6 m^2/g. Therefore, the high surface area of δ-manganese dioxide is responsible for the increased adsorption of lead (+2). Layered manganese dioxide or birnessite materials possess both internal cationic vacancies and particle edges as the adsorption sites for the metal ion. Although the cationic manganese vacancies in the layered structure interact with both cadmium (+2) and lead (+2), the external edges provide specific binding sites for lead (+2) (van Genuchten and Peña 2016). A pair distribution function analysis is performed to conduct these adsorption studies.

Layered δ-manganese dioxide can also efficiently remove copper (+2) from water. At a high pH, manganese dioxide surface becomes negatively charged. Adsorption of copper (+2) increases from 30% to 99.5% as pH increases from 2.4–6.0. The negatively charged surface attracts electrostatically copper (+2). Adsorption occurring at a low pH <3.2 is due to inner sphere complexation reaction (Kim et al. 2014). If the polluted water contains calcium chloride along with copper (+2), an interference from calcium (+2) lowers the adsorption on manganese dioxide. The adsorbed copper (+2) is easily desorbed by light irradiation.

α-Manganese dioxide microsphere is an excellent sorbent for the removal of lead, copper, cadmium, and chromium (Guo et al. 2014). The microsphere has a loose mesoporous structure with a surface area of 252.8 m^2/g. In an acidic environment of pH 3, these heavy metal ions are removed within 500 min of contact time. Within 500 min, there is nearly 100% removal of lead, 80% removal of copper (+2) and chromium, and 50% removal of cadmium. γ-manganese dioxide is used for the adsorption of lead, cobalt, and copper from aqueous solution (Le and Van Phuc 2015).

γ-Manganese dioxide with a surface area of 65 m^2/g can absorb 200 mg/g lead (+2), 90.91 mg/g cobalt (+2), 83.33 mg/g copper (+2). An interparticle diffusion in the nanostructures facilitate strong metal ion adsorption. A pH variation generate surface charges over manganese dioxide via protonation-deprotonation reactions of the surface bounded hydroxyl groups (Zaman et al. 2009). pH variation of hydroxylated manganese dioxide surface can lead to different extent of heavy metal ion adsorption. There is a ligand exchange interactions between cadmium (+2) and adsorbed hydroxyl groups. Adsorption of cadmium (+2) increases significantly in the presence of phosphate ions. Phosphate ions decrease the positive surface charge on metal oxides, thus increasing the cadmium (+2) sorption. In the presence of phosphate anion there is a formation of inner-sphere complex that increases cadmium (2+) adsorption on manganese dioxide surface.

Nanofibres of α-manganese dioxide can be synthesized from δ-manganese dioxide by a hydrothermal reaction in the presence of graphene oxide, where graphene oxide acts as a structure-directing agent (Luo et al. 2017). The α-manganese dioxide nanofibres acquire a surface area of 144 m^2/g, which is nearly three times higher than the 56 m^2/g in δ-manganese dioxide. Using the Langmuir model, it is calculated that 111.7 mg/g of antimony (+3) are removed, whereas only 89.9 mg/g of antimony (+5) ions are removed. The manganese dioxide nanofibre shows excellent sorption capacity over a pH range from 2–10. Antimony (+3) exists in monohydroxylated cationic forms when $pH < 2$, exists as neutral species for pH 2–10.4, and exists in anionic hydroxylated species at $pH > 10.4$.

γ-Manganese dioxide hollow microspheres containing ferrous species show excellent arsenic removal from water as compared to the undoped γ-manganese dioxide (Ge et al. 2016). Iron-doping changes the morphology of γ-manganese dioxide from needle like nanofibres to flower. The flower is an assembly of many intertwined nanosheets. Iron doped flowery manganese dioxide acquires a surface area and pore volume of 232 m^2/g and 0.34 cm^3/g. Pure manganese dioxide has a surface area of 40 m^2/g and a pore volume of 0.1 cm^3/g. In the adsorption experiment, the initial arsenic (+3) concentration taken is 20 mg/L. The initial concentration of arsenic (+3) is finally reduced to 0.73 mg/L of arsenic (+5) after 7 h of contact with iron-manganese dioxide conjugate. In iron-doped γ-manganese dioxide, γ-manganese dioxide is responsible for oxidizing arsenic (+3) to arsenic (+5). Ferrous ions help in the adsorption of arsenic (+5) and their subsequent release.

Arsenic adsorption is mildly affected by the presence of chloride, nitrate, and sulfate ions in water. However, if the contaminated water contains phosphate co-anions, there is a decrease in the adsorption of arsenic on the iron-doped manganese dioxide. Phosphate ions occupy the preferential adsorptions sites on manganese dioxide, thereby reducing the available adsorption sites for arsenic (+3) (Ge et al. 2016). Like arsenic, chromium (+6) adsorption is also hindered by the co-presence of phosphate ions (Gheju et al. 2016). In the absence of phosphate co-anions the adsorption of chromium (+6) is 0.83 mg/g, whereas the adsorption amount is only 0.18 mg/g when phosphate ions are present in water. Lead (+2) adsorption is studied with β-manganese dioxide. The removal is nearly 58% and it remains constant for a contact time of 6 h (Zhao et al. 2010). The experiment contains an initial lead (+2) concentration of 10 mg/L and sorbent content of 1 g/L. However, an increase in the sorbent content to 1.6 g/L leads to more than 70% lead (+2) removal.

In an extended X-ray absorption fine structure (EXAFS) study, it is revealed that nickel (+2) uptake by manganese dioxide follows an inner-sphere surface complexation reaction rather than an outer-sphere complexation reaction (Sheng et al. 2011). Hydrated nickel (+2) forms a sixfold coordination complex with manganese dioxide sharing both edges and corners on manganese dioxide surface. In the complex structure, edge-sharing nickel-oxygen has a shorter bond length as compared to the corner-sharing nickel-oxygen bonds. Therefore, nickel (+2) uptake by manganese dioxide through edge-sharing is energetically more favorable than that of corner-sharing.

6.3.3 Iron Oxide

Iron oxide is considered to be another widely explored metal oxides for the speedy removal of heavy metal ions from water. Superparamagnetic iron (+2,+3) oxide or ferrosoferric oxide contains iron in valence state +2 and + 3. Ferrosoferric oxide nanoparticles functionalized with carboxyl-terminated species strongly interact with cadmium (+2) ions (Feng et al. 2012). Cadmium (+2) adsorption on the functionalized iron oxide was measured using electrochemical rotating disk electrode method. The adsorption of cadmium (+2) was estimated to be 20 μg/mg on carboxyl functionalized ferrosoferric oxide. The adsorbed cadmium (2+) can be easily desorbed by merely lowering the pH of the medium. Besides cadmium (+2), these carboxyl terminated iron oxide nanoparticles are equally effective in removing lead (+2), and copper (+2). By adopting the Freundlich model, the calculated amounts of cadmium (+2), lead (+2), and copper (+2) adsorption on iron oxide is found to be 74.63, 45.66, 44.84 mg/g at 25 °C. The removal of these ions from water increases as the pH of the solution increases to 5.0. At pH 5–9, there is a marginal increase in ion removal. Thermodynamic consideration shows that the adsorption is maximum at a reduced solution temperature. Moreover, within 30 min of contact time between heavy metal salt-sorbent mixture solution leads to more than 90% removal of metal ions (Shi et al. 2015).

Urchin like structured ferrosoferric oxide microspheres shows high efficiency in the adsorption of lead (+2) and chromium (+6) (Yu et al. 2018a). The microsphere is an assembly of many superparamagnetic iron oxide nanoparticles. Numerous tiny pores are interconnected, forming ion diffusion channel into the interior of the microsphere. The interior of the microsphere contains polyacrylic acid with a terminal carboxyl groups, which binds the diffused lead (+2) ions. There is a maximum 107.4 mg/g adsorption of lead (+2) on urchin-like iron (+2,+3) oxide microspheres. Similarly, there is a maximum 68.7 mg/g adsorption of chromium (+6) on urchin-like iron oxide microspheres (Yu et al. 2018a).

The benefit of using magnetic nanoparticles in ion-separation is because of the strong magnetic moment exhibited by the magnetic iron oxide. Samples with high magnetisation are attracted by a weak magnet. For example, superparamagnetic iron oxide hollow spheres possess a saturation magnetization of 109.48 emu/g. Thus, the adsorbed heavy metal ions on iron oxide hollow spheres can be easily separated from water using an external magnet. If the magnetization is very strong, the nanoparticles with adsorbed ions can be easily removed by a weak magnet. The adsorption of chromium (+6) is simulated with Freundlich and Langmuir isotherms (Liu et al. 2012). The initial concentration of chromium (+6) affects the adsorption of chromium (+6) on iron oxide sorbent. When the initial concentration of chromium (+6) is less than 10 mg/L, Freundlich isotherm determines the adsorbed amount, which is found to be 17.98 mg/g. However, at a very high chromium (+6) concentration (80 mg/L), Langmuir isotherm determines the adsorbed amount, which is found to be 180 mg/g.

Dimercaptosuccinic acid functionalized ferrosoferric oxide nanoparticles with a surface area of 114 m^2/g is an excellent sorbent for a number of toxic metal ions, including mercury, lead, cadmium, thalium, and arsenic. Lead ions have a strong affinity for the dimercaptosuccinic acid-coated iron oxide (Yantasee et al. 2007). Within one minute nearly 99% lead ions were removed by the acid-functionalized iron oxide.

A high surface area alpha phase of iron (+3) oxide shows a strong affinity for arsenic (+5) and chromium (+6). The high surface area of 130 m^2/g and the presence of abundant surface hydroxyl groups are responsible for the enhanced adsorption (Cao et al. 2012b). The hydroxyl groups undergo an ion-exchange reaction with the diffused arsenic and chromium ions. A maximum 51 mg/g of arsenic (+5) and 30 mg/g of chromium (+6) adsorption occurs on the alpha-iron (III) oxide nanostructures. Similarly, hollow nest like alpha-iron (III) oxide nanostructures having a surface area of 152.4 m^2/g can effectively remove 75.3 mg/g of arsenic (+5) and 58.6 mg/g of chromium (+6) from water (Wei et al. 2013).

It is reported that a composite of fly-ash and iron oxide nanoparticles can effectively remove many metal ions, including chromium, lead, copper, and cadmium. At a pH 5, 81.2 mg/g lead (+2) and 24.6 mg/g chromium (+3) are adsorbed (Maiti et al. 2018). The adsorption of ions on iron oxide is more feasible when the reaction temperature is high. Adsorption is measured in the temperature range of 15–45 °C, and the maximum adsorption is recorded at 45 °C. A high temperature facilitates the ion-exchange phenomena leading to higher ion adsorption. At high temperature, water vaporisation starts forming microcavities. These microcavities facilitate the ion-exchange phenomena and increases the ion adsorption.

Gamma phase of iron (+3) oxide nanosheets is an excellent material for the adsorption of heavy metal ions. A report shows the formation of a linear monodentate complex between arsenic-contaminated water and gamma- iron (+3) oxide nanosheets. The complex leaves many hydroxyl groups on the surface of iron (+3) and provides many binding sites for arsenic (Liu et al. 2016). The heavy metal ion adsorption over the nanosheets is a fast process and accommodate 109.5 mg/g of arsenic (+3) and 39.1 mg/g of arsenic (+5) within 15 min of contact time.

Imine functionalized iron (+3) oxide shows selective adsorption for zinc (+2) and lead (+2). Single lead (+2) and zinc (+2) adsorption on aminated iron oxide nanoparticles depend on the pH of the medium (Zeng et al. 2012). In a highly acidic medium (<pH 3), there is no adsorption of these ions. It is due to the competition between proton and the heavy metal cations for binding sites on the sorbent, particularly on the nitrogenated sites of the amine. Protonated iron oxide repels the metal ions from getting adsorbed. The pH range of 6–7 results in 0.24 mmol/g and 0.48 mmol/g adsorption of lead (+2) and zinc (+2) ions. The affinity of lead (+2) and zinc (+2) ions for adsorption on aminated iron oxide is compared. The preferential adsorption of lead (+2) and zinc (+2) on aminated magnetic nanoparticles depend on the types of donor atoms on the sorbent. Since nitrogen is a hard donor, it shows more affinity for hard metal ion zinc (+2) than the relatively soft lead (+2).

In one of the studies, a comparison is made between water-soluble and water-insoluble ferrosoferric oxide nanoparticles in the heavy metal ion removal from wastewater (Wang et al. 2012). Water-soluble ferrosoferric oxide is highly effective in removing more than 80% lead (+2) within the first 20 min of contact time and nearly 42% chromium within 40 min of contact time. The excellent sorption ability of water-soluble ferrosoferric oxide is because of the presence of surface carboxyl groups. There is an electrostatic interaction between negatively charged carboxyl functionalized iron oxide and positively charged heavy metal ions.

6.3.4 Aluminum Oxide

Aluminum oxide or alumina is well known as a sorbent for heavy metal ions. The most common and thermodynamically stable crystalline form of alumina is corundum or α- alumina. Other typical crystalline phases of alumina are cubic γ, η, and δ phase. Alumina exists in monoclinic θ-phase, hexagonal χ-phase, orthorhombic κ-phase. Amongst all these, γ-alumina has its advantage because of the high surface area and stability over the desired range of temperature (Tabesh et al. 2018).

The sol-gel method, vapor deposition, co-precipitation, mechanical synthesis are some of the widely used methods for the preparation of alumina powders (Tabesh et al. 2018). Preparation of ordered mesoporous alumina involves different techniques like nanocasting, dip-coating, anodization, sol-gel method (Drah et al. 2017). γ-alumina is highly ordered and the presence of mesopores and macropores have marked it as a very effective adsorbent for toxic heavy metals. γ-alumina can be used in the form of nanoparticle or as activated alumina. Presence of surface impurities can improve the absorption capacity of alumina. Three-dimensionally ordered γ-alumina can be used for the adsorption of hazardous metal ions like lead (+2), nickel (+2), cadmium (+2) (Drah et al. 2017).

γ-aluminum oxide hydroxide functionalized with thiol groups can be effectively used for the removal of heavy metal ions like mercury (+2), lead (+2), cadmium (+2) (Xia et al. 2017). For lead (+2) ion removal, very high adsorption capacity is achieved with three-dimensional γ-alumina as adsorbent (Drah et al. 2017). The phenomena of adsorption involves four steps-adsorption, ion-exchange, surface complexation, and co-precipitation. A high reaction temperature of 45 °C favors adsorption of 95.39 mg/g lead (+2) over γ-alumina. It also adsorbs 25.39 mg/g of nickel (+2) and 23.32 mg/g cadmium (+2) at 45 °C. Spectroscopic study confirms that the attachment of Lead^{2+} with γ-alumina occurs on the 3-surface oxygen atoms.

Pseudoboehmite like formation with hydroxyl groups linked to the surface of alumina helps in cation absorption. Negatively charged alumina surface is advantageous for metal ion adsorption because of the electrostatic interaction for the oppositely charged ions. The surface charge of an adsorbent can be controlled by maintaining the pH of the adsorbent solution (Tabesh et al. 2018; Drah et al. 2017). With a higher pH than a pH of point of zero charge, the concentration of proton ion decreases in the active sites of alumina surface, which results in a negatively charged surface. Higher is the concentration of the proton ion; lower is the adsorption of metal ions onto the active sites of alumina surfaces as competition between the protons and positively charged metal ions for the active sites increases. Therefore, there is an optimum value of pH for effective adsorption of metal ions in acidic media. On the other hand, precipitation of insoluble metal hydroxides in a basic solution can increase the adsorption of metal ions onto the alumina surface. The optimal pH value for adsorption lies in the vicinity of pH of point of zero charges.

The efficiency of γ-alumina for the removal of lead and cadmium ion increases with increase in pH value and gets saturated after a specified pH value. There is a 97% removal of lead (+2) ion and 87% removal of cadmium (+2) ions at a pH value of 5 (Tabesh et al. 2018). Lead (+2) adsorption studies on the γ-alumina surface are mostly favored at a neutral environment with pH 7. Adsorption of lead (+2) increases as the solution acidity is reduced to a neutral value but reverses when the solution turns basic (Bhat et al. 2015). Increase in pH value helps metal ions to deposit as metal hydroxides. Lead (+2) adsorption over the three-dimensional γ-alumina surface gradually decreases when pH is <6 and significantly increases above pH value of 8. For lead^{2+}, the optimum value of pH is 6.5, while for cadmium (+2) and nickel (+2) the value is slightly lower than 6 (Drah et al. 2017).

Not only a change in pH but the contact time between heavy metal ion solution and the sorbent also influence the removal efficiency. Exchange of metal ions with the surface hydroxyl groups and attachment of metal ions onto the surface lead to a change in pH with time. The adsorption rate slows down with time because the abundant active sites at the surface decrease gradually as the sites get filled up by adsorbed metal ions. Lead^{2+} ion absorption rate is very fast within 20 min of exposure which remains almost constant to a period of 70 min. The effective exposure time is found to be 30 min for cadmium^{2+} ion (Tabesh et al. 2018).

Initial loading of adsorbent is a determining factor for metal ion removal. pH changes as active adsorption sites increases with high adsorbent dosage. Cadmium (+2) ion adsorption on γ-alumina increases significantly when the adsorbent amount increases. An enhancement in the adsorption of lead (+2) is observed with an increase in the adsorbent dosage (Bhat et al. 2015).

The Freundlich isotherm constant for lead (+2) and cadmium (+2) adsorption on the γ-alumina surface is very high, which infers that adsorption on the γ-alumina surface is a multilayered process and involves various surface-active sites (Tabesh et al. 2018). Adsorption of 47.08 mg/g and 17.22 mg/g are obtained for lead (+2) and cadmium (+2) on γ-alumina. However, in some studies, lead (+2) adsorption is better fitted to Langmuir isotherm, indicating monolayer adsorption on γ-alumina (Bhat et al. 2015). Freundlich isotherm is best-fitted for lead (+2) ion adsorption capacity of three-dimensional γ-alumina at 45 °C (Drah et al. 2017).

It can be concluded that small dosage of γ-alumina can be effectively used to remove heavy metal ions like lead (+2), cadmium (+2), nickel (+2), mercury (+2) in slightly acidic or neutral media. Adsorption efficiency of composite and modified alumina are being investigated for the removal of heavy metal ions and highly toxic compounds in the subsequent discussions.

Some other mention of metal oxides as a sorbent for heavy metal ions are silica, zinc oxide, cerium oxide, tin oxide. There are several polycrystalline forms of silica, which is a principal constituent of sand. The different polymorphs of silica are α-quartz, β-quartz, β-tridymite, α, and β forms of cristobalite, keatite, coesite, and stishovite (Xu and Ching 1991). The most occurring stable form of silica is the α-quartz. With adjustable pore size and high surface area, mesoporous silica can be used in the removal of heavy metal ions like lead (+2), copper (+2), nickel (+2) (Thirumavalavan et al. 2011). Organic templates like hexadecyl trimethyl ammonium bromide is used to synthesize highly porous silica materials with high surface area (Thirumavalavan et al. 2011).

Adsorption of metal ions lead (+2), copper (+2), nickel (+2) increases when initial adsorbent concentration is increased to a specified value. Further increase in adsorbent concentration does not have any significant effect on the adsorption process. The adsorption capacity of the synthesized mesoporous silica saturates beyond this optimal value as the available surface adsorption sites get occupied by the adsorbed ions (Thirumavalavan et al. 2011).

Zinc oxide nanosheets can effectively hold cadmium (+2), copper (+2), mercury (+2), lanthanum (+3), manganese (+2), lead (+2), and yttrium (+3). The best selectivity is shown towards cadmium (+2). The adsorption of cadmium (+2) is measured with a fixed zinc oxide of 25 mg but with a varied cadmium (+2) concentration from 5–150 mg/L. Adsorption increases with an increase in the cadmium (+2) concentration, and the maximum recorded adsorption is 97.36 mg/g (Khan et al. 2013). Glutathione coated hollow zinc oxide is used for the uptake of mercury (+2), cadmium (+2), and lead (+2) from water (Malik et al. 2019). While uncoated zinc oxide shows instability at neutral pH with a zeta potential value of −3.1 mV, coated zinc oxide attains high stability with a zeta potential of −21.72 mV. Mercury (+2) removal increases from 40% at pH 4 to 97% at pH 8. The surface charge increases as pH increases. Thus, a strong electrostatic interaction between the metal ions and carboxylate groups stabilize the system. Glutathione coated zinc oxide gives the best results in the removal of mercury (+2) in comparison to cadmium (+2) and lead (+2).

A study has shown that the morphology of zinc oxide can tremendously affect the adsorption amount of heavy metal ions. For example, the adsorption capacity follows the order of spherical> rod-like> flower-like. These different forms of zinc oxide show a high affinity for lead (+2), followed by copper (+2) and nickel (+2). Rod like zinc oxide adsorbs 180 mg/g of lead (+2), whereas flower-like and spherical zinc oxide adsorbs 170 mg/g and 164 mg/g of lead (+2) (Zhang et al. 2018). Adsorption amount of copper (+2), nickel (+2) on flower, rods and sphere are 29.7 mg/g (0.08 mg/g), 42.4 mg/g (0.092 mg/g), and 54.3 mg/g (0.098 mg/g), respectively. Thus, the different morphological forms show a strong affinity for copper (+2) than nickel (+2). It is mentioned that the anisotropic zinc oxide has high as well as low energy surface sites. Initially, the exposed high energy lattice planes provide adsorption for heavy metal ions. The covering up of high energy sites with heavy metal ions is followed by the adsorption of ions on the low energy sites. The flowerlike structure has an exposed non-polar (010) surface, whereas the rod-like zinc oxide has polar $[10\bar{1}1]$ as the exposed face, which is having higher energy than the non-polar plane. The polar surface accommodates maximum heavy metal ions and lowers the energy.

An inner-sphere complex model describes the selective adsorption of arsenic (+3) ions on tin oxide nanospheres. The nanospheres show arsenic (+3) adsorption of 112.7 mg/g at a pH ~ 7. These nanospheres have a surface area of 169.5 m^2/g and a pore volume of 0.11 cm^3g^{-1} (Zhang et al. 2015). After a contact time of 100 min, the arsenic (+3) concentration decreases below 10 μgL^{-1}. Arsenic (+3) adsorption leads to a ligand exchange reaction with hydroxyl on the surface of tin oxide. The ligand exchange process leads to a decrease in hydroxyl groups from 53.69% to 27.23%, as determined with X-ray photoelectron spectroscopy.

Magnesium oxide hollow spheres prepared using hollow carbon spheres as hard template possesses a surface area of 175 m^2/g, the pore size of 9.5 nm, and pore volume of 0.83 cm^3/g. The nanosphere removes 892 mg/g of arsenic (+3) from the arsenic-contaminated water (Purwajanti et al. 2016). The as-prepared magnesium oxide hollow sphere when submerged in arsenate containing water changes its morphology to flower like nanosheets. The flower-like morphology contains sufficient numbers of hydroxyl groups for the adsorption of arsenate. Flower-like magnesium oxide synthesized by microwave-assisted solvothermal process shows superior performance to adsorb 1980 mg/g lead (+2) and 1500 mg/g of cadmium (+2) (Cao et al. 2012a). This work describes a different mechanism for ion adsorption. Along with the amount of heavy metal ions in solution, this work also tested the amount of magnesium ions in solution. It was found that as adsorption of heavy metal ions increases over the metal surface, more and more numbers of magnesium ions release into the water. Thus, a reaction at the solid-liquid interface occurs for the first few layers of magnesium which helps in lead (+2) insertion into the magnesium lattice sites with subsequent magnesium excretion into the solution (Cao et al. 2012a).

Zirconium oxide shows a strong affinity for vanadium ion adsorption. A pH variation effect on the adsorption measurement shows that at pH 3.5, 43.7 mg/g of vanadium (+5) adsorbs on zirconium oxide. The adsorption value decreases to 11.6 mg/g for pH 12.5. Chromium (+6) adsorption increases in an alkaline medium (Wu et al. 2019). At pH 10, there is 25.3 mg/g of chromium (+6) adsorption. At pH ~ 1 chromium (+6) adsorption decreases to 9.31 mg/g. When the solution contains a mixture of chromium (+6) and vanadium (+5), there occurs a competition for the selective adsorption of these ions on zirconium oxide surface. The adsorption of either of these ions is affected by the pH of the medium. There is a maximum 41.99 mg/g of vanadium (+5) adsorption at pH 3, whereas only 1.49 mg/g of chromium (+6) adsorbs in the 3–13 pH range. The result reveals the strong affinity of zirconium oxide for vanadium (+5) ions.

The nanosheets of zirconium oxide is capable of removing 74.9 mg/g of arsenic at pH 6. A maximum of 74 mg/g of arsenic (+3) adsorption occurs on zirconium oxide nanosheets with an initial arsenic (+3) concentration of 167 mg/L at pH 6 (Shehzad et al. 2019). When the initial arsenic concentration reduces to 0.25 mg/L, the arsenic concentration in water decreases below 0.01 mg/L. The size of the mesopores in the connecting channels is larger than the ionic radii of arsenic (+3).

Therefore, arsenic (+3) first strongly adsorbs on zirconium oxide surface and then diffuse into the pore channels.

Ceria hollow nanospheres of size 260 nm, containing dispersed cerium oxide nanocrystals of 14 nm, possesses a surface area of 72 m^2/g. These hollow nanospheres adsorb 22.4 mg/g of arsenic (+5) and 15.4 mg/g of chromium (+6) (Cao et al. 2010). Ceria nanoparticles are highly effective in removing 189 mg/g lead (+2) from water (Recillas et al. 2011).

6.3.5 Binary Metal Oxides

In this section, we will discuss the adsorption of heavy metal ions over binary metal oxides. A monolithic core-shell nanostructure of titanium dioxide -zinc oxide having both mesoporous and microporous structure show excellent results in the removal of lead and cadmium (Sharma et al. 2019). The measured specific surface area of titanium dioxide-zinc oxide and zinc oxide are 332 m^2/g and 120 m^2/g, respectively. The conditions maintained during adsorption is pH 6, temp 30 °C, and time 150 min. The measured adsorption of lead (+2) over zinc oxide and titanium dioxide-zinc oxide are 790 and 978 mg/g, whereas cadmium (+2) adsorption over zinc oxide and titanium dioxide-zinc oxide are 643 mg/g and 786 mg/g, respectively.

Titanium-zirconium (titanium dioxide-zirconium) nanofiber composites were prepared using hydrocarbon surfactant. The nanofibers have a large surface area (248 m^{2}g^{-1}) and a large number of available sites for metal-ion adsorption. Titanium-zirconium composite is functionalized with phosphonate and amine groups for the adsorption of cadmium (+2) ions. Cadmium ions have a large affinity for phosphonate groups, and the adsorption capacity is 10-times stronger than amine-functionalized nanofibers (Choi et al. 2013). For titanium dioxide-zirconium oxide without surface modification, the adsorption of different metal ions follows the trend-lead (+2) > copper (+2) > nickel (+2) > cadmium (+2) = zinc (+2). Lead (+2) adsorption on amine and phosphonate functionalized titanium dioxide/zirconium are 69.8 and 69.4 μmol/g. Copper (+2) adsorption is 89.9 μmol/g on phosphonate functionalized composite and 26.5 μmol/g over the amine-functionalized composite.

The interconnected networks of zirconium-oxygen bonding in the titanium-zirconium oxides show a strong affinity for chromium adsorption. These mesoporous microspheres have a high surface area of 413 m^2/g. The mesoporous microspheres show well-interconnected mesopores with abundant hydroxyl groups. Because of the interconnected mesopores inside the microspheres, the hydroxyl groups are readily accessible for the chromium (+6) (Chen et al. 2012).

Zirconium oxide-aluminium oxide composites can remove 110.49 mg/g of lead (+2) ions. The superior capability is owing to the large surface area of 278 m^2/g, a large pore size of 12.99 nm, and large pore volume of 0.925 cm^3/g (Tian et al. 2013). Highly toxic metal ions like chromium (+6) can be detected in aqueous media and removed by composite aluminium-iron oxide films (Mikhaylov et al. 2018).

Layered δ-manganese dioxide contains many interlayer active sites. Exfoliation of these layers will increase the surface area and will expose many active sites for effective metal ion adsorption. One of the approaches of separating the layers is by pillaring with inorganic oxides. The process could prevent layer aggregation and provide sufficient interlayer spacings for open pore network (Zhang et al. 2017a). While the pristine δ-manganese dioxide possesses a surface area of 14 m^2/g and a pore diameter of 42.3 nm, pillaring with aluminium oxide increases the surface area to 166 m^2/g and reduces the pore diameter to 4.3 nm. While only 30 mg/g lead (+2) adsorption occurs on pristine δ-manganese dioxide, the adsorption increases to 87.8 mg/g over the layered manganese dioxide.

For an equilibrium arsenic concentration of 0.01 mg/L and at pH 6.7–7.1, cerium-zirconium oxide nanospheres adsorb 27.1 mg/g of arsenic (+5) and 9.2 mg/g of arsenic (+3), respectively. The adsorption kinetics reveal that arsenic (+5) adsorption is faster and 88% of equilibrium adsorption is reached within 30 min, whereas it requires 5 h for reaching 75% of equilibrium adsorption for arsenic (+3) (Xu et al. 2013). It is speculated that the intra-particle ion diffusion inside the binary oxides is faster for arsenic (+3) than that of arsenic (+5), thus leading to strong adsorption of the former ions than the later. The interference of the competing ions, such as chloride, magnesium, calcium, sulphate, carbonate, hydrogen phosphate on uptake of arsenic is investigated. While chloride, magnesium, calcium, sulphate have a negligible influence on arsenic (+5) and arsenic (+3) adsorption, the presence of carbonate and phosphate ions have a drastic impact on the arsenic uptake. A higher concentration of carbonate ions decrease arsenic (+5) adsorption but increases arsenic (+3) adsorption. However, an increased amount of hydrogen phosphate causes a reduction in the uptake of both arsenic (+3) as well as arsenic (+5).

Microspheres composed of carboxyl functionalized mesoporous silica, and silica-coated magnetic cores are effectively used in heavy metal ion removal (Hou et al. 2017). The composite shows high adsorption capacity at a low concentration with values 395 mg/g for cadmium (+2), 476 mg/g for copper (+2), 357 mg/g for lead (+2) ion. The adsorption rate on the surface of those microspheres increases with an increase in the metal ion concentration. The best-fitted parameters with the Langmuir isotherm model for core-shell magnetic mesoporous silica microspheres imply monolayer surface adsorption of metal ions onto the homogeneously distributed surface binding sites. The adsorption capacity of core-shell magnetic mesoporous silica microspheres is stronger in alkaline media. The adsorption of metal ions gradually increases with an increase in pH value from 2–8 due to the capture of metal ions by the negatively charged surface carboxyl groups (Hou et al. 2017).

Applications of fumed metalloid oxide composites are also advantageous due to their large specific surface area in the removal of toxic heavy metals ions. Mixed silica-alumina oxide and silica-titania composites are few examples (Wawrzkiewicz et al. 2017; Byrne and Mazyck 2009). Adsorption capacities of fumed silica-alumina composites for some of the metal ions cobalt (+2), nickel (+2), copper (+2), and zinc (+2) are 72.4 mg/g, 73.2 mg/g, 54.1 mg/g and 55.2 mg/g with an initial adsorbate concentration of 100 mg/L in acidic media (Wawrzkiewicz et al. 2017). As adsorbate concentration increases, the interaction between adsorbate ions and adsorbent surface active sites increases that helps to overcome the resistance due to mass transfer, thus promoting the adsorption. Composite like silica-titania can be utilized for tracing hazardous mercury ions in aqueous media. Silica-titania composite possesses a large surface area and more than 90% removal of mercury is possible with an adsorbate concentration of 100 μg/L (Byrne and Mazyck 2009). The best-fitted parameters with the Langmuir isotherm model for core-shell magnetic mesoporous silica microspheres imply monolayer surface adsorption of metal ions on the surface binding sites. For silica-alumina composite, the metal ion adsorption data are well-fitted with Freundlich isotherm model. Apparently, the adsorption over mixed silica-alumina oxide surface involves heterogeneous multilayered adsorption.

Iron (+2,+3) oxide doped with copper ions can increase the amount of arsenic uptake. The amount of arsenic (+5) and arsenic (+3) adsorption on bare and doped iron (+2,+3) oxide are 7.32 and 42.9 mg/g, and 8.12 mg/g and 37.97 mg/g, respectively. While the bare iron oxide adsorbs only 7.32 mg/g of arsenic (+5) and 8.12 mg/g of arsenic (+3), the uptake amount of arsenic (+5) and arsenic (+3) after copper doping increases to 42.9 mg/g and 32.97 mg/g, respectively (Wang et al. 2015). Copper doping increases the specific binding sites for arsenate ions as well as facilitates arsenic (+3)-oxygen and arsenic (+5)-oxygen binding with a concomitant increase in arsenic adsorption. Doped copper ions act as an electron transfer agent between arsenic (+3) and lattice oxygen, promoting +3 to +5 oxidation state conversion.

Iron (+2,+3) oxide-manganese dioxide composite was used for the removal of a number of metal ions including lead (+2), copper (+2), cadmium (+2), zinc (+2), and nickel (+2). The recorded data shows that the composite can remove 208.17 mg/g of lead (+2), 111.9 mg/g of copper (+2), 169.9 mg/g of cadmium (+2), 100.2 mg/g of zinc (+2) and 55.63 mg/g of nickel (+2) (Zhao et al. 2016). A flowerlike core-shell morphology of iron (+2,+3)-manganese dioxide was synthesized by following a hydrothermal route (Kim et al. 2013). The flower like magnetic composite can uptake 53.2 mg/g of cadmium (+2). The surface of the composite is negatively charged. Below pH 8, the positively charged and neutral cadmium hydroxide species are adsorbed on the binary metal oxide surface, whereas above pH 10 the adsorption of cadmium (+2) decreases because of the increased repulsion between anionic hydroxylated cadmium and iron oxide/manganese dioxide composite. The uptake capacity of cadmium (+2) resumes at 83% after 5th cycle revealing the high stability as a catalyst.

A carbon masked magnetite microsphere core with a manganese dioxide shell coating can effectively remove radioactive isotope of uranium (+6) released into the wastewater near nuclear power plants (Dai et al. 2019). The predominant cationic uranium compounds bind with negatively charged iron oxide-carbon-manganese dioxide surface electrostatically. At pH > 8, the uranium (+6) exists as anionic species. Thus, a repulsion occurs with adsorbent surface resulting in weak adsorption of ions.

Iron (+2,+3) oxide-aluminium microboxes are used to adsorb mercury from tap water, lake water, and tomato juice (Ravindranath et al. 2017). These microboxes have a surface area of 203.8 m^2/g. The pH effect on the uptake ability of microboxes are studied and it was found that with a variation of pH from 2–7 the negative charge accumulation on the surface of microbox increases, thus increasing the adsorption of mercury ions. Adsorption of mercury again decreases at $pH > 7$. The microboxes shows a maximum of 216 mg/g removal of mercury at an initial concentration of 100 ppm of mercury species.

A composite of iron and cerium oxide is highly effective in arsenic adsorption. Adsorption leads to a change in the oxidation state from toxic arsenic (+3) to considerably less toxic arsenic (+5). The catalyst is so effective in removing 99% arsenic within the first ten min of contact time. The total arsenic removal is 263 mg/g (Mishra et al. 2018a). The efficiency shown by the composite is because of two primary reasons (i) presence of porous network and high surface area (ii) ultrasonic irradiation-induced facile mass diffusion across the interface. Three adsorption isotherms were considered-Langmuir, Freundlich, and Redlich-Peterson to determine the adsorption process. The maximum adsorption of arsenic (+3) with Langmuir model is 263.15 mg/g for a iron/cerium composition of 0.2/0.8. Freundlich and Redlich-Peterson model give 40.34 mg/g and 200.4 mg/g amount of arsenic (+3) adsorption. The effective removal of arsenic (+3) is a two steps process: cerium (+4) and iron (+3) ions initially lead to oxidation of arsenic (+3) to arsenic (+5) followed by strong binding of arsenic (+5) on the metal oxide by forming monodentate and bidentate complexes.

6.4 Conclusion

We can conclude the chapter by mentioning that adsorption based technique is a simple way for the removal of heavy metal ions from contaminated water. Metal oxide nanostructures acquiring high surface area and porosity can show a strong affinity for metal ion adsorption. Metal oxide nanostructures having the morphology of rods, flowers, hollow spheres contain numerous adsorption sites. The anisotropic structures contain numerous channels for facile ion migration and adsorption. The adsorption phenomena are electrostatic. In various stages of the adsorption, the metal ions exist in its different oxidized forms. The adsorption of some of the metal ions is a monolayer adsorption process and follow the Langmuir isotherm model. The multilayer adsorption is described by a Freundlich isotherm. The adsorption process is controlled by the pH of the medium, equilibrium ion concentration, contact time, temperature of the reaction, the initial dosage of the metal oxide, and the concentration of ions.

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Chapter 7
Organic-Inorganic Ion Exchange Materials for Heavy Metal Removal from Water

Mesut Yılmazoğlu

Abstract Heavy metal contents in natural water resources and industrial wastewater threaten the environment and human health. For this reason, heavy metal removal from water resources is one of the primary needs for the reuse of resources. In addition to the conventional methods for the removal of heavy metals from water, removal and recovery can also be carried out with high efficiency with ion exchange materials. With ion exchange, unwanted ions are replaced by others that do not contribute to environmental pollution. The method is technologically simple and allows even traces of contamination to be removed from solutions. This chapter emphasizes the ion exchange materials (organic and inorganic) used for the removal of heavy metals from water sources and industrial wastewaters on the basis of the ion exchange process.

Keywords Heavy metals · Environment · Adsorption · Ion exchange · Ion exchanger · Water treatment · Lead · Mercury · Cadmium · Chromium · Nickel · Zinc · Copper

7.1 Introduction

Water is of great importance for humanity and society in terms of environment and social development. Priority sources for water use in the community order are sea water, municipal wastewater and industrial wastewater. When these sources are taken into consideration, decontamination of waste water and making it reusable according to need is one of the important tasks of public and private sectors. At the same time, pollution of the existing water resources is one of the most important problems to be solved in terms of public health. Especially in areas with high

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industrial development, industrial wastewater supplied from factories to the environment can also contain heavy metals that can cause great harm to the environment. Heavy metals (zinc, copper, nickel, chromium, manganese, lead, mercury, arsenic and cadmium, etc.) and their salts are an important group of environmental pollutants. Although some harmful substances entering the soil or water can be removed or biodegradable, heavy metals cannot be removed. Therefore, heavy metals entering the receiving environments adversely affect chemical and biological processes due to their high accumulation. The toxicity of a metal is based on its capacity to damage dynamic life processes in biological systems, including macromolecules, metabolites and cell organelles. Their most dangerous aspect is that they pass to feed and nutrients and then to the living things through the food chain.

Industrial wastewater may contain heavy metals such as copper, zinc, cadmium, lead, nickel and chromium, which may harm the environment. The most popular method used in the treatment of these heavy metal wastewaters is the chemical precipitation process. In this method, the formation of a heavy metal hydroxide precipitate is allowed. Following precipitation, filtration or other solid/liquid separation is carried out. The heavy metal deposits generated by this method must be handled appropriately because the heavy metal deposits generated are classified as a hazardous solid waste. The treatment or treatment of these heavy metal deposits is more difficult than the treatment of wastewater containing heavy metal. Therefore, many processes such as adsorption, bio sorption, electro dialysis, reverse osmosis and ion exchange have been developed in place of the conventional precipitation process to remove heavy metals from industrial wastewater. Among heavy metal removal processes, the ion exchange process is very effective for removing various heavy metals and can be easily recovered and reused by regeneration. Ions can be easily removed from a solution, mixture by ion exchange method. In this way, desired ionic cleaning and deionization can be achieved. Ion exchange resins, known as materials used to achieve this removal, can be classified as natural or synthetic. With a more customized classification, it can also be classified as anion exchanger, cation exchanger and chelate exchange resins. (Dorfner 1991).

7.2 Ion Exchange Process

Ion exchange is the process of replacing the ions which are connected to the solid surface (ion exchanger) by electrostatic forces, with ions of different properties in the liquid phase. There are two major ion exchange groups. These are functional groups, cation exchangers which can react with cations in aqueous medium, and functional groups, anion exchangers which can react with anions in aqueous medium. Some substances are capable of both anion and cation exchange is called amphoteric ion exchangers (Beker 1986). In the case of an ion exchanger of structure X (−) Y (+), X (−) represents the stable and insoluble anion in the crystalline structure and Y (+) represents the exchangeable cation. If the X (−) Y (+) ion exchanger is introduced into an aqueous solution containing Z (+) cations, the following ion exchange reaction occurs. This reaction is a cation exchange reaction:

$$X(-)Y(+)+Z(+)\rightarrow X(-)Z(+)+Y(+) \tag{7.1}$$

Similarly, if an ion exchanger of structure T (+) A (−) is introduced into an aqueous solution containing B (−) anions, the following ion exchange reaction occurs. This reaction is an anion exchange reaction:

$$T(+)A(-)+B(-)\rightarrow T(+)B(-)+A(-) \tag{7.2}$$

The passage of ions through the boundary surface between the solid phase and the liquid phase is a reversible event. The ion exchange reaction takes place in stoichiometric proportions, the total charges of the ions passing from the solid phase to the solution and from the solution to the solid phase are equal to each other and the system is always electrically neutral. For example, when three Ca^{++} ions in the solid phase pass into the solution, six Na^{+} ions pass into the solid phase if the solution contains Na^{+} ions. In other words, by replacing three divalent Ca^{++} ions with six univalent Na^{+} ions, the total number of ions passing from each phase to the other is equal (Beyhan 2003).

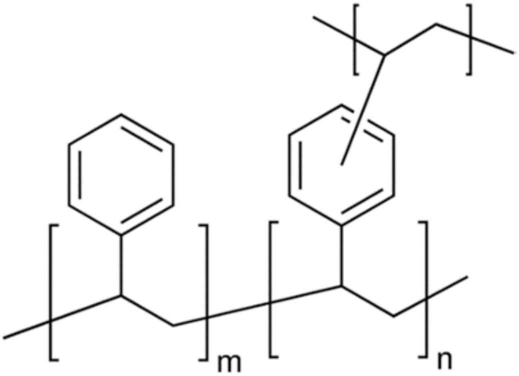
Ion exchange resins, which absorb certain ions from the solution in their structure and exchange them with ions in their structure, realize this in an equivalent amount. In this way, the physicochemical event based on the release of another ion instead of the ion from the solution is called ion exchange. This change is usually reversible between the equivalent amounts of ions. Thus, by applying the opposite reaction, the connected ions can be taken back to the solution.

7.3 Ion Exchange Materials

The so-called ion exchangers, which perform separation according to the principles of ion exchange, are solid and/or water-insoluble substances capable of retaining certain ions from solutions and releasing others. These substances are essentially passive electrolytes containing an inactive moiety, i.e., a support or matrix containing grafted ion exchange active groups. Synthetic or natural organic/inorganic materials can be used as ion exchangers. Initially, high porosity sand was used as ion exchange resin. The general name of these materials is zeolite. The third most important properties of zeolites after adsorption and catalyst properties are cation exchange. These are the first ion exchangers used for water softening.

Today, synthetic ion exchange resins with high ion exchange capacity are also used. Synthetic ion exchange resins are substances of high molecular weight polymeric structure and are composed of two parts as structure. The first is a three-dimensional hydrocarbon network (polymer) and the other is an acidic or basic, ionizable functional group bonded by chemical bonds to the hydrocarbon. The type

Fig. 7.1 Molecular structure of poly(styrene-co-divinylbenzene) (PS-DVB) resin



and number of functional groups determine the ion selection and exchange capacity, while the polymer provides matrix insolubility and the strength of the resin. Most ion exchangers vary according to the ratio of divinylbenzene and cross-linked styrene to each other and the nature of the functional groups. The PS-DVB system is the most physically and chemically resistant to date for commercial use. Ion exchange materials can be classified according to various criteria and are divided into two main categories as cation exchangers and anion exchangers according to functional groups. (Fig. 7.1)

Cation Exchangers Ion exchangers containing SO_3H or COOH groups, capable of holding inorganic or organic cations and exchange them with hydrogen ions.

Anion Exchangers Ion exchangers containing basic groups (NH_2 type, amine functional), capable of exchange of inorganic or organic anions with hydroxyl ions.

Depending on the strength of these functional groups, synthetic resins are divided into four types: strong acid cationic, weak acid cationic, strong base anionic and weak base anionic. Strong acid cationic resins are those having functional group sulfonate. The term strong acid defines that the functional group of the resin is fully ionizable at each pH. In other words, due to the low pK_a values, the strong acid exchangers are ready to give a proton over a wide pH range (1–14). Weak acid cationic resins, the functional group is usually carboxylic acid. Since the pK_a values of these resins are between 4 and 5, they do not tend to give proton (H^+) easily unless the pH > 6. Therefore, the cation exchange capacity of these resins depends on pH. As the pH increases, the ion exchange capacity increases. Strong base anionic resins have an amine functional group. The pK_b values of these resins are in the range of −10 and give the hydroxyl ion readily when pH <13. Thus, the ion exchange capacity of such resins is not pH dependent. Strong base anionic resins have been used to demineralize water for many years. In addition, strong base anionic resins are now used to remove nitrate, arsenic and perchlorate from water. These systems are operated by the chlorite cycle and the resins are regenerated with NaCl. Weak base anionic resins carry the tertiary amine functional group. These amine groups have no permanent constant positive charge. The tertiary amine group is present in association with a water molecule and does not ionize. It therefore adsorbs an ion without change. The behavior of the weak base anionic resin can also be defined as the adsorption of the weak acid by acting on a Lewis base of the tertiary amine group. Some basic exchange reactions related to these four groups of resins are listed below:

Strong acid cation:

$$2\mathrm{R}-\mathrm{SO_3H}+\mathrm{Ca}^{+2} \leftrightarrow \left(\mathrm{R}-\mathrm{SO_3}\right)_2 \mathrm{Ca}+2\mathrm{H}^{+}\ 2\mathrm{R}-\mathrm{SO_3Na}+\mathrm{Ca}^{+2} \leftrightarrow \left(\mathrm{R}-\mathrm{SO_3}\right)2\mathrm{Ca}^{+}\ 2\mathrm{Na}^{+}$$

Weak acid cation:

$$2\mathrm{R}-\mathrm{COOH}+\mathrm{Ca}^{+2} \leftrightarrow \left(\mathrm{R}-\mathrm{COO}\right)_2 \mathrm{Ca}+2\mathrm{H}^{+}\ 2\mathrm{R}-\mathrm{COONa}+\mathrm{Ca}^{+2} \leftrightarrow \left(\mathrm{R}-\mathrm{COO}\right)_2 \mathrm{Ca}+2\mathrm{Na}^{+}$$

Strong base anion:

$$2\mathrm{R}-\mathrm{X_3NOH}+\mathrm{SO_4}^{-2} \leftrightarrow \left(\mathrm{R}-\mathrm{X_3N}\right)_2 \mathrm{SO_4}+2\mathrm{OH_2R}-\mathrm{X_3NCl}+\mathrm{SO_4}^{-2} \leftrightarrow \left(\mathrm{R}-\mathrm{X_3N}\right)_2 \mathrm{SO_4}+2\mathrm{Cl}^{-}$$

Weak base anion:

$$2\mathrm{R}-\mathrm{NH_3OH}+\mathrm{SO_4}^{-2} \leftrightarrow \left(\mathrm{R}-\mathrm{NH_3}\right)_2 \mathrm{SO_4}+2\mathrm{OH_2R}-\mathrm{NH_3Cl}+\mathrm{SO_4}^{-2} \leftrightarrow \left(\mathrm{R}-\mathrm{NH_3}\right)_2 \mathrm{SO_4}+2\mathrm{Cl}^{-}.$$

In addition to this classification, ion exchangers can be classified into two classes as inorganic ion exchangers and organic ion exchangers according to their material origin.

(a) **Inorganic ion exchangers:** Clays, natural and synthetic zeolites etc.
(b) **Organic ion exchangers:** Natural and synthetic polymers, polysaccharides, proteins, carbon-based materials, synthetic resins etc.

7.3.1 Inorganic Ion Exchangers

A large number of inorganic materials having ion exchange properties are naturally present in nature. The source of natural zeolite and natural clay-based ion exchangers which are classified as inorganic materials are zeolite tuffs and volcanic tuffs. These tuffs contain many precious minerals (quartz, mordenite, clinoptilolite, feldspate). Clay minerals, which are natural inorganic structures of the ion exchanger class, can have different pore sizes and pore diameters. Clay based materials are natural structures that exhibit adsorption properties as well as ion exchange properties. Because of these characteristics, natural clay minerals are used in all kinds of water treatment processes. In addition, it is primarily preferred as impermeable protective material in order to prevent contamination and deformation in groundwater.

Examples of clay used in this manner are known: vermiculite, saponite, bentonite, montmorillonite, and kaolinite. In addition to widespread examples of industrial application, there are many studies in the current academic literature on the efficiency of these natural materials in removing contaminants from waste water.

Zeolites are micro porous crystal solids containing aluminum, silica and oxygen in lattice structures and cation and water in pores. Zeolite has become a widespread mineral in the world, some physical and chemical properties, because of the factors such as economic adsorbent attracted interest by researchers and many studies on this mineral has been carried out in the first studies on the formation environment of zeolites; Alkaline soils, salty alkaline lakes, deep sea sediments, low temperature open hydrological and geothermal systems are observed to be the source of zeolite. Later, in the 1930s, the development of measurement methods such as X-ray diffraction (XRD), infrared (IR) absorption, nuclear magnetic resonance (NMR), electron spin resonance (ESR), and their formation in marine and lake environments were also identified. With the researches, high ion exchange capacity of the zeolites, surface absorption, molecular sieve properties, suitability of crystal structure to receive water without deterioration, low density, many properties have been determined useful to the industrial field.

Ion exchange characteristics of inorganic ion exchangers were found to be very significant in adjusting the economic and physical properties that are very important for use in the treatment of drinking and wastewater. Ion exchange capacities depend on crystallinity, particle size, and the nature of the adsorbed ion species. Recently, it is noteworthy that natural inorganic ion exchange materials have become very important as supplements or substitutes of other materials, such as organic resins, for treatments aimed at removing radioactive species. They show better properties than organic substances due to their increased selectivity to radioactive parts (Abusafa and Yücel 2002; Nilchi et al. 2006).

The first examples of synthetic inorganic structured materials used in wastewater treatment are zeolite based materials. Zeolites are crystalline alumina silicates which can be prepared as crystal powders or pellets. Important advantages of synthetic zeolites are their ability to show different chemical properties according to their composition and content, to be obtained in different pore sizes, high thermal resistance and protective effects against radiation. Numerous inorganic synthetic zeolite syntheses have been presented in the academic literature due to their increased selectivity under certain conditions. Besides these advantages, they are also fragile and high production costs are negative features (Khan et al. 2012).

7.3.2 Organic Ion Exchangers

Natural organic materials such as animals, plant tissues and soil have ion exchange properties. Some of these natural substances are straw, wood, paper, flour, potato starch and humus in soil. Most natural substances give color to water during treatment. Therefore, monitoring of the treatment process becomes difficult. They are also extremely difficult to regenerate. The most common example of natural ion exchangers is clay. Extensive research on clays has been conducted in polymer science for the last 20 years. Clay soil is capable of holding ions dissolved in water (Weatherley and Jorgensen 2003).

The most known type of organic synthetic resins are styrene-divinylbenzene-type copolymer structures. By grafting this organic structure with acidic or basic active groups, anion exchange and cation exchange structures are produced. They are easily renewable (McDowell et al. 1986). Organic resins are superior to inorganic resins in very high purity and controlled applications where decomposition is essential according to the dissolution principle. Production costs also make organic resins popular. Organic resins that are formed with inorganic structures also play an important role in the removal of certain radioactive species. The fact that organic resins create safe processes with high efficiency in the treatment of liquids containing radioactive species makes these materials attractive.

In addition to organic synthetic resins, polysaccharides, proteins and certain carbonic materials are examples of organic ion exchangers. These materials can be obtained from nature as biological materials or from agricultural waste. Due to their low cost, they are in great demand as adsorbents in water treatment processes. Examples of these materials include sunflower seed husks, lentils and rice, nuts, tangerines, wheat bran, coffee powder, coffee residues, wood dust and wood chips, and some wastes in the food industry (Liao et al. 2006).

7.4 Heavy Metal Removal with Ion Exchange Materials

Today, a number of processes are being developed in the treatment of water to be used in many fields of activity with the vital and industrial needs and in obtaining the desired quality of water. It is possible to prepare wastewater from pollutants and make them ready for use in accordance with the determined needs. Natural wastewater as well as waste water needs various processes according to their intended use. The quality of the water should be improved as water, which can find many uses, such as agriculture, medicine, health and nuclear stations, must meet the characteristic requirements of all application areas. Water softening, demineralization, chemical and biological precipitation with precipitation agents, and filtration-filtration processes are examples of conventional processes used in improvement processes. If we talk about softening in water, this treatment can be carried out with ion exchange materials in addition to thermochemical methods (Stackelberg et al. 2007).

Due to toxic heavy metal ions in industrial wastes, water, air and soil pollution causes serious environmental and vital problems. In addition to being a natural component of the earth's crust in natural water resources, heavy metal content is also significant in waste water from industrial systems such as paint, metal, automotive and mining. Toxic heavy metal ions create a threat for human health even at very low concentrations and cause diseases. Therefore, it is important to remove these toxic materials from natural water resources and industrial wastewater. The process of separating heavy metals from wastewater has been the subject of many research and extensive projects in industry and academia. It is also important to recover some precious metals such as platinum and gold after metal removal processes and to recycle them according to the area of use. The removal and recovery of heavy or precious metals from water or wastewater can be accomplished by chemical and electrochemical techniques, ultrafiltration, flotation, solvent extraction, reverse osmosis and ion exchange methods. However, most of these processes have high cost, low efficiency and the disadvantage of the separation of the heavy metal sludge obtained. Adsorption method is one of the effective and economical methods for removing pollutants from water. In this method, the determination of new and suitable adsorbent materials that will show the affinity of the pollutants is the most important issue. Many organic/inorganic adsorbent materials such as clay, activated carbon, zeolites, and natural biological/agricultural resources have been used to remove heavy metal ions from wastewater.

These materials also have disadvantages such as their relatively low adsorption capacity, poor interactions with heavy metal ions, and the difficulty of separating and reusing from waste water systems. In recent years, studies on eliminating these problems with organic-inorganic hybrid materials have attracted attention.

The functional variation of the organic materials is combined with the advantages of a thermally stable and stable inorganic substrate to yield strong binding affinities to selected metal ions and relatively high metal ion adsorption capacities. Hybrid polymeric materials functionalized as adsorbents are considered to be one of the most effective techniques because metal ions can be chemically bonded by organic-inorganic polymer hybrids. Such materials often provide the best synergistic properties of each of its components and have high physical, chemical and mechanical properties. Organic-inorganic hybrid polymeric materials are currently being studied extensively for efficient applications. The internal multifunctional character of these materials makes them potentially useful in multiple areas (Samiey et al. 2014).

7.4.1 Lead (II) Removal from Wastewater with Organic-Inorganic Ion Exchangers

Presence of lead above certain standard values in living spaces and water resources is damaging to vital processes such as brain functions, reproductive system, kidney and liver functions in living organisms. The permissible limits for drinking water and wastewater in terms of lead content are 0.015 and 0.1 mg/L, respectively.

One of the organic resins used for lead removal is the polyacrylamidoglycol resin containing all three amide, hydroxyl and carboxyl groups. In this way, when the resin containing three different functional groups was used as ion exchangers, high selectivity and adsorption efficiency was observed against Pb (II) ion in wastewater containing other heavy metal ions (Rivas et al. 1998).

Clinoptilolite was used as an ion exchanger to remove Pb (II) ions from the waste water of a plant where batteries were produced. It has been reported that zeolite regeneration and ion exchange properties are good and Pb (II) recovery is achieved in 40% efficiency in removal and Pb (II) recovery processes (Petruzzelli et al. 1999).

Inorganic ion exchangers used to remove lead from waste water by adsorption processes can be considered as kaolinite clay, bentonite, alumina and natural/modified zeolites. The studies on this subject are primarily based on the preparation of modified zeolites. For example, modified zeolite composites with high magnetism and high adsorption properties were synthesized and used for Pb (II) removal. When the composites were compared with natural zeolites, the results showed that the maximum amount of Pb^{2+} ions adsorbed on the modified zeolite composite and natural zeolite were 84.00 mg/g and 66.96 mg/g, respectively (Yuan et al. 2018). In another study, natural zeolite and Fe (III) modified zeolite samples were compared in lead removal process from wastewater. The modified zeolite samples were prepared under strong basic conditions and the effects of sorbent amount and initial lead concentration on lead adsorption of the samples were evaluated. Adsorption yield of modified zeolite (133.00 mg/g) was found to be higher than that of pure zeolite (66.00 mg/g) (Dakovic et al. 2012). Again, in a study on lead removal from wastes, it was observed that different metal oxides exhibited higher removal efficiency compared to activated carbon. Ca (II) decreased the lead removal ability of activated carbon in the adsorption process, but did not affect the lead removal ability of metal oxides (Meng et al. 2019). When the removal of lead ion removal and adsorption kinetics with phosphate clays were tested, the effects of parameters such as initial metal ion concentration, pH, and sorbent amount were investigated. As a result, Pb (II) adsorption was observed to increase with pH, decreasing ionic strength and increasing amount of sorbent as expected. In addition, the structure of complex-ion ligands was effective in adsorption efficiency. Phosphate clays have been found to be a cost-effective, efficient option for lead removal from industrial wastewater (Singh et al. 2006). In another study, chrome-columned clays were synthesized and characterized. The prepared nanomaterial showed the best results for Pb (II) adsorption in heavy metal removal (Georgescu et al. 2018).

Finally, in a recent study, polymeric ion exchange resin (SMR) was tested for the competitive removal of heavy metals from natural waters. Polymeric resin particles were dispersed in both river water and wastewater with a high capacity removal rate of 82% ± 0.2% from river water and 86 ± 0.1% from river water (Örmeci and Murray 2019).

7.4.2 *Mercury (II) Removal from Waste Water with Organic-Inorganic Ion Exchangers*

One of the most toxic pollutants in the environment is mercury because it can easily spread in nature and accumulate easily in living organisms in a short time. In industrial wastewater, mercury metal may be present as ions or undifferentiated molecules. Like other contaminating metals, it can be removed by reduction, precipitation and ion exchange processes. It is also possible to separate mercury ions from wastewater with inorganic ion exchange materials.

Sulfonate derivative ion exchangers having sulfonic acid group in their structures were found to be effective in the removal of Hg (II) from industrial wastewater. Both the aromatic structures of such anion exchange organic compounds and the affinity of functional sulfonic groups make the immobilization of the ion exchange phase superior. Compounds such as dithizone sulfonate (Chikuma et al. 1985) and nitroiopyrine sulfonate (Nakayama et al. 1982), which have been reported to be tested in the literature, are examples of strong basic anion exchangers that have shown high efficiency in removal of Hg (II).

For Hg (II) removal, different approaches and materials may be preferred, depending on the concentration of mercury present in the industrial waste water. For example, thioester resins are used for the separation of small amounts of Hg (II) in industrial wastewater from sodium chloride electrolysis. In this process, the paths in the resin structure are effective (Dujardin et al. 2000).

In a sample study, a clay composite was used to remove mercury (II) from waste water. Dithizone-montmorillonite (Dz-MMT) composite was prepared by a single step synthesis as the adsorbent; the effects of parameters such as pH, adsorption time, adsorbent dosage and initial concentration on mercury adsorption of prepared composites were investigated. It was observed that the prepared clay composites exhibited high mercury removal capacity (50 mg/L) at room temperature (Elhami and Shafizadeh 2016). In recent years, various zeolite species have also received great interest in the treatment and removal of heavy metal waste water. In this study, nanocomposites were prepared by absorbing coal fly ash type zeolites with silver nanoparticles and synthesized new type of nanocomposites were used for mercury removal from industrial wastewater. In the adsorption results, it was shown that nanocomposites were effective in 99% efficiency in mercury removal from wastewater and provide higher mercury removal than pure zeolites (Inglezakis et al. 2018). The modified zeolites (MSMZ-DT and NSMZ-DT) were prepared by treating the micro and nanoparticles obtained by mechanical modification of clinoptilolite, a natural zeolite, with Hexadecyltrimethylammonium bromide. The results showed that sorbent had high removal activity against Hg (II) cations. The modified materials showed higher activity than the raw zeolites in removing both mercury and lead cations (Shirzadi and Ejhieh 2017).

7.4.3 Cadmium (II) Removal from Wastewater with Organic-Inorganic Ion Exchangers

Cadmium found in aqueous sediments such as lead and mercury can be easily absorbed by plants. Therefore, the toxic effect is quite high, but can easily spread. The main source of cadmium found in water resources on earth is wastewater from mining and metallurgy industry.

Zeolite structures, as mentioned previously, are popular materials for heavy metal removal due to their high cationic exchange ability in addition to their molecular sieve properties. In a recent study for the separation of Cd (II) ions from waste water, hollow fibers and zeolite were prepared and tested using hollow fibers and zeolite for adsorption tests. The results showed that the prepared structures could act as a highly effective inorganic binder without blocking zeolite pores (Araki et al. 2019). In another study using zeolite based materials, it was observed that the presence of thiourea affects Cd^{2+} adsorption and adsorption kinetics depending on the properties of tuff as in sodium forms. The contribution of thiourea in zeolite materials changes the textural parameters. Specific surface areas are lower in thiourea modified zeolites (ZSCThio and ZSGThio) than in non-thiourea zeolite products. In $pH > 5$ values, Cd (II) sorption behavior was the same for ZSCNa, ZCSThio, ZSGNa and ZSGThio and 100% Cd removal was achieved (Olguin et al. 2017). In another study, which investigated the cadmium adsorption capacity after iron-activated clay sample (Tunisia, Tejera-Esghira) with acid, the experimental results showed that the maximum Cd^{2+} adsorption capacity of the natural clay was 23.60 mg/g and that the adsorption corresponded to the pseudo second order kinetic model (Sdiri et al. 2018). In another study aiming to remove cadmium from wastewater with lower adsorbent cost, adsorption was performed with Fe-S nanoparticles which attracted attention with good magnetic and surface area properties. Nanocomposite adsorbents synthesized by a simple and cost-effective method enabled cadmium to be removed with higher yields than pure adsorbents. Adsorption efficiency with Fe-S nanoparticles reached over 98.5% (Afzali et al. 2019).

7.4.4 Nickel (II) Removal from Wastewater with Organic-Inorganic Ion Exchangers

Nickel is used extensively in the industry thanks to its anticorrosive properties. Waste catalysts, batteries and electrolytes used in the industry require the treatment of industrial wastewater containing nickel from these plants. While it is necessary to remove the precious metal nickel for environmental and vital reasons, it is very important to recover it because of its industrial needs and value.

Carboxylic ion exchange materials have shown superior separation efficiency for Ni (II) ions as in other metal separation processes. The carboxylic cation exchanger in sodium form (Wofatit CA-20) was used to remove nickel ions from the effluent from the washing after metal plating and exhibited high separation efficiency (Halle et al. 1982).

In another study, the effects of ion exchange material known as commercial Lewatit TP-207 for the removal of Ni (II) ions in aqueous phase were investigated. It is thought that iminodiacetate functional groups in the adsorbent structure will be effective in Ni (II) removal. On the basis of ion exchange, it was observed that cadmium and nickel formed different complexes in the ion exchange phase. Compared to other ion exchangers of different pore sizes with similar functional groups, the complexion constants of the complexes were found to be higher (Biesuz et al. 1998).

Ammonium carbonate is also widely used for the regeneration of ion exchangers used for nickel recovery from nickel-rich wastewater. However, chelating ion exchangers are also used in nickel recovery processes. One example of the former chelating ion exchange for nickel recovery is the Dowex XFS-4195 material. Chitosan, one of the biological organic sources, can also be used for the separation and recovery of Ni (II) ions from catalyst wastes used for hydro sulfurization. Molybdenum, vanadium and aluminum may also be present in these waste aqueous solutions containing Ni (II) ions. In high efficiency removal of Ni (II) ions, molybdenum and vanadium ions are first removed and Ni (II) is removed by the chelating ion exchange membranes mentioned above (Nagib et al. 1999).

Zeolite-based ion-exchange materials are found to be used for nickel as in other heavy metals separation processes. In a previous study, the efficacy of solid lithium, rubidium, cesium and sodium based Y zeolites in copper and nickel removal was investigated. The removal of copper was achieved in 64% yield under the same test conditions, while the nickel removal efficiency reached 33% (Keane 1998).

High removal efficiency has been achieved with sodium titanate-based inorganic ion exchange material for the removal of nickel from wastewater from the metallurgical industry (Lehto et al. 1996). This ion exchange material ($Na_4Ti_9O_{20}$), consisting of interchangeable sodium ions and titanium oxide layers, was able to efficiently remove nickel from waste water at appropriate pH values ($pH > 5$). Before discharge, the loading of metal ions in the wastewater at 0.65–7.7 meqg-1 and Ni (II) levels was very low (0.003–0.009%).

In a study using organic ion exchangers, different amounts of silica were added to solid foams (ST/2EHA/DVB polyHIPE) of porous styrene/2-ethylhexylacrylate/divinylbenzene internal phase emulsion. These ion exchange membranes were then sulfated with concentrated sulfuric acid. The effect of silica addition on membrane morphology and mechanical properties was investigated and the efficiency of 3% silica reinforced polymer membrane was tested for Ni (II) ion adsorption. The results showed that adsorption kinetic behavior was in good agreement with the pseudo-first order and Elovich model at low and high nickel concentrations, respectively (Moghbeli et al. 2017).

In a study aimed to remove nickel from wastewater, the magnetic hydroxyapatite nanocomposite was tested as an adsorbent. The nanocomposite has a specific surface area of 101.20 m^2/g and has an adsorption capacity of 29.07 mg/g. In addition to this high adsorption capacity, it is also an important advantage that it can be easily separated from the aqueous medium by an external magnetic field. As a result, it has been proved that hydroxyapatite-Fe_3O_4 nanocomposite can be a suitable adsorbent for nickel removal from waste water (Munshi et al. 2018).

Chitosan-g-maleic acid (CTS-g-MA) graft copolymer was synthesized to remove Ni (II) ions from waste water. The synthesis was performed with gamma radiation and the graft conditions, monomer concentration and acetic acid concentration were optimized. At the end of the study, Ni (II) adsorption capacity of CTS-g-MA was determined as 70.10 mg/g and the effect of coexistence of cationic ions on the adsorption capacity was also investigated (Ibrahim et al. 2019).

7.4.5 Chromium (III, VI) Removal from Wastewater with Organic-Inorganic Ion Exchangers

Removal of chromium (III) and chromium (VI) ions from industrial wastewater is very important due to their environmental and vital threats. The most important sources of heavy metal pollution caused by chromium ions are industrial wastewater from metal processing and coating plants. (The water coming from chrome plating facilities, the waters where the coated surfaces are washed after the coating process is performed, etc.)

One of the polymer-based ion exchangers for Cr (VI) removal is seen in the literature as an ion exchanger with a polyvinyl benzene matrix. The ion exchanger prepared by binding 1-(4-pyridinyl)-2-(1-piperidinyl) ethyl ester of 4-aminobenzoic acid to the polymer matrix was characterized by high selectivity for Cr (VI) ions in wastewater (Heininger and Meloan 1992).

In an early study, clinoptilolite modified with HDTMA (Hexadecyltrimethylammonium) proved to be an efficient ion exchanger for Cr (VI) removal. Clinoptilolite modified by HDTMA localized in external zeolite exchange sites can be very effective in adsorption of multivalent anions (Haggerty and Bowman 1994; Li and Bowman 1997).

Amberlite IRAA400 is known as a strong basic anion exchanger. In this study, it was observed that the effect of temperature on removal efficiency was insignificant in order to investigate the removal of chromate ions from aqueous solutions at different pH values at different initial concentrations and at different temperatures. However, it has been noticed that adsorbed chromate ions decrease with decreasing pH value (Mustafa et al. 1997).

One of the macro porous ion exchangers used in the removal of Cr (III) ions is the cation exchangers of the carboxylic structure known as Purolite C-106. Hydrogen peroxide is used in the desorption process. The chromate anion forms created in the process are separated by passing through the cation exchanger. The chromate solution can then be used in the coating industry after cleaning the cation exchange bed. Besides, Cr (VI) ions can be reduced to Cr (III) and used in tanneries.

Adsorbent resins prepared by adsorption of Cyanex 272 on Amberlite XAD-2 polymer support showed high affinity for Cr (III) ions in waste water. Furthermore, the removal of Cr (III) ions adsorbed with said macro porous polymer support based on the adsorbent from the resin was very easy with HCl. The desorption efficiency is very high (95%) and this allows the resins to be reused in successive applications (Mendoza et al. 2000).

Cysteine modified polymeric nanofibers were used for Cr (III) removal in tannery wastewater. In this study, it was reported that the prepared nanofibers exhibited

1.75 g Cr (III)/g nanofiber separation efficiency under optimized adsorption conditions. This separation capacity is superior to the removal capacity of similar materials previously reported from the study (Mohamed et al. 2013).

The cross-linked porous structure and anion content of poly (ionic liquids) prepared in the study, which used in the removal of imidazolium-based poly (ionic liquids) in Cr (VI), made this removal very efficient. Among the adsorbents prepared, PVIm-6-SDC material formed by radical polymerization of ionic liquid and then dried with supercritical CO_2 having high anion content showed superior properties such as high surface area and large pore volume. A very high Cr (VI) adsorption capacity of the product (236.80 mg/g, 25 °C) was observed. This value indicates that the adsorption capacity of the product is higher than that reported in the literature (Li et al. 2019). In another recent study, metal organic framework (MOF) cationic material was prepared for Cr (VI) removal. The results obtained in this study show that this new Cu^{II}-MOF material captures Cr (VI) pollutant heavy metal ions in very high throughput through a single crystal coordination substitution process (retention capacity 190.00 mg/g). This is the first example of a stable coordination between chromate and MOF during the chromate capture process (Hou et al. 2019). The corn stalk-based anion exchange biomaterial (CS-AE) produced for Cr (VI) removal was found to be a highly efficient bio sorbent. In this study, it was observed that chromium ions were removed by ion exchange with chlorine ions on CS-AE (Yuan et al. 2018).

7.4.6 Copper (II) Removal from Wastewater with Organic-Inorganic Ion Exchangers

The presence of copper ions in water sources shows a toxic effect and this toxicity negatively affects the natural growth and growth of plants. One of the most well-known examples of ion exchange process in industrial applications is the process of recovering copper from industrial waste water released during leaching, which is one of the copper production stages. Because of the low pH in these processes, conventional chelating agents are not effective in adsorption of copper ions. For this reason, ion exchangers with high affinity to copper ions have been synthesized in previous studies compared to other metal ions Dowex XFS-4196 ion exchanger exhibited higher affinity to copper ions in these processes (Jones and Grinstead 1977; Grinstead 1979).

The chelating ion exchangers known as Duolite ES-346 also show high selectivity for Cu (II) ions. This material is an ion exchanger based on polystyrenedivinylbenzene. In addition to the amidoxime groups, hydroxamic acid groups present in the structure can also be activated in a wide pH range. Studies have shown that this ion exchanger can form strong complexes with Cu (II) (Ferreira et al. 1998).

In another study, Dowex HCR-S and Dowex 50WX-2 (organic ion exchangers) and inorganic ion exchange materials (ZrP-1 and ZrP-2) with phosphate groups, were used to remove Cu (II) ions by ion exchange based electrodialysis process. Adsorption results have shown that zirconium phosphate based ion exchangers show very high selectivity to copper ions in concentrations ranging from 0 to 0.5 mmol (zirconium phosphate concentration). Compared with organic ion exchangers, zirconium phosphate-derived inorganic ion exchangers were found to be more effective in removing Cu (II) ions (Vasilyuk et al. 2004).

The systems in which ion exchange materials are used as additives in separation processes have also been the subject of many researches. A study in which heterogeneous membranes obtained with ion exchange materials added to styrene-acrylonitrile copolymers in certain percentages are used for Cu (II) removal in water has attracted attention in the literature. Membranes produced by additive phase inversion were used to remove Cu (II) ions from synthetic wastewater. 90 min electro dialysis time and 8 volt potentiostatic control yielded over 70% extraction efficiency. Under constant current conditions, although the extraction efficiency is lower (52%), energy consumption can be much lower (Purcar et al. 2015).

One of the effective materials that can be used in the removal of Cu (II) ions from waste water like other harmful heavy metals is ion exchange fibers. A study conducted in this context in the literature is concerned with the removal performance and adsorption kinetics of Cu^{2+} ions of ion exchange fibers. Elution and selectivity tests were also performed. Adsorption kinetics were defined by Temkin model and pseudo second order kinetics. The results showed that selectivity to Cu (II) ion was higher (62 mg/g) than other metal ions under pH = 3 conditions (Simate et al. 2015).

In one of the recent studies in which chelating ion exchangers are used for Cu (II) removal, bis-picolylamine, iminodiacetate based resins have been used. Studies have shown that resins are effective in copper separation and recovery. Resins exhibited very fast sorption properties. All the resins used are suitable for re-use and the capacity reduction at each use is very low. The resins have high adsorption capacities for Cu^{2+} ions in short contact times (Pehlivan and Edebali 2016).

Cu (II) removal by ion exchange from wastewater was carried out with iminodiacetate resins in another study. Separation kinetics were also examined in the study at room temperature (pH = 3.5) for the separation capacity of Cu^{2+} ion was measured as 2.30 mmol/g. Kinetic results showed that adsorption with resins provided the best fit with the pseudo second order model (McKay et al. 2016).

In the study where a composite material was used for Cu (II) removal, adsorbents (MeCM) were produced by immobilization of 2-methyl-8-quinolinol on porous silica. In this study, the effect of pH on adsorption process, effect of reaction time, effect of initial Cu (II) concentration and effect of competing ions were investigated. It was observed that removal of Cu (II) was carried out efficiently under neutral pH conditions. Cu (II) adsorption capacity of MeCM composite was determined as 197.15 mg/g and it was found that metal ions in waste water were not effective in Cu (II) adsorption due to high Cu^{2+} affinity (Awual et al. 2019).

7.4.7 Zinc (II) Removal from Wastewater with Organic-Inorganic Ion Exchangers

Acid baths containing zinc sulfate are used in industrial plants where fiber production is realized by viscose method. The toxic effects of industrial wastewater containing Zn (II) pollution in these facilities are threatening in terms of environmental and living health. The transfer of these wastes to network waters and natural water resources can cause serious damages. Extraction process is the most effective method used to remove or recover zinc from industrial plant wastes. However, considering the benefits of the process, the extraction process can be quite expensive due to the need for devices and equipment in the commercial sense.

The first ion exchangers used to eliminate these harmful effects are weak acidic cation exchangers. These cation exchangers were primarily tested as carboxylic cation exchangers. Such ion exchangers cannot be effective for the removal of zinc in acidic medium and hydrogen form because of their high hydrogen affinity. Therefore, the waste sources must be neutralized before the changeover is applied. Methacryldivinylbenzene KB-4 was the first ion exchanger proposed for zinc removal, but it was able to exhibit high ion exchange capacity independent of Zn (II) concentration in waste water (Winnicki et al. 1975).

As an example of organic resins, polyvinyl pyridine ion exchange material was used to remove Zn (II) ions from waste water. In addition to the effective performance of the resin in copper and nickel removal, it has been proven to have superior adsorption capacity (0.65 mmol/g) to other metal ions in zinc separation (Shah and Devi 1998).

The synthesis of new types of ion exchangers for zinc removal has attracted attention over the years. In a study using a porous ion exchanger in sodium ion form, the separation of zinc ions from waste industrial water was investigated. Kinetic data of adsorption were also evaluated in tests performed in a batch reactor. This ion exchange resin named D401 showed an equilibrium exchange capacity of 2.70 mmol/g for Zn (II) ions. When the kinetic data were evaluated, the most appropriate correlation was obtained with Elovich model (McKay et al. 2009).

In a study aimed to recover zinc from zinc-containing wastewater from galvanized processes, various ion exchange resins (Purolite A500 and Hypersol-Macronet MN500) were tested in a mini electrodialysis system. The system was tested for different zinc solutions and experiments were carried out at constant voltage. Before and after the process, pH and conductivity of the solutions were measured and the results were evaluated. By using the resin pair in the electrodialysis system, zinc ion removal was achieved with high efficiency and very low conductivity solution was obtained which could be reused as rinse water. With the ion exchanger system used, the removal rate is above 80% (Radu et al. 2015).

In another study aimed to remove Zn (II) from aqueous solvents, the cation exchange capacity of macro-algae Pelvetia canaliculata (Linnaeus) was investigated. Sulfonic and carboxylic groups on the surface of algae are thought to be effective in zinc removal. In the studies carried out, it was observed that algae had higher affinity to copper and zinc ions in waste water containing different ions. When pH = 4, zinc and copper ions were observed at almost all binding sites (Vilar et al. 2014).

7.5 Conclusion

In this chapter, organic, inorganic and hybrid materials used in the removal and recovery of major heavy metal ions (lead, mercury, cadmium, nickel, chromium, copper, zinc) contained in natural spring waters and industrial wastewater are mentioned. In the removal and recovery of heavy metals from wastewater, inorganic based ion exchangers are mostly natural/synthetic zeolite and clay structures and modified zeolite/clay structures obtained by additives or processes to these structures. Similarly, polymeric resins, functional copolymers, and biopolymers appear to be classified as organic ion exchangers and provide similar and sometimes superior removal efficiency in inorganic ion exchangers in heavy metal removal and recovery. The design of superior ion exchangers is made possible by the synthesis of organic/inorganic hybrid materials, depending on the application area and target removal efficiency. Many years of academic and industrial research and development have contributed to the discovery of new types of productive materials and their commercialization on an industrial scale for the removal of toxic heavy metals from wastewater.

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Chapter 8
Low-Cost Technology for Heavy Metal Cleaning from Water

Muhammad Shahid Nazir, Zaman Tahir, Masoom Fatima, Sadaful Hassan, Zulfiqar Ali, Majid Niaz Akhtar, and Mohd. Azmuddin Abdullah

Abstract Uncontrolled and rapid industrialization and excessive anthropogenic activities have caused extensive pollution in the waterbodies. Water contamination has been a major concern especially in the developing world. The high number and level of pollutants in the wastewaters are hazardous to human health and the environment. Among major pollutants found in the wastewaters are heavy metals. Many conventional methods such as membrane filtration, adsorption, electrochemical treatment, and bio-sorption have been applied to remove and remediate the heavy metal contamination from wastewaters. Although some of the approaches are found to be successful, a number of these are not economical and time consuming. Among the new technologies, nanotechnology, emerging membrane technology, low cost sorbents technology, use of zeolites and metal organic frameworks have been developed as efficient and economical techniques for heavy metals removal from wastewaters. Biotechnological methods have great potentials to lower the cost of wastewater treatment for contamination removal. This chapter outlines the conven-

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tional wastewater treatment techniques and highlights the potential low cost methods for successful removal and remediation of toxic heavy metals from the wastewaters.

Keywords Water contamination · Type of pollutants · Sources of heavy metals · Conventional wastewater treatment · Advanced wastewater treatment · Remediation · Biotechnological strategies

8.1 Introduction

The demand for clean water in recent years has increased manifold due to the increase in the population (Pendergast and Hoek 2011). The World Health Organization (WHO) report estimates that, since 1990, only 2.5 billion people have access to the facilities of clean water, and in 2015, nearly 663 million people still do not have access to clean water. Water pollution has been caused by rapid urbanization, development in agriculture, and industrialization. The pollutants can be classified into organic, inorganic and biological pollutants. Heavy metal ions, viruses, organics, and bacteria are present in waste water. As freshwater availability is still a major issue for socio-economic development, the WHO has set a limit to the quantity of heavy metals allowable in aqueous solution (Machell et al. 2015). Inorganic metals can be beneficial for human health, but when the amount exceeds permissible limit, they become poisonous. Heavy metals have the ability to penetrate into the living beings and persist in the environment as they are non-biodegradable (Hashim et al. 2011) and eventually affects human health (Zou et al. 2016), causing nervous breakdown, cancer, and organ rupture. Toxic heavy metals such as Hg^{2+}, Cd^{2+}, As^{3+}, Pb^{2+}, and Cr^{6+} are carcinogenic and hazardous (Meng et al. 2014) when released in huge amount into the environment (Yin et al. 2018). Iron, cadmium, cobalt, mercury, zinc, nickel, lead, and manganese can cause toxicity in the groundwater, surface water, and the soil. Pollutants that enter the soil can be linked to their active sites (mineral clays, hydroxides and oxides of manganese and iron, and organic material). The activities will subsequently change, either increased or decreased, which will determine the degree of their harmful effects. Large amount of biological waste containing lead (Pb) is often found with its salts. In soil, lead makes stable complex composite with organic ligands which may become less harmful as compared to the free metal ions (Linnik and Nabinvaets 1986).

To ensure that the impact of exposure is not hazardous to public health, the removal of harmful metals from aqueous media and the reduction in the number of impurities is important (Atkovska et al. 2018). In this review article, the sources of different types of heavy metal pollutants, the routes of contamination, and different strategies for their removal from the environment are highlighted.

8.2 Sources and Impact

Metals having atomic weight higher than 50 are termed as heavy metals (Orlov et al. 1985; Orlov et al. 2002). The common ones are the 19 elements (Mn, Cr, Co, Ni, Fe, Zn, Cu, Ge, Cd, Sb, Sn, Ga, Mo, W, Pb, Te, Bi, Tb, and Hg). The list does not include Ba, actinides, and lanthanides, and several elements are considered as the highly distinctive polluting noxious metals - Cd, Cu, Pb, Ni, Co, Sn, Mo, V, Zn, and Hg. Heavy metalloids, also called as semi-metals, are also grouped as poisonous metals. Uranium, at molecular weight 238, is radioactive. The heavy metals in the environment are assembled, and are not easily degraded and can enter human food chain. The origins of heavy metals may come from the traffic and building material, sewage water and emission from atmospheric deposits (Sörme and Lagerkvist 2002). The sources can be categorized as households, drainage water, businesses, pipe sediments, release from the atmosphere, road, and construction materials and pipe sediment. Examples of other different sources are overflow through the rooftops, food, tires' wear, or car washing. Contaminated water containing chromium, zinc, nickel, cadmium, mercury, and copper, may come from different industries (Evanko and Dzombak 1997). Heavy metals like nickel, vanadium, silver and titanium are produced in electroplating, milling, and coating industries. Other heavy metals like tin, lead and nickel are generated from Printed-Circuit Board (PCB) manufacturing. Wood industry produces arsenic waste, pigment production industries produce chromium sulphide, petroleum industry produces used catalysts such as vanadium and chromium. All these industries produce large amount of residues and waste water that can be harmful, requiring extensive waste water treatment. Recycled water may contain as high as 30% of metals and metalloids (Fig. 8.1). Some types of metals can be detected and tracked like copper, zinc, nickel and mercury, and some may be undetected such as chromium, cadmium and lead. The biggest source of copper metal are roofs and tap water. For zinc, the largest sources are car washing and galvanized material; for nickel, the major source can be from drinking water itself and the chemicals in the wastewater treatment plant; and in the case of mercury, from amalgam in teeth.

Figure 8.2 shows the natural and anthropogenic sources of heavy metal ions. Volcanic eruptions, comets, erosions and weathering of minerals are some of the natural sources of the heavy metals which enter the atmosphere (Ayangbenro and Babalola 2017). Heavy metals that exist naturally are influenced by particle size, soil organic carbon, and mineral composition. Soil heavy metals may be modified by the external sources, weathering, or erosion (Herngren et al. 2005). Naturally occurring quantity of heavy metals may not be a cause for concern, but the anthropogenic activities may have disrupted their safe level in the environment. The main anthropogenic sources include mining activities, chemical and metallurgical industries, smelting process, and plastic manufacturing, cement industry, pesticides, fertilizers, transport and agriculture. (Yadav et al. 2017). Toxic heavy metals present naturally are not easily available for plants and microorganism, as they are in insoluble forms such as complexes, precipitates, or minerals. Such heavy metals also

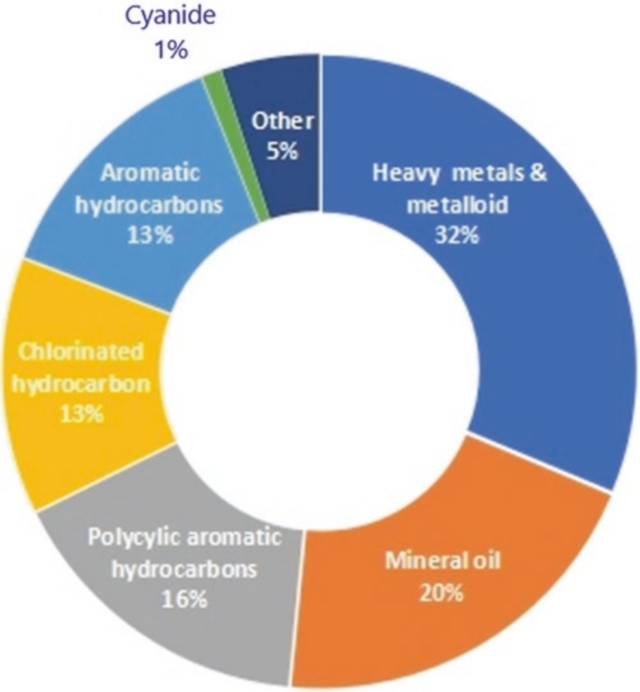

Fig. 8.1 Composition of water contaminants in recycled water. In recycled water 32% comprised of heavy metals and metalloids, 20% of mineral oil, 16% of polycyclic aromatic hydrocarbons, 13% of chlorinated hydrocarbon, 13% of aromatic hydrocarbon, 1% of cyanide, and 5% of other contaminants. (Modified from Bolisetty et al. 2019)

have strong interaction with the soil and the binding energy of these heavy metals and the soil is quite large.

Heavy metals coming from anthropogenic resources have high solubility and are very reactive due to which their bioavailability is very much higher than that of the heavy metals coming from the natural resources. Therefore, they are more dangerous to the biota. Anthropogenic sources of the heavy metals are diverse which include manufacturing of explosives; improper handling of industrial wastes, sewage and biosolids; electroplating industries and battery production; pesticides and phosphate fertilizers; dyes, printing and photographic materials; mining and smelting; and leather tanning, wood preservatives and textile industries (Fig. 8.3). The parameters which influence the accumulation of the toxic metals in the life cycle include soil characteristics, level of poisonous metals in the ground, limit of absorption by animals and limit of plant uptake. The pollution of the ground from the noxious metals can be caused by the ore processing and mining. Mining processes change the environment through the release of heavy metals and the accumulation of large quantity of heavy metals could take several decades for their recovery from the environment (Ayangbenro and Babalola 2017).

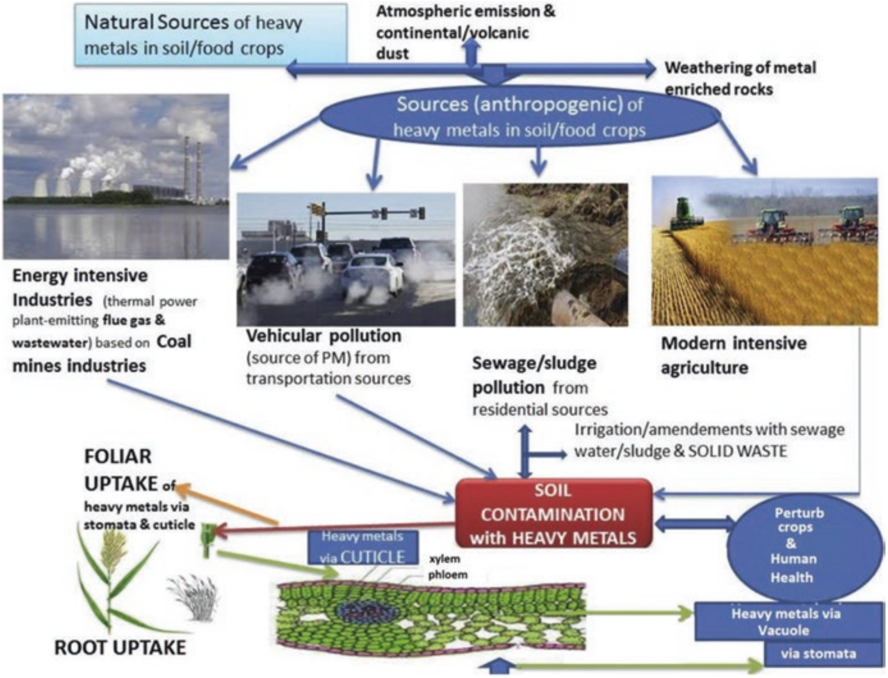

Fig. 8.2 Natural and anthropogenic sources of heavy metal ions. Two sources of heavy metals consist of natural sources i.e., atmospheric emission, volcanic dust, weathering of metals enriched rocks, and metals found in atmospheric condition, and anthropogenic sources i.e., energy intensive industries, road and water vehicles, sewage and sludge pollution from domestic areas, and modern intensive agriculture. These sources contribute significantly towards soil contamination with heavy metals. (Reprinted with the permission of Heavy metals in food crops: Health risks, fate, mechanisms, and management, Creative commons attribution, Rai et al. 2019)

Soil is the main base for harmful metallic ions to be released into the environment and atmosphere. Unlike organic contaminants, heavy metals are not biodegradable and the level will remain high in the ground for a long period of time before being released from any natural or anthropogenic activities (Bolan et al. 2003). The bioavailability and changes in the chemical structures are made possible by these release and interactions, and the biodegradability of some organic contaminants may be inhibited by the toxic metals present in the ground. The accumulation of heavy metal natural concentrations in the ground can be transported by carrier such as water and weathering pattern (Osman 2014). Soil rich in noxious metals not only risks polluting the groundwater, but also causes phyto-toxicity, and reduces the land use potential for agricultural productions (Maslin and Maier 2000).

Micronutrients are required by the plants and animals in an amount below the threshold limit. When the quantity increases, it becomes hazardous (Ojuederie and Babalola 2017). Pollutants such as heavy metals could severely affect animals, plants and human health and the productivity of crops (Rashid et al. 2019). Heavy metals are toxic depending on time of exposure, dose and heavy metal type. Each

Fig. 8.3 Anthropogenic sources of heavy metals. The main anthropogenic sources are attributable to urbanization, mining, modern agricultural practices, volatilization through different routes, fertilizer contamination with time, and mainly from modern industries. (Modified from Verma and Sharma 2017)

type has its own adverse effect on human body (Masindi and Muedi 2018). Heavy metals may get into the human body by inhalation and ingestion, causing genetic mutations (mutagenicity), damage of neural tissues (neurotoxicity), and affecting normal embryonic development (teratogenicity). As it is non-degradable, heavy metal ion attached to the cells may cause cell damage and increase the risk of cancer. Chromium, arsenic, nickel, cobalt, copper, lead and mercury are known to affect the circulatory, digestive and nervous system, leading to brain damage, blindness, cancer and death. Cadmium poisons the liver and kidney due to similar chemical properties, and interchanges with minerals like iron, zinc and copper and competes at the binding sites. Lead accumulates mainly in bones, brain and kidney. Arsenic poisoning causes gastrointestinal or nervous disorders. In plants, heavy metal contamination leads to reduction in water potential and protein oxidation, nucleic acid damage, cell death, enzyme and growth inhibition, and decrease in photosynthesis (Ashfaque et al. 2016).

8.3 Different Routes of Contamination

Many sources have caused the release of heavy metals in soil, waterbodies and eventually the food chain (Islam et al. 2018a, b). Ground water reservoir represents major total fresh water sources, and the pollution of toxic metallic ions in base-water and the impurities as contaminants in ground water will limit its use (Sun et al. 2018). Half of the world may be facing the harmful effects of ground water pollution where an estimated 100 million people are consuming heavy metals contaminated water every year (Rashid et al. 2019). Heavy metals may contaminate the ground water through natural sources (lithogenic sources) including disintegration of rocks, degradation of soil and precipitations, while the combustion of fuel, underground corroded pipes, mining, urbanization, industrial and agriculture wastes represent the anthropogenic routes (Rajeshkumar et al. 2018; Saleem et al. 2019). The natural routes involving weathering of rocks and minerals, erosion, surface water degradation and leaching are slow and are influenced much by climatic conditions, but the anthropogenic activities are fast and pose serious threats due to increasing population and industrial activities (Titilawo et al. 2018). Metal smelting and lead removal from paints and petroleum industries also have significant effect on the soil contents, and vegetative propagation (Alloway 2013) which could render the ground water unsuitable for consumption.

Other source of groundwater contamination include overabundance of sulphides, arsenic, manganese and other metals, the most common ones, being iron and manganese that occur naturally in the soil. Radioactive decay is the source of heavy metal contamination in rocks and sediments. Uranium decay, particularly, results in the release of radon and other harmful gases. In coastal regions, saltwater intrusion and the contamination with metal remnants of ship wreckage or plastic residues especially pose serious threats. Abandoned mine areas is not only unsuitable for crop production but also constantly release the toxic heavy metals and sulfide minerals such as FeS_2 (pyrite), FeAsS (arsenopyrite), PbS (galena), $CuFeS_2$ (Chalcopyrite) and (FeZn)S (Sphalerite), to the environment as sulphuric acid or metals from the ores and minerals. The acidity causes further release of more toxic heavy metals from the mineral sources and metal such as arsenic may be released from mine drainage. These toxic metals and pollutants continuously change their states and undergo various redox reactions, where their movement increase the risk of contamination to the ground water and surrounding areas (Karaca et al. 2019). Sediments may contain toxic elements such as cadmium, copper, lead, and chromium from sewage and industrialization water sediments which are discharged into the water bodies, leading to serious health hazards and deterioration of the water quality, which eventually causing harmful effects on aquatic life (Rajeshkumar et al. 2018). The wastes from smelting, electroplating and industrial processes and effluents could also contaminate drinking water, food and the surroundings (Chowdhury et al. 2016; Sakshi et al. 2019). The thermal power plant wastes from the combustion of coal generates large amount of solid ashes, which are sometimes dumped near the area of large ponds and water reservoir, resulting in the soil surrounding the area and the pond having high level of lead, molybdenum, astatine, chromium, manganese, nickel, cobalt, copper, vanadium (Sakshi et al. 2019).

The untreated solid and liquid wastes from agricultural crop land can be another major source of ground water contamination. Heavy metals, pesticides, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls which are present in the soil as contaminants, are toxic, mutagenic and carcinogenic (Sakshi et al. 2019). Fungicides, pesticides, insecticides, and phosphate-containing fertilizers have caused contamination of Zn, Cd, and Cu in the agricultural soil. To lower the contamination and for its prevention, it is pertinent to identify and apply multivalent approaches to measure the variety and probable origins of heavy metal accumulation in the soil (Chai et al. 2015). Positive-matrix-factorization (PMF) has been applied to locate and simplify the identification of the origin of soil pollution (Hu et al. 2013). The levels significantly affect the movability and availability of heavy metals in the soils. Greater quantity of cadmium and copper have been detected in the soil for industry and construction as compared to the soils without sewage irrigation (Yang et al. 2018). Leaching of metals from pipes of water distribution system is another anthropogenic route of ground water contamination (Chowdhury et al. 2016). Urbanization, untreated discharged wastes, agricultural activities, rapid industrialization and toxic metal leaching are deteriorating the groundwater quality (Rashid et al. 2019), where leaching of metals from pipes of water distribution system has contributed towards ground water contamination (Chowdhury et al. 2016). These different routes including deposition, industrial discharge and sewage waste as depicted in Fig. 8.4, may render the natural ground water reservoir as unfit for utilization (Singh et al. 2018; Titilawo et al. 2018; Varol 2019).

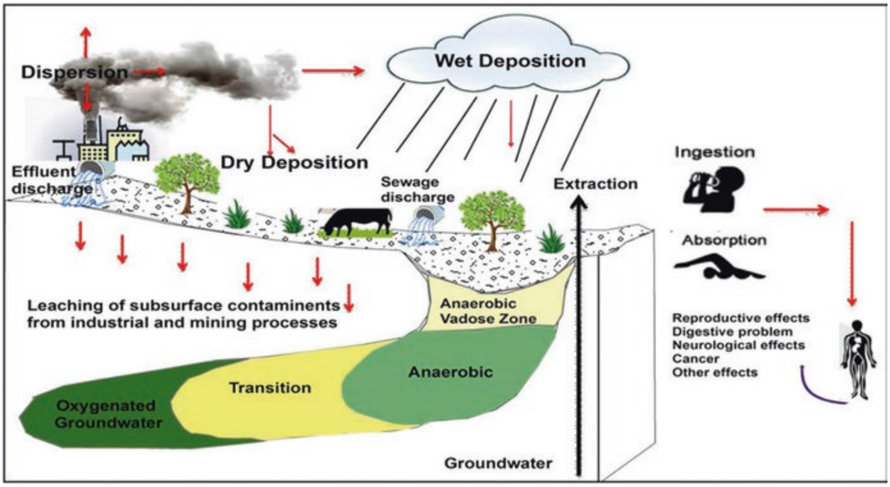

Fig. 8.4 Anthropogenic routes to contaminate the ground water quality with toxic metals. Industrial discharge and sewage discharge in water and soil not only leachout into soil and ground water, but also eventually disperse in air. The formation of dirty wet deposition in the atmosphere results in the down-pouring of dirty water into the ground and waterbodies, thereby leading to the contamination of groundwater with heavy metals. (Reprinted with the permission of Groundwater chemistry and human health risk assessment in the mining region of East Singhbhum, Jharkhand, India, Elsevier publisher, Singh et al. 2018)

8.4 Conventional Water Treatment Methods

The processing of surface water may involve the Drinking Water Treatment Plants (DWTPs), and the Waste Water Treatment Plants (WWTPs), both having to comply to the standards established by the World Health Organization (WHO) and Environmental Protection Agency (EPA). The organic, heavy metals and inorganic compounds and impurities need to be removed and eliminated before can be deemed safe for release into the environment and fit for human consumption. Toxic metal ions removal from aqueous medium can be treated by various conventional and advanced methods. As shown in Figs. 8.5 and 8.6, these primarily consist of sorption (Song et al. 2019), chemical precipitation and coagulation (Yu et al. 2017a, b), oxidation-reduction (Sheng et al. 2016), solvent extraction, photocatalytic degradation (Kumar et al. 2018), membrane filtration (Mikušová et al. 2014), and ion exchange (Radchenko et al. 2015). Figure 8.7 shows the merits and demerits of various techniques for the removal of hazardous substances from the contaminated water. There are major considerations to be made such as economical process, can be operated in industrial scale, no complex chemistry involved and the method can be tuned to achieve better results by functionalization (Xu et al. 2018). Adsorption is an effective and reliable way for the uptake of heavy metals. The advantages of adsorption include wide pH range, low cost and simple operation while the disadvantages are weak selectivity and waste product excretion. Similarly, chemical precipitation is low cost, and requires simple operation but it produces waste products and ineffective for the removal of trace ions (Pinakidou et al. 2016).

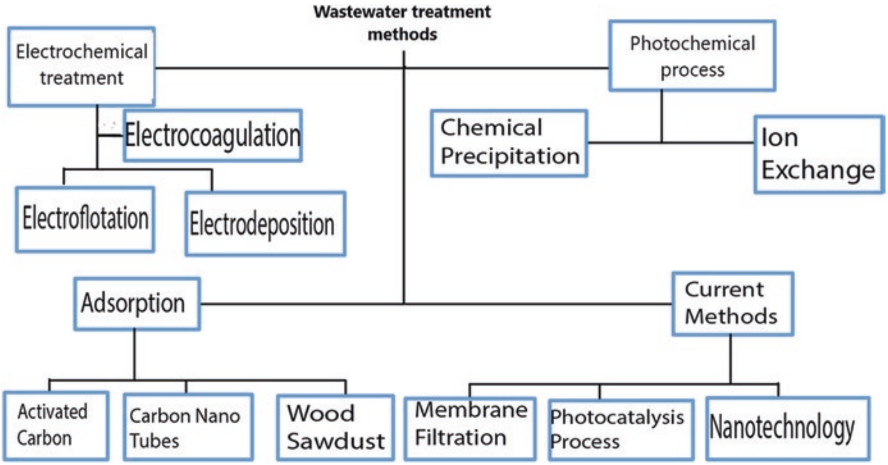

Fig. 8.5 Water treatment methods. The water treatment techniques mainly consist of adsorption (i.e., through wood sawdust, activated carbon, and carbon nanotubes), electrochemical (i.e. electroflotation, electrodeposition, and electrocoagulation), photochemical (i.e. chemical precipitation and ion exchange), and advanced method (i.e. membrane filtration, photocatalysis, and nanotechnology) to treat contaminated water and remove heavy metals. (Modified from Bolisetty et al. 2019)

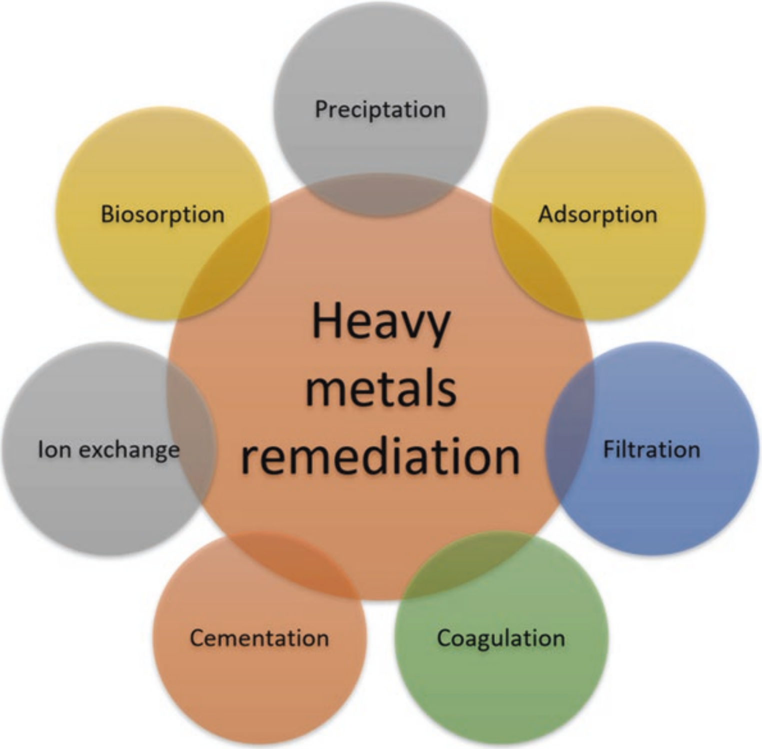

Fig. 8.6 Remediation of heavy metals. The methods like precipitation, adsorption, biosorption, ion exchange, filtration, coagulation, and cementation are mainly used to remove heavy metals from water. (Reprinted with permission of Environmental Contamination by Heavy Metals, Creative commons attributions 3.0, Masindi and Muedi 2018)

8.4.1 Preliminary Treatment

The large sized and coarse solids in waste water must be removed and this is the basis of preliminary treatments. The units should be maintained, and the impurities are removed during the process. This treatment includes coarse screening, grit removal and removal of larger objects in some cases. The flowrate of water in the grit chamber is maintained high and some organic solids are prevented to settle by the air flow. The organic and inorganic materials can settle down by sedimentation. Those that float will be removed by skimming. The treatment could achieve the removal of 50–70% suspended solids, 25–50% biological oxygen demand (BOD) along with 65% oil/grease. However, dissolved and colloidal particles are not separated. In primary sedimentation, nitrogen, heavy metals and organic phosphorous which are linked to the solids may be separated, and the wastes are known as primary effluents. In the small wastewater treatment plants, the grit removal is not the

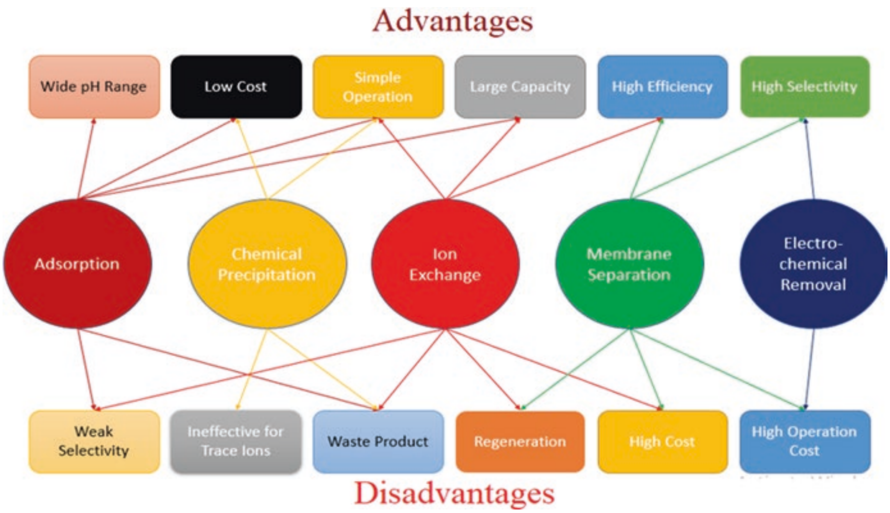

Fig. 8.7 Techniques for elimination of heavy metals and their advantages and disadvantages These techniques mainly involve adsorption, chemical precipitation, ion exchange, membrane filtration, and electrochemical removal of heavy metals. (Reprinted with permission of A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: Preparation, application, and mechanism, Commons creative attributions (3.0), Xu et al. 2018)

first step. Comminutors are used to minimize the size of the large materials. In this way, the waste in the form of sludge will be obtained.

Toxic metals can be removed by specific adsorbents which exhibit significant affinity (Xiao et al. 2016). Activated carbon is a common adsorbent used to treat water and waste water for the removal of organic and inorganic impurities. Activated carbon has large meso and micropores, and greater surface area to remove heavy metals ions such as lead, nickle and zinc (Kuroki et al. 2019). The next steps may involve screening, centrifugation, chemical precipitation, microfiltration, coagulation, flocculation and gravitational methods. Flocculation, coagulation, microfiltration and chemical filtration are used when there is a high level of the metals, but these are less effective as compared to the tertiary treatment. The heavy metal removal in industries is primarily done by chemical precipitation where water insoluble materials are formed when the heavy metals react with different reagents. The pH variation of heavy metals also form insoluble materials which can be separated by sedimentation. The main advantages of chemical precipitation are it is easy to handle and cheap but the main drawback is that the heavy metals may not be at such amount of concentration that are acceptable to be removed or discharged. Large-scale treatment should be carried out for the heavy metals to be disposed off.

8.4.2 Secondary Water Treatment

Microorganism is capable of remediating the pollutants in the safe manner, using simple natural bioprocesses. In the aerobic treatment, micro-organisms are present with oxygen supply to convert the pollutants into carbon dioxide and biomass. Wastewater is combined with the oxygen which is supplied by the air compressor and circulated around the tank for good mixing. In anaerobic treatment, biogas is produced from the pollutant in the absence of oxygen. The methane produced can be used as energy source. These processes mostly involve the removal of organic pollutants. About 90% pollutant removal efficiency can be achieved with anaerobic process. The industrial wastewater containing heavy metal may be treated with the bio-adsorbent such as the activated carbon. The sequestration of Hg can be achieved by utilizing the bacterial biofilms, and zinc, copper, manganese and iron can be removed by using immobilized yeast. However, the industrial treatment with specific and genetically modified microbes is not widely used as yet although the potential is great for future application (Bolisetty et al. 2019).

8.4.3 Tertiary Water Treatment

Chemical precipitation is used in industry and is simple to operate to eliminate heavy metals from the inorganic waste. The dissolved heavy metals and the chemicals introduced react in the solution producing insoluble precipitates of metals. The size of the precipitate can be increased by coagulation, and the large size particles are removed as sludge. By varying the reaction conditions such as temperature, pressure, ions concentration and pH, the metal ion removal can be increased. The hydroxide treatment is commonly used as it is cheap, simple and easily atomized (Bolisetty et al. 2019). Crystallization and thermal treatment are a part of the tertiary water treatment. Thermal method, such as evaporation and distillation, provides energy to water which brings it to boiling temperature and the the steam is collected as a pure water. Crystallization of pollutants is achieved by adding the amount of seed for nucleation. Nitrogen, ammonia and phosphorous are crystallized by the process of struvite crystallization. (Bolisetty et al. 2019). Photocatalysis involving oxidation and reduction make use of the catalyst like titanium oxide (TiO_2) and ultravoilet light to produce free radicals that could degrade the pollutants (Bolisetty et al. 2019). Electrochemical treatment may involve electrocoagulation, electroflotation, electrodeposition and electrooxidation, making use of anode and cathode plate, where current is passed through the effluent containing the metal ions. The precipitation of metals in acid and base neutralization reaction could recover the metals (Gunatilake 2015).

8.4.4 Membrane Filtration

Membrane filtration technologies could remove heavy metals, total dissolved solids (TDS), algae, microorganisms, bacteria and micro-pollutants. Different materials are used such as polymer or ceramic, and the separation is on the basis of pore size and weight of impurities utilizing different size-based membrane processes such as nanofiltration or ultrafiltration. The pore size of the micro-filtration is the largest (100–1000 nm) (Bolisetty et al. 2019). Ultrafiltration is used to remove particles ranging in the microsize category where 90% of the heavy metals could be removed from the solution, requiring small space because of its compact size (Gunatilake 2015). Nanofiltration, which lies in between the size of ultrafiltration and reverse osmosis, can remove solute particles ranging in sizes from 100 to 1000 Da. Sufficient pretreatment steps must be taken as the small pore size of the nanofiltration membrane may get clogged easily. Although nanofiltration is considered less effective in removing ions, it shows better capability of removing the pharmaceutical active compounds.

Reverse osmosis involves the separation where the solution is forced through a membrane due to the applied pressure to overcome the osmotic pressure, allowing only the pure solvent to pass through. The semipermeable membrane however stops the impurities like the bacteria and metals from passing through. The separation depends on the pressure, water flux and concentration as it is a diffusive process (Gunatilake 2015). Ion exchange method (Fig. 8.8) is effective in converting a number of liquid phase impurities into solid state. The ion exchanger exchanges the cations and the anions that the metal ions at low quantity can be removed, and it

Fig. 8.8 Ion Exchange Filtration setup. (Reprinted with permission of Ion Exchange Filtration, MAA Chem, CC BY 4.0 (Open access), MAA Chem)

commonly involves economical material as synthetic organic ion exchanger and simple protocols but very effective to remove metals from the solution. The -SO_3H group present in the cation exchange resin has good selectivity, reversibility and ion exchange capacity for the lead ion. The mercury ion can be removed from the waste water by the Immobilized metal affinity chromatography (Imac TMR resin), ALM-525 resin and sarfion resin. The Imac TMR has microporous copolymer structure which could bind with Hg due to the presence of SH group. Cadmium can be removed by cationic resins Doweex50 W-X4 and purolite S-950 (Zhang et al. 2019).

8.5 Advanced Technology for Heavy Metal Ion Removal

8.5.1 Nano-Adsorption

Nanotechnology has been developed to purify drinking water, and provide efficiency through minimal generation of waste. Nano-magnetic oxides (NMO) are extensively used in the waste water treatments. The high surface area, stability and the nanostructures are advantageous to remove metal ions, but the adsorption properties are dependant upon the conditions of the operating unit. Zeolites-based water treatment plants have also been applied for the removal of toxic metals. Zeolites are negatively-charged lattice, composed of alumino-silicate with porous surface and cavity structure in a three-dimensional frame work. The negatively-charged mineral is balanced by the positive charge ions such as Na^+, K^+, Ca^{2+}, and Mg^{2+}. The zeolites can easily replace the cations present in water. The low cost and high surface area make zeolites one of the most efficient water treatment materials especially for heavy metal ions removal. The ion exchange properties of zeolites commonly exhibit the sorption order of $Pb^{2+} > Cu^{2+} > Ni^{2+}$. The Pb^{2+} and Cu^{2+} removal from aquatic system depend upon the composition of alumino-silicate framework, while the Ni^{2+} sorption mainly depends upon the size and shape of the micro-pores present on the surface of the lattice (Hong et al. 2019) (Fig. 8.9).

8.5.2 Molecularly-Imprinted Polymers

Ion printing is one of the advanced methods for the preparation of adsorbents, with high selectivity and affinity for ions. Ion printing polymers (IIP) bear the same properties as that of the molecularly-imprinted polymers which can detect metal ion and differentiate between the types of ions. Suitable monomers having cross-linkage properties and proper ion templates are pre-requisites for the synthesis of IIP. The ion templates and the monomers are the basic components to form the metal-ligand

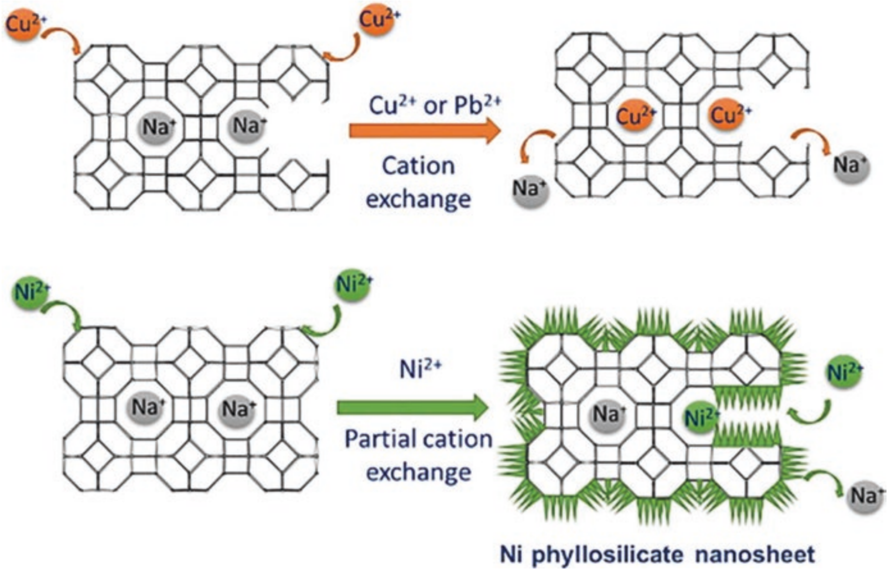

Fig. 8.9 Effect of zeolites on copper and lead sorption. Zeolites take up the heavy metal ions such as copper and nickel by exchanging with the lighter metal ion such as sodium to remove the ions from the sample. (Reprinted with permission of Heavy metal adsorption with zeolites: The role of hierarchical pore architecture, Elsevier, Hong et al. 2019)

complex where the coordination bond or electrostatic attractions are the main factors. Copolymerization of metal-ligand complex and the initiators are necessary to obtain the final product. The resultant polymers are washed with appropriate solution to obtain a polymer with three-dimensional specific cavities due to the removal of the template ions (Zhang et al. 2019).

8.5.3 *Layered Double Hydroxides (LDH) and Covalent-Organic Framework (COF)*

Apart from the noxious metallic ions present in cationic form, different types of anions are also present in the waste water or in air. Layered double hydroxides (LDHs) are active adsorbents used to remove these anions. (Dai et al. 2019). Another development is the specifically designed covalent organic frameworks (COFs) under defined conditions. COFs are divided on the basis of the monomers that are the basic component making up the specific COFs, with specific pore size to capture the desired heavy metal. Amide-based COFs could be recycled for several cycles of usage (Li et al. 2019).

8.5.4 Emerging Membrane Technologies

Different types of micro-porous membranes have been used for the removal of high molecular weight pollutants like colloides and dissolved particles from waste water. Specific pressure from 0.1 to 5 bars is commonly applied. Many types of polymer membrane such as Complexation-enhanced ultra-filtration (CEUF), simple polymer ultra-filtration, polyelectrolyte ultra-filtration and polymer supported ultra-filtration use the same working principle. *Saccharomyces cerevisiae*, sodium alginate, and seaweed-extracted polysaccharides are initially used in the synthesis and polymerization of CEUF. Metal ions are attached to the functional group of the polymers through ligand formation or electrostatic interaction (Abdullah et al. 2019). The complex formation of the polymers is achieved with the heavy metals utilizing chelation process as the basic mechanism of the CEUF.

In electro-dialysis, ionic-exchanger membranes (IEMs) comprising of anionic and cationic membranes are placed in parallel stacks. In between the stacks, a dilute feed stream along with the electron stream flows through the IEMs. The electric current is applied to the electrodes to allow the current flow in the solution feed through which the positive metal ions move towards the cathode. These ions then pass across the negatively charged membranes and halted by the positive membranes. Similarly, the negative ions move towards the anode, crossing the positive membrane and stopped by the negative membrane. Small amount of hydrogen gas is released at the cathode and chlorine and oxygen are removed at the anode as represented by the equations (Abdullah et al. 2019):

$$2e^- + 2H_2O \rightarrow H_2(g) + 2OH^-$$

$$H_2O \rightarrow 2H^+ + 1/2O_2(g) + 2e^- \text{ or } 2Cl^- \rightarrow Cl_2(g) + 2e^-$$

8.6 Low-Cost and Biotechnological Approaches

8.6.1 Biosorption

Biosorption has been increasingly used for heavy metal ion sorption utilizing agro-biomass and natural microorganism like fungi, algae and bacteria. The method is attractive for industrial scale application as it is cheap, efficient, can be regenerated, utilizes less chemicals, and the metals can be recovered (Joshi 2017). The biosorbent may be pretreated chemically for process improvement on the sorptive capability, and different types of biosorbents sorb the metal ions to a different capacity. Coal, coconut shells, wood have been turned into activated carbon (Joshi 2017). Clay is the potential alternative to the activated carbon especially the zeolites which have high surface area and negatively-charged functionalities to attract the metal

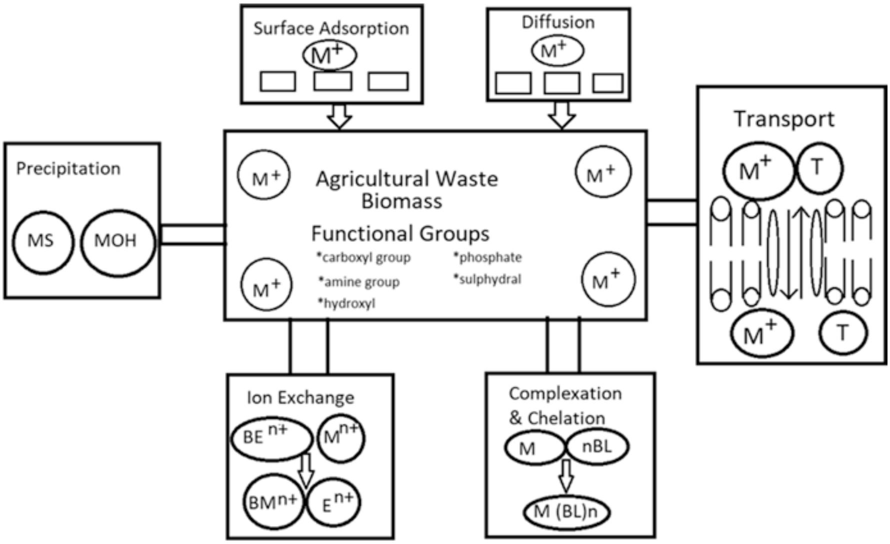

Fig. 8.10 Mechanism of biosorption. The heavy metals present in soil are sorbed via precipitation, ion exchange (Biomolecules with Exchangeable ions (BE), Biomolecules with Metal ions (BM)), complexation and chelation, and ion transfer, in order to remove heavy metal ions using agricultural biomass waste. (Reprinted with permission of A review on heavy metals uptake by plants through biosorption, Attribution international (CC BY 4.0), Sao et al. 2014)

ions. Chitosan which has versatile metal binding capacities, is also more cost-effective than the activated carbon. The raw materials can be sourced from the fishery wastes such as lobsters, shrimp and crab shells. Figure 8.10 illustrates the mechanism of biosorption for metal ion removal.

8.6.2 Microbial Remediation

Microbial remediation removes heavy metals by precipitation, reduction, oxidation, absorption and adsorption (Fig. 8.11). The uptake into the microbial metabolic pathways allows the heavy metals to be utilized for metabolism, respiration, fermentation and growth. Microorganisms such as algae, yeasts, bacteria and fungus have been utilized as biosorbents for the removal or recovery of heavy metals (Ayangbenro and Babalola 2017; Igiri et al. 2018). These may involve processes such as bioaccumulation, biosorption, and biomineralization (Ayangbenro and Babalola 2017). Bioaccumulation uses living cells to actively accumulate and transport the ions into the cells (Fig. 8.12). Biosorption can be passive but occurs very fast where the metal ion binds to the surface of the organisms. Then, the ion slowly perforates the cell membrane and enters the cell. Metal ions can be reduced to lower the reduction state to make them less harmful and converted into water soluble forms. It is the specific

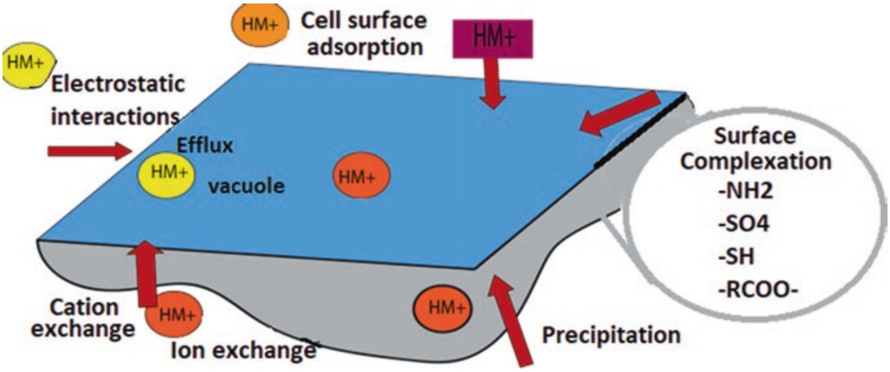

Fig. 8.11 Mechanism of heavy metal ion uptake by the microorganisms by electrostatic interaction, cation exchange, precipitation, or adsorption. (Reprinted with permission of Toxicity and bioremediation of heavy metals contaminated ecosystem from tannery wastewater: a review, Hindawi, CC BY 4.0, Igiri et al. 2018)

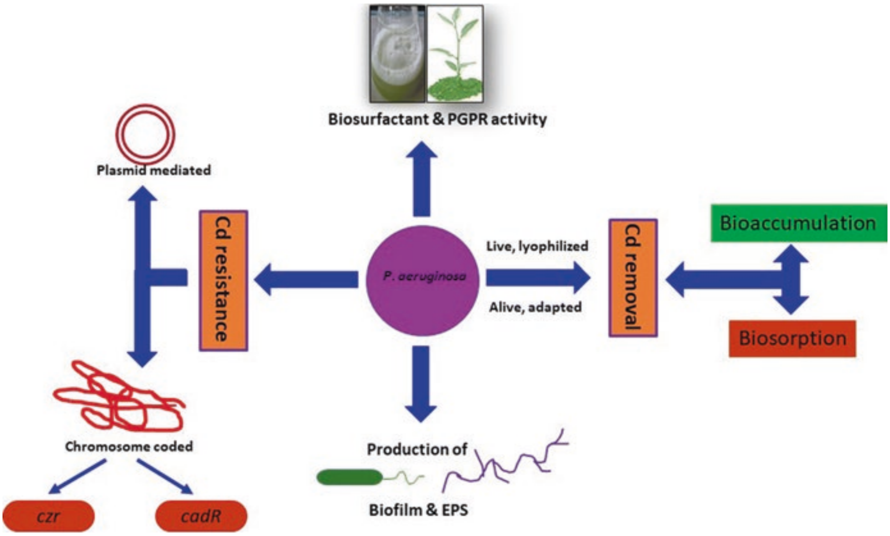

Fig. 8.12 Mechanism of bioaccumulation for cadmium. (Reprinted with permission of Cadmium (heavy metals) bioremediation by *Pseudomonas aeruginosa*: a minireview, Common Creative attributions, Chellaiah 2018)

characteristic of the microbial cells that converts the oxidation state of the metal ion from one form to another, thereby lessening the ion toxicity. Different metals and metalloids are used as electron donor or contributor by the bacteria for energy production. Some metals, also in oxidized form, act as acceptor of electrons in anaerobic respiration of bacteria. Metal ions can be reduced by enzymatic reactions to generate less harmful chromium or mercury. Through bioleaching (Fig. 8.13), metal

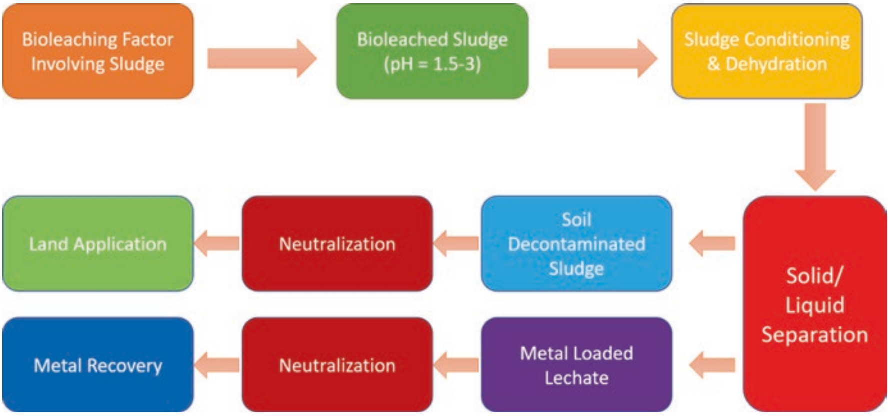

Fig. 8.13 Process of bioleaching. Bioleached sludge is conditioned and dehydrated leading to solid and liquid separation, thereby neutralizing it to obtain metal recovery. (Reprinted with permission of Bioleaching of heavy metals from sewage sludge: A review, Attribution international (CC BY 3.0), Pathak et al. 2009)

ions can be dissolved naturally and removed from the soil (Bahafid et al. 2017). Fungi have been used for biomonitoring of the toxic metal ions as the fungal cell wall contains proteins and polysaccharides that could bind the metal ions. Fungi, algae and yeasts such as *Yarrowia, Pichia and Candida* have high tolerance towards heavy metal ions. In the case of algae, this may depend on the internal structure and the environment or habitat of the species (Yadav et al. 2017). Different defence mechanisms such as ion complexation or binding protein formations have been used by the microorganisms to cope with the heavy metal stress. Metal toxicity due to the complex formation of metal ions and the biomolecules can block the metabolic activities and inhibit growth. There are however threshold limits beyond which the microbial tolerance towards toxicity may be reduced (Yadav et al. 2017).

8.6.3 Biotechnological Strategies

Biofilms can be applied as stabilizer, and used for bioremediation or biotransformation of persistent organic pollutants, pharmaceuticals/personal care products, and heavy metals (Edwards and Kjellerup 2013). Biofilms possess the characteristic of emulsifier or surfactant properties and could tolerate large amount of toxic metal aggregation. Encapsulating or immobilizing the biomass in polymeric matrix also improves the chemical and physical stability especially in cases where the level of heavy metal ions removal are not satisfactory. To increase the efficiency of remediation, recombinant deoxyribonucleic acid (DNA) technology is used to change the genome of microorganisms or specific enzyme pathway such as ligases by metabolic or genetic engineering. Heavy metals like arsenic, cadmium, and mercury can be removed using the genetically-modified microorganisms but the rate of decontamination still depends on the enzyme catalytic activity (Ojuederie and Babalola 2017). *Chlymadomonas reinhardtii* strain has been engineered to tolerate cadmium toxicity, and *Escherichia coli* is genetically engineered to specifically target As^{+3} removal. Over expression of arsenic-resistance (*ars*) operons in *Cyanobacterium glutamicum* has been developed as a strategy to remediate arsenic contaminated sites (Igiri et al. 2018).

In the cell cytoplasm, there is a mixed amount of metal ions that could be sequestered intracellularly by the biomolecules. These include the polysaccharides, lipids and peptidoglycan, with ligands and functional groups on the cell surface such as hydroxyls, carboxyls (-COOH), $-PO_4$, thiols, and amino group that are metal binding. Zinc ions for example are transported from the cytoplasm and get accrued in the periplasm, where the influx or efflux of ions take place with the physiological changes within and outside the cells. Different kinds of bacteria have the ability to remove metals by extracellular sequestration of metal ions, allowing precipitation of the metals and converting them into nontoxic elements. Examples are the sulphur-reducing bacteria which include *Desulfromonas* and *Geobacter* species. An anaerobe, *G. metallireducens,* has the capacity to reduce Mn^{4+} to Mn^{2+}, and Cr^{6+} to Cr^{3+}. The bacteria that reduces sulphur, produces large quantity of H_2S, causing the precipitation of metal ions that are positively charged. With *P. aeruginosa* strain, the precipitation of cadmium could take place in aerobic condition. Another economical biotechnological approach is phytoremediation, utilizing plants for the removal or remediation of toxic pollutants from groundwater, ground, and wind (Fig. 8.14). It is eco-friendly and could work in symbiosis with the microbial biomass. The phytoremediating plants maybe hyper or non-hyper accumulators. The hyper type does not require any enzymes for the removal of toxic metallic ions. Phytoextraction may include direct extraction of the metal ions into the plant vacuole, and rhizoremediation uses microbes in rhizosphere to remove toxic ions (Ojuederie 2017). As shown in Fig. 8.15, the biotechnological and biological approach, though may be time consuming and limited to specific contaminated sites, is more cost effective and environmentally-friendly to achieve long term remediation of the toxic pollutants.

8.7 Conclusion

Adsorption, biosorption electrochemical treatment and membrane filtration are conventional methods to reduce water contamination and to produce clean water. However, advanced methods for heavy metal removal from waste water including nanotechnology and emerging membrane technology, can be costly. Lower cost sorbent technology utilizing zeolites and metal organic frameworks have been applied to achieve reasonable economical treatments of heavy metals. Remediation of heavy metals from wastewaters via biotechnological strategies have attracted considerable interest not only because of the economics, but because these are more eco-friendly for long term use. The future direction may involve the application of biofilms and

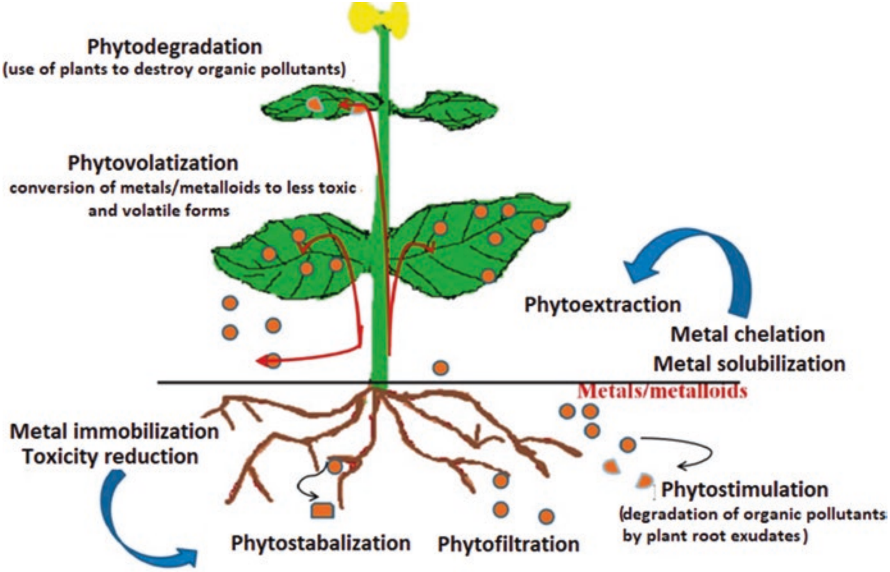

Fig. 8.14 Phytoremediation in plants. Phytovolatization converts metals into volatile form, phytodegradation degrades metals via enzymes, phytofiltration filters metal ions, phtyoextraction extracts the accumulated metals, phytostabilization limits the movement of metal ions, and phytostimulation degrades the metal ions *via* extruders. (Reprinted with permission of Microbial and Plant-Assisted Bioremediation of Heavy Metal Polluted Environments: A Review, Attribution international (CC BY 3.0), Ojuederie 2017)

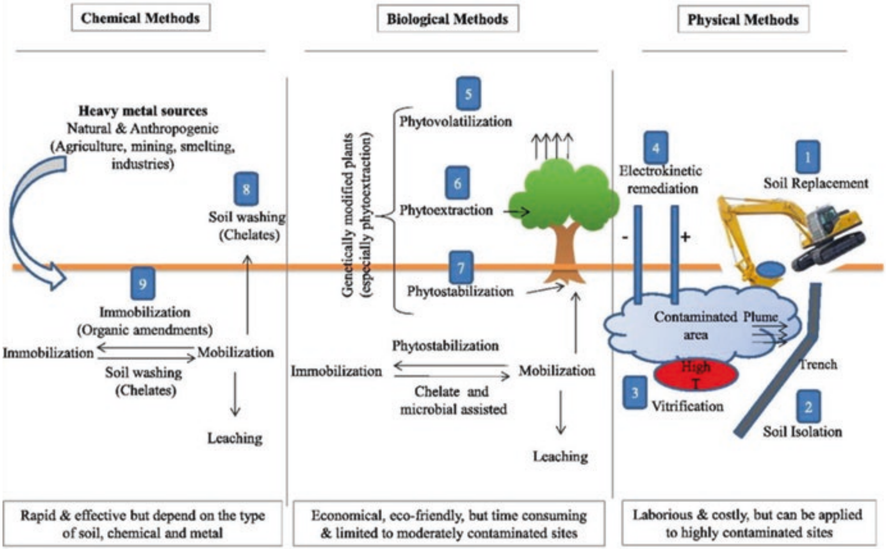

Fig. 8.15 Comparison of the technologies for toxic heavy metal remediation involving chemical, biological, and physical methods. (Reprinted with permission of A comparison of technologies for remediation of heavy metal contaminated soils, Creative Common Attribution (CC BY 4.0), Khalid et al. 2017)

surfactants in combination with microbial remediation and phytoremediation to achieve higher efficiency with long term reduction of environmental impact.

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Chapter 9
Use of Nanomaterials for Heavy Metal Remediation

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Abstract The world has been facing a grave problem of water pollution. One of the most abundant pollutants are heavy metals. They exhibit toxic or carcinogenic effect on organisms and are especially troublesome owing to their bioaccumulative nature. Most conventional water treatment methods are unable to fully remediate water from heavy metal cations. Techniques based on adsorption create a big opportunity in this field due high efficiency, low-cost, flexibility and ease of operation. Nanomaterials possess series of characteristics such as large specific surface area, developed porosity, high interfacial reactivity and tunable physiochemical properties that make them attractive in the field of adsorption-based water treatment techniques. Nano-clay minerals, layered double hydroxides, zeolites, two-dimensional early transition metal carbides and carbonitrides, zero-valent metals, metal oxides, carbon nanotubes, fullerenes, graphene, graphene oxide, reduced graphene oxide, graphitic carbon nitrides, metal-organic frameworks all belong to the nano-class materials and have found their use in water remediation. Despite some disadvantages originating from still not entirely investigated effects they can have on the environment, they exhibit great removal abilities and in the foreseeable future should be the basic pillar of adsorption-driven water treatment.

Keywords Water treatment · Adsorption · Heavy metals · Nanomaterials · Nanoadsorbents · Removal efficiency · Adsorption capacity · Environment pollution · Nanomaterials application · Wastewaters

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9.1 General Introduction

The world the we know depends on water; it is its main constituent and a vital factor for proper functioning of the environment and an essential element for the survivor of life on Earth. Out of the enormous water quantity on Earth only around 1% is available as freshwater used in our day-to-day activities (Sharma and Sanghi 2012; Mishra and Clark 2013). The significance of water has long been recognized as it has been worshipped by some civilizations, certain religions consider it sacred and some artists and poets inspiration source. As precious as it is, it has also become one of the most exploited resources on our planet. Constant economic growth, extensive urbanization, massive industrialization and many spheres of human activities has been contributing to progressive deterioration of water quality. Moreover, the total world's water demand is expected to increase by 30% until 2050 (UNESCO-WWAP 2019). Almost all water supplies sources in the world are polluted with substances of varying toxicity and access to potable water is a common major problem afflicting many people (Mishra and Clark 2013; Sharma et al. 2013; Srinivasan 2013). The water resources on Earth are limited and their quality degradation, with its immediate and long-term consequences, poses a serious threat for the mankind that is already paying and is going to pay even a higher price if preventive actions are not undertaken in the coming decades.

9.2 Heavy Metals in the Environment

The term heavy metal has never been defined by IUPAC hence it has no one coherent and clear definition. What is more, list of metals that are consider heavy may vary from one to another, what additionally complicates the issue (Bánfalvi 2011). In general, the term heavy metals may be applied to any metal or metalloid that has atomic density within the range of 3–5 g cm^{-3} (Bánfalvi 2011; Chen 2012; Gautam et al. 2015). Other definition bases on the atomic mass and says that a metal should be seen as heavy if its atomic mass exceeds 40 u (Chen 2012). Yet, another one states that if a metal has d-orbitals in its structure, then it is heavy (Bánfalvi 2011).

Despite of these discrepancies, there are no doubts that heavy metals exhibit adverse effects on living organisms even if present only at low concentrations. The hazardous nature of heavy metals originates also in their tendency to accumulate in biotic systems as they, unlike many other pollutants, cannot be degraded into harmless end products (Küpper 2011; Chen 2012; Gautam et al. 2015). Despite this, one should notice that at trace level concentrations certain heavy metals are necessary for some organisms (Ho and El-Khaiary 2009; Küpper 2011; Gautam et al. 2015).

Contamination of the environment with heavy metals has become one of the most acute and long-term environment problems nowadays that has been in the focus of many intensive research worldwide (Ho and El-Khaiary 2009; Küpper 2011; Chen 2012; Janyasuthiwong et al. 2017). Owing to regulations on the national and international level and considerable improvement in applied technologies the emission of heavy metals from point sources, that is industry-driven sources, has been considerably reduced. However, emissions originating from diffused sources such as agriculture, combustion, and traffic, if not have increased they have reminded stable. Consequently heavy metals have found their place among the most common water pollutants (Scoullos et al. 2001; Gautam et al. 2015). A brief description of the most commonly occurring heavy metals is presented in the subsection below.

9.2.1 Characteristics of Selected Heavy Metals

Copper occurs in nature as free metal; it is used mostly in a pure form or as alloy. Copper sulfate finds applications as a fungicide, algaecide, and also as nutritional supplement. Copper is released to the environment on the natural way via eruption of volcanoes and weathering processes, and on the anthropogenic way during smelting and ore processing. Excessive exposure to this metal may result in anemia, impaired immune system, and internal organs damage (ATSDR 2004a).

Lead emissions are mostly anthropogenic. Before leaded gasoline was banned, most of lead came from automobile emissions and lead containing paint; another common sources are lead ore mining, ammunition and battery production, iron and steel forges, breakdown of construction materials containing mining waste and of lead-containing chemicals. The main target for lead toxicity is the nervous system and kidneys (Scoullos et al. 2001; ATSDR 2002).

Mercury naturally occurs in several forms with methylmercury being of particular concern as it can accumulate in certain organisms. Mercury enters the environment by weathering and volcanic processes. Human contribute mainly by fossil fuels combustion, mining and smelting, improper waste incineration. The main target for mercury poisoning are the kidneys and the nervous system (ATSDR 1999; Scoullos et al. 2001).

Arsenic is widely found in soil and many kinds of rock. Arsenic compounds prevent wood form rotting and decay; it occurs in lead-acid batteries, in semiconductors and some light-emitting diodes. It is released the environment due rock weathering and volcanic activities, during mining and smelting its ores and in industrial wastewaters. Arsenic is a strong toxicant existing in several oxidation forms in a variety of inorganic and organic compounds. Skin is the most sensitive target arsenic exposure; it is also a carcinogen targeting the respiratory and digestive systems (ATSDR 2007).

Cobalt is a naturally occurring metal of which small amounts can be found found in rocks, soil, water bodies, and living organisms. This element may be deposited on land by the activity of wind that carries droplets of water containing cadmium, eruption of volcanoes and forests incinerations. Coal-fired power plants as well as cobalt mines and smelters release small quantities of that element. Radionuclides used as gamma radiation source may enter the environment after nuclear accidents, radioactive waste disposal and operations of nuclear power plants. Cobalt alloys are corrosion resistant, its compounds are used as pigments and in agriculture and medicine. Cobalt can cause adverse effects in various internal organs and the radionuclides damages characteristic for radiation sickness (ATSDR 2004b).

Nickel is abundant in Earth's crust. It enters the environment during mining and processing by the nickel industries, some amounts are emitted by oil-fueled power plants and solid waste burning. Nickel is used to manufacture various every-day use goods and its alloys are used in making stainless steel, jewelry and coins. Common adverse effects on nickel are allergic reactions (ATSDR 2005).

Cadmium occurs in the environment rather as oxides, sulfides, and carbonates, rarely as a pure metal. Most of that metal enters the environment due to weathering of rocks forest fires and volcanic eruptions. Anthropogenic activities such as mining, fossil fuels and household waste combustion and use of some fertilizers also take an important part in cadmium circulation in the environment. There are strict regulations on discharge of cadmium-containing wastewaters, hence only a small amount of cadmium enters water bodies that way. The main cadmium exposure sources are cigarettes, the daily intake of cadmium may be even doubled in smokers. This element targets the lungs, kidneys, stomach, and bones (ATSDR 1993).

9.3 Wastewater Treatment

Water treatment can be broadly defined as a process applied to wastewater in order to achieve demanded quality standards defined by legislation depending on the water use (Howe et al. 2012). The methods to treat water may be grouped according to their nature as based on physical forces, chemical reactions, electrical interactions, thermal processes, and biological approaches (Gupta and Ali 2012; Sun et al. 2012). The treatment often possesses many technical and economic challenges because some techniques are not effective enough and/or inordinately costly (Sharma et al. 2013; Srinivasan 2013). Moreover, sometimes a various methods must be applied in a co-treatment as no single one is able to completely remove all contaminants (Mishra and Clark 2013). Furthermore, some treatments may produce secondary pollution generating toxic sludge with by-products more hazardous than the treated compound (Teng and Low 2012; Sharma et al. 2013; Srinivasan 2013). Despite the fact that a variety of processes have been tested for metal cations removal, a cost-effective effluent treatment method still remains an object of interest in research in the field of wastewater treatment (Sun et al. 2012; Teng and Low 2012).

Biological treatment is suitable for elimination of heavy metal cations, but the stability of the microorganism may be easily upset when heavy metal cations are present in high metal concentrations.

Nano and ultrafiltration or reverse osmosis, as effective as they are, consume a lot of energy, the membranes are excessively expensive and have short life time. It all together makes the processes economically challenging limiting their application (Hassan and Hawkyard 2007; Philippis and Micheletti 2009; Carolin et al. 2017).

Coagulation and flocculation based approaches have been widely used for the purpose of removing heavy metals from water. The biggest drawback is that removal is only partial and additionally large quantities of a chemical sludge are generated what increasing the operation costs, as it has to be properly handled afterwards. There is also a disadvantage of over-feeding chemicals to the waste stream furtherly contaminating the effluent. Chemical precipitation bases on the principles of this processes class, although it has the same disadvantages, it is the most common metal cations removal technology. It is simple and inexpensive but in many cases not efficient; when a wastewater contain various cations, it might be hard to remove all of them as the pH conditions for precipitation of one metal may solubilize another. On top of that, to reduce the metals concentration of acceptable level substantial amount of chemicals must be utilized (Hassan and Hawkyard 2007; Philippis and Micheletti 2009; Carolin et al. 2017).

Phytoremediation bases on the ability of plants roots to adsorb, accumulate and immobilize heavy metal cations. It is an inexpensive method, however the treatment takes a long time and some chelating agents must be used to enhance the accumulation levels in plants (Dineshkumar et al. 2019).

Ion exchange relays on exchanging harmless ions with ions that are being removed form wastewater of the same charge. This method is efficient but be really expensive due to the ion exchange resins price (Philippis and Micheletti 2009).

Adsorption is a process during which atoms interact with solid surfaces by means of physical or chemical forces. This water technique stands out from the others; it is simple, easy to operate, flexible, versatile, does not consume much energy, it is economically viable, reaches high removal levels, and has wide applications range (Gupta and Ali 2012; Hadi et al. 2015; Bonilla-Petriciolet et al. 2017). It has been recognized as a viable water sanitation technology and is recognized as one of the most advantageous and effective approaches for water pollution control (Gupta and Ali 2012; Teng and Low 2012; Hadi et al. 2015; Bonilla-Petriciolet et al. 2017). Among many types of adsorbents used in the process, nanomaterials hold a special position owing to a set of certain characteristics highly desired in the field of adsorption.

9.4 Nanomaterials

The nano-scale refers to sizes between 1 and 100 nm. Materials enclosed in such dimensions open a new world of possibilities and possess unique features quite different than their bulk scale counterparts. This nano-world has been in a center spot of attention of many researchers and industrial communities. Miniaturization, by some, is considered to be the key for our future as it provides viable ways to impact our lives and the environment that we inhabit. The development of nanotechnology created means to produce custom-designed nanomaterials of various sizes, shapes and surface properties. This consequently allows to produce materials of certain characteristics desired in specific applications. One of the applications where nanomaterials have been intensively used is water treatment. Increased porosity and large surface area create a great number of active sites for interaction of chemical species on the surface. As a result nanomaterials exhibit high interfacial reactivity what makes them cost-effective and highly-efficient adsorbents in water treatment systems. In the section below are described several groups on nanomaterials utilized in water remediation.

9.4.1 Clay Minerals

Clay minerals belong to a large family of aluminosilicate layered solids, they are the main constituent of clays – fine-grained natural materials. Clay minerals have ability to accommodate guest molecules what gives them good adsorption properties. Moreover, upon various modifications the properties can be significantly enhanced mostly due to an increase in their porosity and specific surface area (Ruiz-Hitzky et al. 2004; Bergaya and Lagaly 2006; Heller-Kallai 2013; Komadel and Madejová 2013; Stawiński et al. 2017; Stawiński et al. 2017; Węgrzyn et al. 2018).

The structure of clay minerals bases on a continuous octahedral and tetrahedral sheets where the octahedral sheet is sandwiched between two tetrahedral sheets. Each tetrahedron is built of a Si^{4+} or Al^{3+} cation coordinated to four oxygen atoms, and is linked to adjacent tetrahedra by sharing three of its corners forming two-dimensional mesh pattern; each octahedron is made of close-packed oxygen ions with cations such as Al^{3+}, Fe^{3+}, Mg^{2+} and Fe^{2+} occupying the sites between the oxygen and is connected to e neighbor by sharing edges. The resulting structure carries a negative net charge as a portion of the Si^{4+} in tetrahedral positions and/or Al^{3+} in octahedral sites is exchanged by geometrically similar cations of usually with lower valency. This charge is balanced by an anion located between the layers. Clay minerals are able to easily exchange these charge balancing species what consequently makes them good ion-exchangers (Velde 1995; Huggett 2004; Bergaya and Lagaly 2006; Brigatti et al. 2013). One of the most commonly used nano clays for water remediation are montmorillonite (bentonite) and vermiculite. The adsorption efficiencies of the both clays have been summarized and presented in Table 9.1.

9.4.2 Layered Double Hydroxide and Their Mixed-Oxides Counterparts

Layered double hydroxides or more commonly hydrotalcite-like materials or anionic clays are a big group of layered hydroxides of synthetic or natural origin. Their structure bases on hydroxides of usually two different di- or trivalent metal cations. Each cation is octahedrally surrounded by hydroxide ions forming an octahedron – the basic building unit of the material. The octahedra joined by

Table 9.1 Comparison of heavy metal cations adsorption efficiency of vermiculite and bentonite

Clay/origin/treatment		Metal	Adsorption capacity (mg g^{-1})	References
VERMICULITE	Sigma-Aldrich raw Virginia, USA raw Red Sea, Egypt Red Sea, Egypt (treated with 0.5 HCl) Red Sea, Egypt (treated with H_2O_2) Chennai, India	Cd^{2+}	44.64 68.9 15 21 23 11	Chen et al. (2018) Padilla-Ortega et al. (2016) Hashem et al. (2015) Vijayaraghavan and Raja (2015)
	Sigma-Aldrich raw Hebei, China raw Red Sea, Egypt Red Sea, Egypt (treated with 0.5 HCl) Red Sea, Egypt (treated with H_2O_2) Chennai, India Malatya, Turkey	Pb^{2+}	121.95 37 15 21 23 49 49	Chen et al. (2018) Yao et al. (2016) Hashem et al. (2015) Vijayaraghavan and Raja (2015) Sis and Uysal (2014)
	Chennai, India Guilan Province, Iran	Cu^{2+}	13 20	Vijayaraghavan and Raja (2015) and Dizadji et al. (2013)
	Piauí, Brasil (expanded for 1 min at 1000 °C) China (expanded for 1 min at 1000 °C) Chennai, India	Ni^{2+}	30 160 6.8	Marcos and Rodríguez (2016) Vijayaraghavan and Raja (2015)
	Sigma–Aldrich Bikita, Zimbabwe	Hg^{2+}	0.1 1.75 20	Tran et al. (2015) Tran et al. (2015) Brigatti et al. (2005)
	Yuli, China raw Greece	Mn^{2+}	28.32 25.6	Kebabi et al. (2017) Inglezakis et al. (2016)
	Greece Malatya, Turkey	Cr^{3+}	12.8 18	Inglezakis et al. (2016) Sis and Uysal (2014)
	Greece Malatya, Turkey Brazil expanded	Zn^{2+}	29.3 11 23.84	Inglezakis et al. (2016) Sis and Uysal (2014) Nishikawa et al. (2013)

(continued)

Table 9.1 (continued)

Clay/origin/treatment		Metal	Adsorption capacity (mg g^{-1})	References
BENTONITE	Oji River, Nigeria (treated in 1.5 M H_2SO_4) Cuencamé, Mexico Valea Chioarului, Romania	Cd^{2+}	0.62 6.978 2.76 13.05	Akpomie and Dawodu (2016) de Pablo et al. (2011) Fernández-Nava et al. (2011)
	Oji River, Nigeria (treated in 1.5 M H_2SO_4) Kutch, India (treated in 6.0 M H_2SO_4) Valea Chioarului, Romania	Pb^{2+}	1.62 6.535 19.45	Akpomie and Dawodu (2016) Pawar et al. (2016) Fernández-Nava et al. (2011)
	Kutch, India (treated in 6.0 M H_2SO_4) Aldrich Chemicals	Cu^{2+}	3.787 4.42	Pawar et al. (2016) Ijagbemi et al. (2009)
	Nigeria raw Oji River, Nigeria (treated in 1.5 M H_2SO_4) Oji River, Nigeria raw Cuencamé, Mexico Aldrich Chemicals	Ni^{2+}	200 4.0 166.67 4.849 5.61	Akpomie and Dawodu (2015) Akpomie and Dawodu (2016) Akpomie et al. (2015) de Pablo et al. (2011) Ijagbemi et al. (2009)
	Cuencamé, Mexico Valea Chioarului, Romania	Hg^{2+}	3.681 1.70	de Pablo et al. (2011) Fernández-Nava et al. (2011)
	Oji River, Nigeria (treated in 1.5 M H_2SO_4) Nigeria raw Oji River, Nigeria raw Cuencamé, Mexico	Mn^{2+}	2.21 166.7 142.86 3.820	Akpomie and Dawodu (2016) Akpomie and Dawodu (2015) Akpomie et al. (2015) de Pablo et al. (2011)
	Gaomiaozi, China Tunis, Tunisia	Cr^{3+}	4.68 117.5	Chen et al. (2012) Ghorbel-Abid et al. (2009)
	Oji River, Nigeria (treated in 1.5 M H_2SO_4) Cuencamé, Mexico	Zn^{2+}	76.92 3.477	Akpomie and Dawodu (2016) de Pablo et al. (2011)

edge-sharing making layers stacking on top of one another forming a three-dimensional structure. The layer is positively charged and this charge is neutralized by an exchangeable anion, that can be almost freely selected, incorporated in the interlayer space. The materials upon exposure to high temperatures transform into mixed oxides. These when contacted with water and anions regenerate the layered structure of the starting material. The anions used in that process may differ from these from the original material. This feature is very important in synthesis of layered double hydroxides as it tune their properties as adsorbents (Braterman et al. 2004; Evans and Slade 2005).

The materials have different adsorption sites: one localized in the interlayer space -corresponding ion exchange originating from the layer charge and exchange capacity, the other localized on the external surface. These sites are related with the presence of two isolated electron pairs and a dissociable hydrogen on the surface hydroxyl groups (Braterman et al. 2004; Evans and Slade 2005). The surface of the mixed oxides has metal ions that are not fully coordinated a Lewis acids. A water molecule is first coordinated to such site then occurs dissociative chemisorption and consequently surface hydroxyl groups are formation (Schindler and Sposito 1991). Moreover, the positively charged layers attracts hydroxide ions creating good conditions to form metal hydroxides. Furthermore the carbonates located in edges of the interlayer space and on the material surface can react with metal cations and form insoluble carbonates (Barnabas et al. 2016). All that together makes layered double hydroxides and the mixed oxides good heavy metals adsorbents.

Li et al. 2019 prepared Mg-Al-CO_3 layered double hydroxide and calcined it at 550 °C and tested the material's ability to uptake Cu^{2+} and Cr^{6+}. The adsorption was on the level of 95.0 and 39.3 mg g^{-1} for Cu^{2+} and Cr^{6+}, respectively and the cations were built into the reconstructed layered double hydroxide structure. Applicability of the unclaimed form of this material for remediation of mine wastewaters was investigated by Rahman et al. 2018. The results showed high selectivity and the adsorption level reached 371, 7.2, 121, and 0.4 mg g^{-1} for Fe^{2+}, Zn^{2+}, Cu^{2+}, and Pb^{2+}. Ma et al. 2016 examined adsorption properties of a Mg-Al layered double hydroxide intercalated with MoS_4^{2-}ion. The capacities for Cu^{2+}, Pb^{2+}, Hg^{2+} and Ag^+ attained 181, 290, 500 and 450 mg g^{-1}, respectively. Polysulfide intercalated Mg-Al-NO_3 layered double hydroxide was examined by Ma et al. 2014 for adsorption of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Pb^{2+}, Cd^{2+} and Hg^{2+} reaching adsorption capacities on the level of 0.71, 0.43, 6.37, 2.00, 8.77, 5.65, 2.68, 6.69 mg g^{-1}, respectively. Wang et al. 2019 synthesized a Ni-Fe- layered double hydroxide intercalated with MoS_4^{2-}, the material was further immobilized on a carbon foam. Such hybrid exhibited adsorption capacity towards Hg^{2+}, Pb^{2+} and Cu^{2+} of 462, 299, and 128 mg g^{-1}. The absorption of Cu^{2+} and Pb^{2+} on Zn-Al-NO_3 layered double hydroxide intercalated with ethylenediaminetetraacetic acid was studied by Kano and Zhang 2018, the modification increased the material's adsorption capacity from 31 to 90 m g^{-1}. This author also investigated adsorption on Mg-Al-CO_3 and Mg-Al-NO_3 layered double hydroxide modified with ethylenediaminetetraacetic acid and with N, N′-1, 2-ethanediylbis-1-aspartic acid. The results indicated higher uptake on the CO_2-layered double hydroxide that reached 28 and 78 mg g^{-1} for Cu^{2+} and Pb^{2+} respectively 8 and 20 mg g^{-1} higher than on the NO_3-form. After the intercalation with the organic anions the capacities further increased to 228 and 169 mg g^{-1} for the ethylenediaminetetraacetic acid and N, N′-1, 2-ethanediylbis-1-aspartic acid form for Pb^{2+} and respectively 71 and 59 mg g^{-1} for Cu^{2+}.

9.4.3 Zeolites

A zeolite is an aluminosilicate material of a crystalline three-dimensional framework structure basing on crystalline silica building units. There are nearly 180 confirmed zeolite structures. The structure has uniformly-sized molecular-dimension pores allowing zeolites to act as molecular sieves. Molecules that are not too large to fit inside the pores can be adsorbed and these too large rejected. Some of the structural Si^{4+} atoms are substituted by Al^{3+} giving the framework a negative net charge – this charge is balanced by cations, usually K^+, Na^+ or/and Ca^{2+}, loosely sitting in the zeolite cavities. Some of the cations can be exchanged what together with the fact that they are quite harmless, makes zeolites good material to adsorb heavy metals from water (Maesen 2007).

Zeolites occur in nature, there is around 60 different natural zeolites known nowadays. The most commonly found are analcime, chabazite, clinoptilolite, erionite and faujasite, followed by heulandite and phillipsite (Colella 2007). There has been an active research on synthesis of such materials that begun nearly 80 years ago. The traditional syntheses undergo in hydrothermal or solvothermal conditions with organic amines, ammonium or alkali metal cations acting as the structure directing agents or templates, the tetrahedral atom source, solvent and a mineralizer. The mixture is then heated in an autoclave under autogenous pressure in temperature lower than 250 °C. These methods are not environmental friendly, hence a whole new branch of zeolite syntheses has been developed. Some of the "green" techniques include: the organic-template-free synthesis, metal-cation-directed synthesis, seed-assisted synthesis, solvent-free synthesis, organic-template-directed synthesis, mother-liquor-reused synthesis and the organic-template-reused synthesis (Liu and Yu 2016). All of the methods aim to reduce the environmental footprint and increase the safety of zeolite production. Thousands of zeolites with new compositions, framework topologies, and functionalities have since been prepared and found their applications in various fields among them is water remediation (Yu 2007). Table 9.2 presents adsorption performance of some natural and synthetic zeolites in removal of heavy metal cations.

9.4.4 Two-dimensional Early Transition Metal Carbides and Carbonitrides

Two-dimensional early transition metal carbides and carbonitrides are two-dimensional solids of thickness within couple of atomic layers. They constitute a large group of transition metal carbides and/or carbonitrides and exhibit properties quite different then their three-dimensional counterparts. The materials originate from phases composed of hexagonal layered early transition metals carbides and nitrides containing early transition metal, an element of the 13th or 14th group, and carbon or nitrogen. The structural octahedra are joined by sharing edges to form a

Table 9.2 Comparison of heavy metal cations adsorption capacities of natural and synthetic zeolites

Nature	Zeolite	Origin/Si and Al source	Adsorption capacity (mg g^{-1})	References
synthetic	Fe-modified W zeolite	mexican fly ash	As^{3+}: 0.315	Medina-Ramirez et al. (2019)
	mordenite-type	silica and sodium Aluminate	Zn^{2+}: 45.05	Gili and Conato (2019)
	X zeolite	diatomite and aluminium hydroxide	Single system Zn^{2+}: 194.9, Cu^{2+}: 146.0 Binary system Zn^{2+}: 4.0, Cu^{2+}: 158.2	Yao et al. (2019)
	X zeolite thiourea modified X zeolite	diatomite and $NaAlO_2$	Cd^{2+}:67.13 Cd^{2+}:94.47	Zhang et al. (2019)
	NaP1 zeolite	hazardous aluminum waste	Pb^{2+}: 245.75 Cd^{2+}: 4.43 Hg^{2+}: 0.22	Sánchez-Hernández et al. (2018)
	Na-A zeolite	bagasse fly ash	Cu^{2+}: 142	Oliveira et al. (2019)
	NaA ZSM-5	Tetraethylorthosilicate and aluminum nitrate	Hg^{2+}:32.25 Hg^{2+}:45.4	Alijani et al. (2015)
natural	Na-clinoptilolite	100 g of clinoptilolite shaken for 12 h in 1 L of 0.2 mol L^{-1} $NaNO_3$	Pb^{2+}:532 Zn^{2+}: 99 Cd^{2+}:75 Cu^{2+}:27	Liu et al. (2019)
	Mixture of mordenite, clinoptilolite and chabazite	Philippines, SAILE Industries, Inc	Zn^{2+}:27.17	Gili et al. (2019)
	SiO_2 modified modernite	Not disclosed	Pb^{2+}: 186.0 Cd^{2+}: 10.3 Cu^{2+}: 12.3 Zn^{2+}: 9.0 Mn^{2+}: 4.2	Wang et al. (2019)
	Mordenite Modernite activated in 1% HF and 6 M HCl	Indonesia	Cr^{6+}: 0.189 Cr^{6+}: 1.040	Neolaka et al. (2017)
	Clinoptilolite	Watercel ZZ, Celta Brazil Ltda	Cu^{2+}: 1.845 Cr^{3+}: 1.661 Fe^{3+}: 1.750	Zanin et al. (2017)
	clinoptilolite mordenite chabazite	Mongolia	Cu^{2+}:12.7, Zn^{2+}:N/M Mn^{2+}:9.8 Cu^{2+}:8.9, Zn^{2+}:54.9, Mn^{2+}:6.0 Cu^{2+}:8.3, Zn^{2+}:11.1, Mn^{2+}:6.6	Egashira et al. (2012)

sheet sandwiched between two layers of pure elements of the 13th and 14th group. The number of sheets that separated by this layer may vary. Two-dimensional early transition metal carbides and carbonitrides are formed by etching out the elements from that structure (Barsoum 2013; Naguib et al. 2014). The materials have been recently rising attention in the field of water remediation.

Adsorption of mercury onto magnetic titanium carbide was studied by Shahzad et al. 2018. The material exhibited high maximum adsorption capacity on the level of 1128.41 mg g^{-1}. Such high capacity was attributed the presence of Fe_2O_3 particles that generated oxidation states essential for Hg^{2+} complexation in forms of $Hg(OH)_2$ and HgO.

Copper removal was investigated by the same author on multilayered and on delaminated two-dimensional titanium carbide nanosheets (Shahzad et al. 2017). The adsorption proceeded on the way of reductive adsorption on the oxygenated moieties of the material structure. On the delaminated material the removal was faster in comparison with the multilayered – the equilibrium was established after 3 and 45 minutes, respectively; the adsorption capacity on the delaminated material reached 78.45 mg g^{-1}.

Uranium uptake was investigated on two-dimensional titanium carbine modified with NaOH and dimethyl sulfoxide. The greatest adsorption capacity was achieved on the hydrated dimethyl sulfoxide intercalated material and reached 160 mg g^{-1}, five times bigger than when the sample was dry (Wang et al. 2017).

Chromium removal by two-dimensional titanium carbine nanosheets etched with different hydrofluoric acid concentration was studied by Ying et al. 2015. The material reached the highest adsorption capacity on the level of 250 mg g^{-1} after etching in 10% hydrofluoric acid solution. The removal of Cr^{6+} was also tested on urchin-like rutile TiO_2–C nanocomposite prepared by in-situ phase transformation of ($Ti_3C_2(OH)_{0.8}F_{1.2}$) under $FeCl_3$ conditions by Zou et al. 2016. The adsorption capacity of this material reached approximately 225 mg g^{-1} and was higher than on the starting material, and the layered anatase that first forms and transforms into urchin-like rutile during the process – 62 and 11 mg g^{-1}, respectively.

Lead adsorption onto exfoliated and alkalization intercalated layered titanium carbide was investigated by Peng et al. 2014. The adsorption proceeded due to the hydroxyl groups in activated Ti sites, where Pb^{2+} cations were exchanged by formation of hexagonal potential trap. Portion of 1 kg of the adsorbent was able to remove lead from 4500 kg of water below 10μg L^{-1} concentration level.

9.4.5 Metal Based Nanoparticles

Metal based nanoparticles are another group on nano-size materials that are promising in the field of water remediation that can be an attractive alternative for conventional water treatment technologies. The materials exhibit good absorption properties due to fast adsorption rate, high adsorption capacity and high reactivity towards water contaminants. Moreover, they can be regenerated and used in cycles, which is economically profitable making such adsorbents low-cost (Yang and Xing 2007; Carolin et al. 2017; Litter 2018a). Metal-based particles are particularly interesting because they can be synthesized and modified chemically with ease. Generally speaking the methods can be classified as physical – ball milling, thermal evaporation, lithography, laser ablation, ultrasonication; as chemical – sol-gel processes, chemical vapor decomposition, chemical reduction, solvothermal technique; and as green methods using bacteria, fungi, algae, plants or viruses. However the most common technique involves the reduction of the metal cation to its metallic form (Shan et al. 2009; Abdullaeva 2017; Iravani 2018). Some of these methods have some drawbacks such as difficulty in controlling particle shape and designed size which affects the properties of the final product (Stefaniuk et al. 2016). Formation of nanoparticles on the way of chemical reduction allows to precisely control their size distribution. Different methods results in nanoparticles of quite diverse properties that are strictly reflected in the material's adsorption capacities and selectivity in removal of contaminants.

Despite the unquestionable advantages nano-scale metal-based adsorbents have certain disadvantages. There is relatively little known about the adverse effect of free nanoparticles in the environment and also many factors such as aggregation, formation of corrosion products, desorption of the contaminants from the material surface as a response to a change in treated water parameters may hinder their applications (Tesh et al. 2018). Generally this group can be divided into zero-valent metals and metal oxides.

9.4.5.1 Zero-valent Metals

Nano-scale zero-valent iron is the most used of this group. Such materials are usually obtained by the reduction of Fe^{2+} or Fe^{3+} to the metallic state using sodium borohydride (Scott 2011). Their structure relays on a metallic iron core that provides the reducing power for reactions with the contaminants and is surrounded by an oxide shell that can absorb the pollutants by electrostatic interactions and it forms a platform for chemical complex formation. The removal mechanism vary and can be driven by adsorption, precipitation, co-precipitation and chemical reduction with the latter being the most recognized one (Scott 2011; Liu and Zhang 2014).

Li et al. 2017 investigated simultaneous adsorption of As^{4+} and Cu^{2+} onto zero-valent iron obtained by the reaction of $FeCl_3$ with $NaBH_4$, the material exhibited high adsorption capacity on the level of 225 and 245 mg g^{-1} for Cu^{2+} and As^{5+}, respectively. Adsorbent formed in similar reaction was used for removal of Cd^{2+}, Ni^{2+}, Zn^{2+}, Cr^{6+}, Cu^{2+}, Pb^{2+} and Ag^{+} by Li and Zhang 2007. The nanoparticles exhibited strong selectivity and reached adsorption capacities on the level of 7.3, 14.2, 18.5, 19.4, 19.94, 19.94 and 19.96 mg g^{-1}, respectively. Dickinson and Scott 2010 studied removal of U^{6+} on nanoparticles formed in the reaction of $FeSO_4{\bullet}7H_2O$ with $NaBH_4$ and observed removal below 1.5% of the metal initial concentration using solution containing from 54 to 2480 ppb of U^{6+}. Adsorption of Cr^{6+}, Cu^{2+} U^{6+} and Mo^{4+} was investigated on an adsorbent synthetized in the same way by Scott et al.

2011. The removal levels for the three first cations were in the range between 96–99% while the removal of Mo, for reasons yet not established, was hindered and did not exceed 5%. Remediation of water laden with Pb^{2+} was conducted by Dongsheng et al. 2019 who proved that if the nanoparticles are freeze-dried and keep in nitrogen atmosphere before application, the maximum adsorption capacity may be enhanced, in this case from 671.04 to 807.23 mg g^{-1}.

The examples above present application of free zero-valent nanoparticles, however they can also be supported on a matrix formed of various materials such as biochar (Zhu et al. 2017), bentonite (Wang et al. 2018), lapillus (a volcanic rock) (Bilardi et al. 2019), pumice (Bilardi et al. 2013), calcium carbonate (Zhang et al. 2019), palygorskite (a clay mineral) (Zhang et al. 2019), mesoporous carbon (Shi et al. 2019), exhausted coffee grounds (Park et al. 2019) or fly ash (Liu et al. 2017) just to name a few.

Another zero-valent metal nanoparticle applicable for heavy metal cations removal is aluminum. Fu et al. 2015 demonstrated that acid-washed aluminum nanoparticles were able to remove around 50 mg g^{-1} of Cr^{6+} cations. Adsorption of this cations were also studied by Jiang et al. 2017. Zhang et al. 2018 reported if the nanoparticles are mechanically activated by ball milling in the presence of NaCl the adsorption occurs with around 292-fold faster rate.

Zero-valent silver also finds its application in water remediation. These nanoparticles obtained by reducing $AgNO_3$ by Benjamina leaves extract were tested for adsorption of Cd^{2+} cations by Al-Qahtani 2017. The results showed that one gram of such material is able to remove 0.845 mg of Cd^{2+}. The nanoparticles enclosed in the matrix of amorphous silica attained the maximum adsorption capacity of 42.26 mg g^{-1} towards Hg^{2+} in the study of Ganzagh et al. 2016. In the research of Ali et al. 2018 zero-valent silver was incorporated into cellulose what resulted in adsorption calcites on the level of 7.89, 2.67, 2.45, 0.92 and 2.23 mg g^{-1} for Hg^{2+}, Cr^{6+}, Co^{2+}, Pb^{2+} and Ni^{2+}, respectively. Silver nanoparticles shielded by mercaptosuccinic acid and supported on activated alumina were tested by Sumesh et al. 2011 for removal of Hg^{2+} and reached outstanding adsorption capacity of 800 mg g^{-1}. Silver nanoparticles trapped with a novel Schiff base as adsorbent of Cu^{2+} was investigated by Bhargava and Uma 2019. A novel nanocomposite based on silver nanoparticles incorporated into the structure of a fly-ash derived zeolite was successfully applied for Hg^{2+} removal by Tauanov et al. 2018. The results showed that such material was able to remove 99% of Hg^{2+}, which was respectively 10% and 90% higher than the score of the zeolite and the parent fly-ash separately. Similar good results for this cation removal were obtained on silver nanoparticles supported on grapheme by Qu et al. 2017.

Beside the mono-metallic nanoparticles some bi-metallic system can be applied to water remediation. It is well-documented that alloys with a noble metal increase the nanoparticle's reactivity. In such combination the noble metal is galvanically protected as the main metal cation acts as an anode and becomes oxidated. The pollutants removal occurs by chemical reduction through direct electron transfer with the noble metal or via reaction with hydrogen released during oxidation of the anode-acting cation (Tesh and Scott 2016).

9.4.5.2 Metal Oxides

Nano-form metal oxides have found their application in wastewater remediation from heavy metals. Not only they exhibit good adsorption capacities but also selectivity. The most commonly used species applied for that purpose are iron, aluminum, manganese, magnesium, and titanium oxides (Dasgupta et al. 2017).

Iron oxides is a term used to collectively name oxides, hydroxides and oxyhydroxides of ferric (divalent) or/and ferrous (trivalent) ion. Together there are 16 forms of iron oxides, the most abundant are hematite (α-Fe_2O_3), magnetite (Fe_3O_4), maghematite (γ-Fe_2O_3), wüstite (FeO) and goethite (α-FeOOH) (Faivre 2016; Lagroix et al. 2016). This group of nanoparticles in one of the most commonly applied in the field of water remediation.

Magnetite nanoparticles exhibited Cr^{6+} removal efficiency on the level of 4.5 mg g^{-1} in the study of Simeonidis et al. 2015. The particles size was crucial for the removal efficiency as when it was increased a significant adsorption capacity loss was observed (Simeonidis et al. 2013). The removal begun from typical for this kind of materials chemical reduction of Cr^{6+} by the Fe^{2+} sites and was proceeded by adsorption and complexion of the Cr^{3+} on the surface what caused gradual surface passivation and formation of a γ-Fe_2O_3 layer (Chowdhury et al. 2012; Lasheen et al. 2014; Pinakidou et al. 2016). Adsorption of As^{3+} and As^{5+} was investigated by Balcells et al. 2016 on hierarchical hollow magnetite nanoparticles obtained in a single-step gas condensation process. The adsorption capacities reached 326 and 190 mg g^{-1} for As^{3+} and As^{5+}, respectively. Such hollow structures synthetized by the template-free solvothermal method were successfully used for Cr^{6+} and Pb^{2+} removal. The adsorption capacities reached 9 and 19 mg g^{-1} for Cr^{6+} and Pb^{2+}, respectively (Kumari et al. 2015). The use of monodispersed magnetite for Pb^{2+} adsorption on the level of 250 mg g^{-1} was also reported by Bagbi et al. 2016. This author conducted regeneration studies and was able desorb up to 80% of the Pb^{2+} from the adsorbent with 20 ml of diluted HNO_3. Green magnetite nanoparticles synthesis where $FeCl_3$ was reacted with coconut husk extract the have been reported by Sebastian et al. 2018 and the adsorption of Cd^2 reached 37.03 mg g^{-1}.

Metal-oxides were also tested combined with different matrixes. The performance of Fe_3O_4 nanoparticles embedded on graphene oxide surface was studied in Se^{4+} and Se^{6+} removal by Fu et al. 2014. The material exhibited selectivity towards Se^{4+} form of selenium, the maximum adsorption capacity reached 23.809 mg g^{-1} and was around 40% higher than for Se^{6+}. Hierarchically structured magnetite-carbonaceous microspheres containing various rattle-type structured magnetic particles were synthetized and tested for Pb^{2+} removal by Gong et al. 2012. The maximum adsorption capacity was found to be 126 mg g^{-1}. Magnetite nanoparticles coated with carboxylic functional groups showed better than commercial magnetite Cd^{2+} adsorption capacity on the level of 37.03 mg g^{-1} (Sebastian et al. 2019). Silica-coated magnetite particles were used for Hg^{2+} removal by Girginova et al. 2010. The material exhibited high efficiency for Hg^{2+} on the level of 74% even at as low as 50μg L^{-1}.

It is a common occurrence that some Fe cations are substituted by other transition metals incorporated into the iron oxide structure (Lagroix et al. 2016). Liang et al. 2017 investigated magnetite doped with Cr, Mn, Co and Ni for removal of Pb^{2+}. These substitutions caused an increase in the capacity from 9.8 to 93.7, 26.0, 12.6, and 51.1 mg g^{-1} for the unmodified and Cr, Mn, Co, and Ni-enriched material, respectively. Some other authors studied removal of Cr^{6+} on $MnFe_2O_4$ (Ahalya et al. 2014) and Mo^{6+} on $CuFe_2O_4$ (Tu et al. 2014) and $ZnFe_2O_4$ (Tu et al. 2016). However the experiments were carried out under unreasonable conditions for drinking water remediation. Removal Pb^{2+}, Cd^{2+} and Cu^{2+} by magnesium oxide cores with silica coated nano-magnetite was assessed by Nagarajah et al. 2017. The adsorption capacities were on the level of 238 mg g^{-1} for Pb^{2+}, 85.1 mg g^{-1} for Cd^{2+}, and 33.5 mg g^{-1} for Cu^{2+}.

In addition to iron oxide-based nano-adsorbents there are reports on application of other oxides such us AgY oxide for removal of Cu^{2+} and Cr^{6+} (Pradhan et al. 2017), AlTi oxide for removal of As^{5+}, Cd^{2+} and Pb^{2+} (Sunil et al. 2018), AlFe oxide for As^{5+} and Cr^{6+} (Zhang et al. 2016), α-MnO_2 for Hg^0 (Zhou et al. 2019), γ-AlOOH for removal of Hg^{2+}, Cd^{2+} and Pb^{2+} (Xia et al. 2017), removal of Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} on TiO_2, MgO, and Al_2O_3 (Mahdavi et al. 2013), Pb^{2+} ions by SnO_2, and TiO_2 (Rehman et al. 2019), Cd^{2+} ions on plant mediated SnO_2 (Haq et al. 2016) and by SiO_2 and TiO_2 (Waseem et al. 2017), As^{5+} on $NdFeO_3$ (Luu et al. 2016), SnO_2-Sb_2O_3 for selective adsorption of Pb^{2+} (Rahman et al. 2015) or Pb^{2+} and Cr^{6+} on MgO (Dargahi et al. 2016).

9.4.6 Carbon-based Materials

Over the past decades many research works have shown the enormous potential of carbon-based nanomaterials for applications in environmental remediation (Fu and Wang 2011; Anjum et al. 2016). High adsorption capacities, large specific surface areas and nontoxicity are the reasons they have been used for this purpose for almost 20 years (Sarma et al. 2019). Furthermore, they stand out from other materials due to their availability and relatively low production cost (Thines et al. 2017).

Different hybridization states of carbon can yield multiple structural configurations (Guerra et al. 2018; Li et al. 2019). Carbon nanotubes, fullerenes, graphene, graphene oxide, reduced graphene oxide and graphitic carbon nitride are the most commonly investigated forms of carbonaceous nanomaterials (Kyzas and Matis 2015; Azzaza et al. 2017). The whole group of these nanomaterials possess distinctive chemical, physical and mechanical properties characteristic for their atomic structure. Some of them can be modified through functionalization or surface treatment to achieve target oriented adsorbents for heavy metal pollution (Adeleye et al. 2016; Li et al. 2019).

9.4.6.1 Carbon Nanotubes

Iijima 1991 made a breakthrough discovery in the field of chemistry and condensed-matter psychics which was development of carbon nanotubes. This 1-dimensional carbon form has cylindrical shape formed of enrolled graphene sheet with diameter in the range of 1 to a few nm (Sarkar et al. 2018). The sidewalls of each cylinder are made of hexagonal lattice of sp^2-hybridized carbon atoms Iijima 1991. Carbon nanotubes are classified into two types: single- and multi-walled nanotubes. The first are seamless cylinders made of a single graphene sheet with diameter of 0.2 to 3.0 nm. Due to different graphene sheet folding configurations single-walled nanotubes can be divided into armchair, zigzag and chiral forms (Kumar et al. 2014; Fiyadh et al. 2019). Multi-walled nanotubes are built of at least two nested cylinders equally spaced from each other by 0.34 nm (Tang et al. 2014). Their diameter lies within the range of 3 to 30 nm, while the length can reach up to dozens of nm, even to 1 cm (Kukovecz et al. 2013).

There are three main methods of obtaining carbon nanotubes: the laser ablation, arc discharge and chemical vapor deposition (Lieber et al. 1998; Gadhave and Waghmare 2014; Sharma et al. 2015). Laser ablation gives product with high purity and quality, but it is expensive. In this method carbon nanotubes are produced during graphite sublimation caused by high-power laser beam. Arc-discharge technique is more common and cheaper. An electric arc created between two carbon electrodes is used to form the nanomaterial. Chemical vapor deposition relays on high temperature decomposition of carbon-containing gas such as methane or carbon in the presence of a metal catalyst (Kumar et al. 2014; Sharma et al. 2015).

Surface modifications are one of the ways to tune nanotubes properties, they bases on introducing functional groups on nanotubes ends or sidewalls. The methods can be divided into three approaches: covalent bonding, noncovalent attachment, and endohedral filling (Gadhave and Waghmare 2014; Fiyadh et al. 2019).

Covalent functionalization is based on introduction oxygen-containing groups to the carbon nanotubes structure on the way reactions such as halogenation, electrophilic, nucleophilic or radical addition, carboxylation, grafting and ozonolysis in acidic or alkaline environment (Kumar et al. 2014; Ali et al. 2019). HNO_3, H_20_2, H_2SO_4, HCl or $KMnO_4$ are the most commonly used oxidants to enhance adsorption capacity of carbon-based nanomaterial (Machado et al. 2015; Anjum et al. 2016; Thines et al. 2017).

Non-covalent methods, such as microwave radiation and thermal treatment, involve interactions related to the $\pi - \pi$ stacking and van der Waals forces. Microwave radiation can cause purification and reorientation of damaged parts in a single-walled carbon nanotubes (Harutyunyan et al. 2002; Vázquez and Prato 2009). Additionally, it can develop defects on carbon nanotube's surface which act like adsorption sites consequently increasing the adsorption capacity. Thermal treatment causes enhancement of specific surface area as high temperatures cause decomposition of volatile matters located on the internal and external surfaces of pristine nanomaterial (Kumar et al. 2014).

Endohedral filling bases on placing different compounds into the nanotube inner cavities. It can be obtained mostly through encapsulation of some inorganic species or biomolecules (Kumar et al. 2014).

Carbon nanotubes possess four adsorption sites types. The first type is in the interior space of each nanotube – accessible only if the tube's open ends are unlocked. The second type is in the interstitial channels – the free spaces between the nanotubes in the bundle. The third type exists in the external grooves on the periphery of nanotubes where two outermost nanotubes connect to each other. The fourth type is on the curved external surface around nanotubes (Gadhave and Waghmare 2014). Carbon nanotubes stand out from other nanomaterials because of their high adsorption capacity. This feature may be influenced by many factors such as porosity degree, nanotubes type, purity or type of the functional groups on the material's surface (Ihsanullah et al. 2016).

Adsorption of Pb^{2+} was examined on carbon nanotubes produced by chemical vapor deposition and oxidized with nitric acid by Tofighy and Mohammadi 2011. The modification resulted in adsorption capacity increase of the tested materials and reached 117.64 mg g^{-1}. Mubarak et al. 2015 synthesized multi-walled carbon nanotubes via tubular microwave chemical vapor deposition. The product reached the maximum Pb^{2+} adsorption capacity on the level of 104.2 mg L^{-1}. Similarly to the authors mentioned above, Kabbashi et al. 2009 obtained the maximum adsorption capacity equal to 102.04 mg g^{-1} on such nanomaterial produced by chemical vapor deposition.

Removal of Cd^{2+} on carbon nanotubes oxidized with H_20_2, HNO_3 and $KMnO_4$ was investigated by Li et al. 2003. The results showed that $KMnO_4$ was the most effective oxidizing agent. For the carbon nanotubes modified with it, the adsorption capacity increased from 1.1 to 11.0 mg g^{-1}. For the other materials the capacities were lower on the level of 2.6 and 5.1 mg g^{-1} for HNO_3 and H_2O_2 treated nanotubes respectively. Mubarak et al. 2015 obtained adsorption capacity of Cd^{2+} equal to 88.62 mg g^{-1} on multi-walled carbon nanotubes produced via the microwave chemical vapor deposition technique.

Remediation of water laden with Cr^{6+} was tested on synthetized by chemical vapor deposition pristine and commercially available functionalized multi-walled carbon nanotubes by Pillay et al. 2009. The unmodified material exhibited better adsorption properties; 0.1 g of this adsorbent was able to remove up to 98% of the cation form a 100 ppb while the functionalized nanotubes managed to adsorb only around 55%. This behavior was due to repulsion of dichromate ions by the electron rich functional groups on the nanotubes. Huang et al. 2015 investigated magnetic multi-walled carbon nanotubes prepared by wet chemical treatment obtaining the maximum adsorption capacity of 16.234 mg g^{-1}.

Carbon nanotubes were also applied in remediation of Co^{2+}. Species oxidized with HNO_3 exhibited adsorption capacity equal to 49.261 mg g^{-1} in the study conducted by Kandah and Meunier 2007, and 85.74 mg g^{-1} in the research of Tofighy and Mohammadi 2011. The last author investigated also the removal of Cu^{2+} and Zn^{2+} reaching 64.94 and 74.63 mg g^{-1}, respectively. Veličković et al. 2013 examined adsorption of As^{3+} on unmodified, oxidized by mixture of HNO_3 and H_2SO_4, and amino-functionalized multi-walled nanotubes obtaining maximum adsorption capacities on the level of 3.55, 4.17 and 16.59 mg g^{-1}, respectively. Sulphur containing multi-walled carbon nanotubes were tested for adsorption of Hg^{2+} in the study of Pillay et al. 2013; the maximum adsorption capacity reached 72.8 mg g^{-1}.

9.4.6.2 Fullerenes

Fullerenes are another allotropic form of carbon discovered after graphite and diamond. They are zero-dimensional nanomaterials made of sp^2- and sp^3-hybridized carbon atoms arranged in hollow cage-like structure (Darwish 2013; Shan et al. 2017; Thines et al. 2017). The first fullerene type reported in 1985 was the Buckminsterfullerene (C_{60}) described as a highly stable and symmetrical structure of "truncrated icosahedron in appearance resembling a football ball". Over the years a number of other have been reported with carbon atoms varying from 20 to 84 (Darwish 2013).

Fullerenes are primarily known for their excellent dielectric properties were also used to remove impurities in the form of heavy metals. Low tendency to form aggregates combined with features like large surface, high surface to volume ratio and great electron affinity make them interesting in the field of heavy metal cations removal (Burakov et al. 2017). However, using fullerenes is associated with high costs that is why they are rather utilized as an additive to adsorbents in very small amounts approximately 0.001%–0.004%. Such admixture can lead to development of porous structure in the adsorbent structure, increase hydrophobic character, generally improving the material's adsorption capacity (Burakov et al. 2017).

Studies under the direction of Alekseeva et al. 2016 showed that addition of a fullerene into polystyrene composite successfully increased sorption capacity for Cu^{2+} the level of nearly 920 mg g^{-1}. Samonin et al. 2014 showed that small addition fullerenes into activated carbon increased its Cu^{2+} adsorption of by around 2 times reaching 125 mg g^{-1}. Adsorption properties of the C_{60} and C_{18} fullerenes are also briefly presented in the work of Gallego et al. 1994.

9.4.6.3 Graphene

Graphene is another allotropic variety of carbon, it was first considered thermodynamically unstable and its possibility to occur in ambient conditions was questioned. The situation changed when in 2004 Russian researchers lead by Novoselov isolated and characterized that material (Novoselov et al. 2004). For this discovery they were given then the Nobel prize in 2010 (Chowdhury and Balasubramanian 2014).

Graphene is a two-dimensional well defined, one-atom thick, monocrystalline carbon structure resembling the honeycomb lattice. Its network is made of hexagonal rings build of sp^2 hybridized carbon atoms joined by the sigma bonds with the length of 0.142 nm. Moreover, graphene layers can be combined into multi-layered forms consisting of sheets built of few (2–5) to multiple (2–10) layers (Suárez-Iglesias et al. 2017).

There are two approaches to obtain graphene: the top-down and bottom-up methods. The first techniques concerns mechanical, electrochemical and liquid-phase exfoliation, as well as chemical modifications by oxidizing agents what results in formation of graphene oxide. All the top-down techniques give single or few-layers graphene (Machado et al. 2015). This approach is low-cost however, some surface defects are formed during process. The bottom-up methods relay on the epitaxial growth, chemical vapor deposition and reactions of hydrocarbon substrates acting as graphene precursors. The defect-free graphene obtained on this way has remarkable properties but the production cost is very high compared to the top-down methods (Kim et al. 2009; Chowdhury and Balasubramanian 2014).

Characteristics of graphene such as enormous surface to volume ratio, occurrence of delocalized π electron cloud surrounding the honeycomb lattice, and incomparable to other materials specific surface area up to 2630 $m^2\ g^{-1}$ could make made graphene an excellent water contaminants adsorbent (Chowdhury and Balasubramanian 2014). However, it exhibits some limitations like its tendency to aggregate and the hydrophobic surface cause problems with good dispersion (Nupearachchi et al. 2017; Kim et al. 2018). That fact inspired scientists to perform various graphene modifications which led to the development of a whole new material groups collectively called the graphene family nanomaterials (Suárez-Iglesias et al. 2017). Graphene oxide and reduced graphene oxide are the flagship species from this group. Nevertheless, some attempts to use graphene as heavy metal cations adsorbent were made.

Leng et al. 2012 investigated removal of Sb^{3+} by graphene obtained via hydrazine hydrate reduction of graphene oxide. The research showed that pH played a significant role in the adsorption process. The maximum adsorption capacity of 7.463 mg g^{-1} was achieved around pH 11, the adsorption increased after crossing pH 3.8 when the graphene surface charge changed from positive to negative.

The ability of graphene to adsorb Pb^{2+} was studied by Huang et al. 2011. The nanosheets were prepared by low-temperature exfoliation under vacuum and then subjected to thermal treatment at 500 and 700 °C. The materials exhibited maximum adsorption capacity on the level of 22.42 mg g^{-1} for the untreated graphene, 35.21 and 35.46 mg g^{-1} for the materials annealed at 500 and 700 °C, respectively. The authors suggest that the Pb^{2+} ions acted as the Lewis acid and the adsorption sites on graphene as the Lewis base. Application of high temperatures and vacuum caused removal of oxygen containing groups from the graphene sheets, what enhanced both, the Lewis basicity and electrostatic attraction.

Linh et al. 2019 conducted adsorption studies of As^{3+} on graphene produced by electrochemical exfoliation of graphite rods. The maximum adsorption capacity attained the level of 25.84 mg g^{-1}. Graphene aerogel was prepared and used for adsorption of U^{6+} by Zhao et al. 2019 with efficiency of 238.67 mg g^{-1}.

9.4.6.4 Graphene Oxide

Graphene oxide is a carbon material formed during oxidation and exfoliation of graphite (Lingamdinne et al. 2016). The processes lead to introduction of oxygen containing species such as the carboxyl, carbonyl, epoxy and hydroxyl group into the graphite layer (Wang et al. 2013; Yang et al. 2019). Due to the occurrence of additional functional groups the thickness of graphene oxide is higher than of pristine graphene and lies in the range of 0.7 to 1.2 nm (Peng et al. 2017).

There are three major routes of obtaining graphene oxide: the Brodie, Staudenmaier, and Hummers reactions (Park et al. 2018). Although some variation of these reaction have been also used. The Brodie techniques basis on treating graphite with potassium chloride and nitric acid. Staudenmair simplified the Brodie's method by adding larger amount of potassium chloride and additional sulfuric acid to the reaction mixture what allowed to obtain more oxidized nanomaterial. The Hummers method decreased the synthesis time from 10 to 2 days. The reaction mixture includes sulfuric acid, sodium nitrate and potassium permanganate. Another way to obtain graphene oxide is exfoliation of graphite oxide into layer sheets by sonication or mechanical stirring. Overall, all the methods lead to graphene oxide, but the technique choice is determined by the desired structural properties of the product (Pendolino and Armata 2017; Peng et al. 2017). Similarly to graphene, its oxidized species have large specific surface area, but in the case of graphene oxide the surface charge is negative due to the presence of functional groups (Wang et al. 2013). Despite the increased interest in graphene oxide, its adsorption capacity towards heavy metal cations has not been fully investigated (Sitko et al. 2013).

Wang et al. 2013 examined graphene oxide obtained via the Hummers method for adsorption of Zn^{2+}; the adsorption capacity reached of 246 mg g^{-1}. The process occurred by ion exchange between Zn^{2+} and H^+ present on the functional groups on the graphene oxide surface.

Yang et al. 2010 investigated adsorption of Cu^{2+} in graphene oxide synthesized by modified Hummer's method. The maximum adsorption capacity reached 46.6 mg g^{-1} which was higher than on other adsorbents such as carbon nanotubes which was equal 24.47 mg g^{-1} (Li et al. 2003). The high removal efficiency was attributed to the large specific surface area and high oxidation degree of the material.

Zhao et al. 2011 examined adsorption of Co^{2+} and Cd^{2+} on few-layered graphene oxide. The highest adsorption capacities for both cations were obtained at pH above 9. At this pH range the material's surface was deprotonated as its point of zero charge (3.9) was exceeded. This consequently rendered more adsorption centra available for cation adsorption. At acidic pH, the surface was protonated and consequently positively charged rendering the adsorption of cations nearly impossible. The maximum adsorption capacities for Cd^{2+} and Co^{2+} were 68.2 and 106.3 mg g^{-1}, respectively.

Applicability of graphene oxide for Pb^{2+} adsorption was investigated by Zhao et al. 2011 who reported the maximum adsorption capacity of few-layers graphene oxide on the level of 842 mg g^{-1}. Sitko et al. 2013 described graphene-based nanomaterial being able to adsorb 1119 mg g^{-1} of Pb^{2+}. The adsorption process was driven by strong surface complexation of Pb^{2+} ions with oxygen-containing functional groups on the material's surface. Madadrang et al. 2012 used N-(trimethoxysilylpropyl) ethylenediamine triacetic acid to modify graphene oxide's surface. The novel material had additional chelating groups obtained by the reaction was able to remove up to 479 ± 46 mg g^{-1} of Pb^{2+}.

Gao et al. 2011 conducted functionalization of graphene oxide's surface by covalently attaching the thiol groups. The process resulted in six-fold increase in the maximum adsorption capacity of Hg^{2+} from the initial 30 mg g^{-1} to 200 mg g^{-1}.

9.4.6.5 Reduced Graphene Oxide

Graphene oxide can be submitted to reduction that leads to formation of another nanomaterial called reduced graphene oxide (Wang and Chen 2015). This material has the sp^2-hybridized structure restored and this method can be an additional route to obtain graphene (Warner et al. 2013). The reduction yield is not 100% hence the final product contain many structural defects and residual oxygen-containing group. Thanks to its corrugated surface with large specific area and a large number of micro and mesopores, reduced graphene oxides are classified as good adsorbents (Machado et al. 2015)· Graphene oxide reduction can be conducted in many was such as thermal, electrochemical or chemical treatment (Smith et al. 2019).

Different preparation methods give nanomaterials of various carbon to oxygen ratios and have impact on final product's morphology, its properties such as solubility, conductivity and mechanical strength. Thermal reduction of graphene oxide at temperatures ranging from 200 to 1000 °C is the most effective method of producing reduced graphene oxide. However, chemical modifications using reducing agents such as sulfuric acid, hydrazine or sodium borohydride are also common and are constantly improved by many researchers (Stankovich et al. 2007; Park et al. 2018).

The ability to absorb Cr^{6+} by this material obtained from refluxing of graphene oxide solution with ethylenediamine was investigated by Ma et al. 2012. The results showed that the reduction Cr^{6+} to Cr^{3+} occurred during contact between the heavy metal ions and the material surface at lower pH values. The process started with binding chromium ions to the reduced graphene oxide surface via electrostatic interaction between positively charged amine groups derived from ethylenediamine and negatively charged CrO_4^{2-}. Second step included reduction of chromium ions from +6 to +3 oxidation state thanks to the p-electrons on ethylenediamine. The last step might have been separated into two different paths: releasing of reduced chromium ions or absorption of Cr^{3+} on the surface the reduced graphene oxide. The maximum adsorption capacity reach 500 mg g^{-1}.

Awad et al. 2017 examined applicability of 2-imino-4-thiobiuret−partially reduced graphene oxide for absorption of Hg^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} reaching the maximum adsorption capacity of the level of 624.0 63.0 24.4 and 101.5 mg g^{-1}, respectively. The adsorption process occurred by chelation between the ions and the modified material surface.

9.4.6.6 Graphitic Carbon Nitride

Graphitic carbon nitride is another promising nanomaterial for cleaning water from heavy metal cations. Triazine or heptazine cores nested in the material's layers are the basic structural units of a graphitic carbon nitrides. Each core is built from carbon and nitrogen atoms forming 6-membered rings. The atoms are linked to each other with sp^2 nature bonds (Inagaki et al. 2019). Contrarily to other carbon materials the nitrides are hydrophilic. They can be obtained mostly in pyrolysis of its precursors such as urea, cyanamide, melamine, ethylenediamine connected with techniques, such as chemical vapor deposition, pressurizing, templating or doping (Inagaki et al. 2019; Xiao et al. 2019).

Xiao et al. 2019 examined applicability of graphitic carbon nitride obtained by calcination of guanidine hydrochloride for absorption of Pb^{2+}, Cd^{2+} and Cr^{6+}. The adsorption of Cr^{6+} took place mostly on the outer nanomaterial's surface whilst Pb^{2+} and Cd^{2+} were adsorbed between layers. The adsorption process was strictly related with the tri-s-triazine units and the N-containing groups on the surface of the adsorbent. The maximum adsorption capacity of Pb^{2+}, Cd^{2+} and Cr^{6+} reached 136.571, 123.205 and 684.451 mg g^{-1}, respectively. Fronczak et al. 2018 investigated graphitic carbon nitride doped with s-block metals. Such modified material reach high Cu^{2+} absorption capacity between 324–339 mg g^{-1} what was 10 times higher than for pristine graphitic carbon nitride.

9.4.7 Metal Organic Frameworks

Metal-organic frameworks are a group of new advanced materials that have been arising enormous interest among researchers. They are hybrids build of metal containing units connected to each other by complexing organic linkers with various types of functional groups. The most common linkers are bipyridines, nitriles, carboxylates, sulfonates, phosphonates, imidazolates, pyrazolates, and catecholate (Eddaoudi and Eubank 2010; Fujita 2010; Furukawa 2018; Firmino et al. 2018; Rodríguez-San-Miguel et al. 2018). The most common method of metal-organic frameworks synthesis is the solvothermal technique where a solvent mixture containing organic linkers and metal salts is heated typically to 60–150 °C in a glass vessel or an autoclave. As straightforward as this method is, it is also troublesome. Many times the optimal synthesis conditions are hard to establish and the obtained products are rather amorphous powders or gel-like materials, not metal-organic frameworks. To overcome these problems two diffusion-limited techniques were developed: the vapor diffusion method where the reaction mixture is exposed to amine vapor, and the liquid-liquid diffusion method – growing crystals on the interface of two solvents. These methods are efficient for synthesis of small amount of metal-organic frameworks but are time consuming and can last up to one month. Other alternative approaches to the synthesis are the microwave-assisted solvothermal synthesis, sonochemical synthesis, mechanochemical synthesis, electrochemical synthesis, and continuous flow synthesis (Furukawa 2018).

The materials are unique owing to their well-defined open crystalline structure large pores and cavities, many organic functional groups that can be incorporated in the structure, diverse metal and organic ligands composition and enormous specific surface. Moreover, they can be tailored for specific applications as their morphology and many of their chemical characteristics can be freely modified without loss of the material's structural integrity. This all gives them a wide range of application (Eddaoudi and Eubank 2010; Fujita 2010; Furukawa 2018; Firmino et al. 2018; Rodríguez-San-Miguel et al. 2018). Due to the characteristics described above metal-organic frameworks are an attractive materials for water remediation. Some examples on the application are presented below.

Arsenic was removed using Fe–Co based metal-organic framework synthesized from $Co(NO_3)_2$ $6H_2O$, $FeCl_2$ $4H_2O$ and terephthalic acid in a solution of dimethylformamide, ethanol and water at 120°°C by Sun et al. 2019. The material was able to remove both As^{3+} and As^{5+} on the level of 266.52 and 292.29 mg g^{-1}, respectively. Yu et al. 2019 used $Zn(NO_3)_2{\cdot}6H_2O$ and 2,5-dihydroxyterephthalic acid dissolved in dimethylformamide and isopropanol for a metal-organic framework synthesis at 105°°C, such material attained the maximum adsorption capacity of 211 and 325 mg g^{-1} for As^{3+} and As^{5+}, respectively. Fe-based metal-organic framework obtained from $FeCl_3{\cdot}6H_2O$ and fumaric acid mixed with water at 70°°C exhibited adsorption capacity of 145 mg g^{-1} for As^{5+} in the study of Wu et al. 2018. Abu Tarboush et al. 2018 in his research prepared a Zn-bases metal-organic framework using $Zn(NO_3)_2{\cdot}4H_2O$ and dihydroxyterephtalic acid in dimethylformamide and ethanol at room temperature and at 120°°C. The first material exhibited better adsorption properties on the level of 99.0 mg g^{-1} compared to the high-temperature one that reached 48.7 mg $g^{-1.}$

Lead was adsorbed on a Cu-based and Zn-based metal-organic framework synthesized from $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and 1,3,5-benzenetricarboxylic acid dissolved in dimethylformamide, ethanol and water mixture by Hasankola et al. 2019. The ultrasonic-assisted adsorption experiments showed the maximum adsorption capacity of the materials on the level of 333 and 312 mg g^{-1} for the Cu- and Zn-based adsorbents, respectively. Adsorption of this cation was also studied by Zhu et al. 2019 on a Tb-based metal-organic framework derived at 100°°C from $Tb(NO_3)_3{\cdot}6H_2O$ and 4,4′,4″-(1,3,5-triazine-2,4,6-triyltriimino) tris-benzoic acid dissolved in dimethylformamide and water. The removal capacity reached 547 mg g^{-1}. Al-based metal-organic frameworks obtained at 100°°C from $Al(NO_3)_3{\cdot}9H_2O$ and 2-amino terephthalic acid dissolved in dimethylformamide showed adsorption capacity of 95.1 mg g^{-1} towards Pb^{2+} in the study of Ricco et al. 2015.

Copper adsorption studies on a Zn-based metal-organic frameworks obtained at 130 °C from $Zn(NO_3)_2{\cdot}4H_2O$ and terephthalic acid dissolved in dimethylformamide were conducted by Bakhtiari and Azizian 2015. The attained maximum adsorption capacity was on the level of 236.12 mg g^{-1}. Ca-based metal-organic framework formed from $Ca(NO_3)_2·4H_2O$ and N,N′-bis(2,4-dicarboxyphenyl)-oxalamide dissolved in dimethylformamide was able to remove Cu^{2+} with the uptake capacity of 68 mg g^{-1} in the study of Margariti et al. 2017.

Mercury removal was investigated on a ZrO_2-based metal-organic framework obtained from $ZrCl_4$, 1,3,5-benzene-tricarboxylic acid and formic acid dissolved in dimethylformamide at 80 °C with grafted amidoxime functional groups by Liu et al. 2019. The material was able to remove up to 383.8 mg of Hg^{2+} per gram, slightly more that the material without the amidoxime groups that reached 343.6 mg g^{-1}. Li et al. 2018 synthetized a Zr-based metal-organic framework extensively functionalized with from $ZrCl_4$, octamercapto-tetrakis(p-benzoic acid)pyrene, benzoic and ethylene dithiol and obtained the maximum adsorption capacity of 403 mg g^{-1}. Liang et al. 2018 incorporated In_2S_3 nanoparticles into the structure of a Cr-based metal-organic framework synthetized from $Cr(NO^3)_3·9H_2O$, terephthalic acid and hydrofluoric acid solution mixed with water at 150 °C. The material showed selectivity towards Hg^{2+} adsorption and reached the capacity of 518.2 mg g^{-1}.

Cobalt was adsorbed by Yuan et al. 2019 on glycine, di- and triglycine derivative-functionalized Cr-based metal-organic framework formed from $Cr(NO_3)_3·9H_2O$, 2-aminoter-ephthalic acid and NaOH at 150 °C. The maximum adsorption capacities ranged from 185.2 to 232.6 mg g^{-1} for the mono and triglycine functionalized metal-organic framework. Yuan et al. 2018 used for the Co^{2+} removal a Zr-based magnetic metal-organic framework modified with glucose, suspended of Fe_3O_4@SiO_2. The material was obtained from $ZrCl_4$, and 2-aminoterephthalic acid dissolved in dimethylformamide and hydrochloric acid mixture at 120 °C. The maximum adsorption capacity attained by the materials reached 270.3 mg g^{-1}.

Cadmium uptake of the level of 286 mg g^{-1} on a Ca-based metal-organic framework produced form $CaCl_2$, 2,5-thiophenedicarboxylate was obtained by Xue et al. 2016. Yusuff et al. 2019 investigated the adsorption on a Cu-based metal-organic framework formed from $Cu(NO_3)_2•3H_2O$, benzene 1,3,5-tricarboxylic acid and triethyl amine in methanol and water mixture at 130 °C. The maximum removal capacity reached the level of 219.05 mg g^{-1}.

Chromium removal was studied by Zheng et al. 2019 on a Cu-based metal-organic framework produced from $Cu(NO_3)_2•3H_2O$ and 1, 3, 5-benzenetricarboxylic acid dispersed in ethanol at 50 °C. The removal of Cr^{3+} was no the level of 24.6 mg g^{-1} whereas of Cr^{6+} was neglectable. Fang et al. 2018 conducted adsorption studies of Cr^{6+} on Fe-based metal-organic frameworks obtained at 160 °C from $Fe(NO_3)_3·9H_2O$ and trimesic acid mixed with water or three mineralizing agents: hydrofluoric acid, tetramethylammonium hydroxide, and Na_2CO_3. The obtained adsorption capacities were 40, 26,42 and 45 mg g^{-1} for the starting, hydrofluoric acid, tetramethylammonium hydroxide, and Na_2CO_3 modified metal-organic framework, respectively.

9.5 Disadvantages of Using Nanomaterials

Application of nanotechnology in water remediation has been becoming a common technology to remove certain pollutants for water bodies. Although this approach has many benefits due to the unique physiochemical properties of nanomaterials, it has also been growing increasing concern regarding its potential impact and side effects on the environment. A number of potentially serious issues originating from the materials small size, high reactivity and mobility in the environment, raise attention regarding the toxicity degree and fate of the nanoparticles one they have been introduced to the ecosystem (Litter 2018b; Litter and Cagigal 2018). The same desired properties that made the nanoparticles desirable in water remediation may induce unknown consequences after release into the environment. Upon interaction with biotic and abiotic system reactive oxygen species may be generated, different conditions may cause release of dissolved part of the nanoparticles that may be more toxic than the nanoparticles themselves, last but not least accumulation of toxic pollutant on nanoparticles may increase their bioavailability and enhance bioaccumulation of trace contaminants within the environment. These consequences, especially in the long term time span may be particularly severe (Oakes et al. 2014).

9.6 Conclusions

The chapter present a state-of-art review of current applications of nanomaterials for remediation of wastewaters laden with various heavy metal cations. Water treatment technologies adopting nano-size materials may be successfully applied to remove heavy metal cations in a way that is efficient and can be a realistic alternative to conventional techniques. The materials are very much unique due to their large specific surface area, high porosity, flexible structure framework and a broad spectrum of modification to which they can be subjected. All that creates almost endless possibilities to obtain a custom designed adsorbents with altered physiochemical characteristics tailored for removal of specific hazardous substances form water bodies. The syntheses on most on the nano-sized adsorbent are quite straightforward and can be conducted on a green way. Moreover, the adsorption capacities of many nano-class materials are considerably higher and the adsorption process faster than of the conventional adsorbents. Despite the enormous effort that has been put in many research conducted on various types of nano-sized adsorbents, there is still lack of comprehensive data on the potential adverse effects they can have on the environment. However, given the current speed with which science and technology have been developing, with a great dose of certainty, one can state that the future of water remediation lies within the hands of nanotechnology.

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Chapter 10
Ecoengineered Approaches for the Remediation of Polluted River Ecosystems

Shabnam Shaikh, Kunal R. Jain, Datta Madamwar, and Chirayu Desai

Abstract Rivers are the vital support system providing sustainable development and agricultural production to our highly industrialized world. However, extreme anthropogenic inputs have disturbed the natural ecological balance, structures and functions of riverine matrices. The origins, fate and various health hazards of the riverine contaminants are outlined in this chapter. To mitigate the river pollution and restoring its healthy status, effective restoration strategies are required to be adopted, this chapter reviews the application of eco-engineered systems for remediation of the polluted rivers. Different laboratory scale and on-site treatment technologies for river bioremediation are reviewed in this chapter for instance, constructed wetlands, floating islands, bioracks, ecotanks, biofilters, microbial nano-bubble systems, periphyton based bioremediation systems, as well as hybrid integrated treatment systems. The application of combined bioremediation technologies and engineering approaches are discussed for removal of various river pollutants. Suggestions have been made on future research for developing pragmatic approaches in the remediation of polluted riverine ecosystems.

Keywords River pollution · Bioremediation · Restoration · Eco-engineered systems

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10.1 Introduction

Rivers, the outcome of the earth's evolutionary progression, are the major driving force for the human civilization as well as ecological and economic sustenance of mankind. Rivers offer many functional roles such as water resource, food production, mediate sediment transfer, electricity production, transportation and tourism (Central Pollution Control Board 2018a). Due to continued urbanization, industrialization and poor sanitation, the qualities and quantities of water bodies have been undergoing rigorous pressures and this is considered most grievous phenomenon around the globe for upcoming decades. Agricultural run-off, industrial discharges, domestic wastewaters and social interventions also considerably account for the river water contamination (Central Pollution Control Board 2018a). Discharges of various carcinogenic, mutagenic, teratogenic and persistent pollutants have deteriorated the aquatic ecosystems throughout the globe. River contaminants mainly comprise of loads of nutrients addition (i.e. N, P and others), organic contaminants, xenobiotics and toxic metals originating mainly from domestic and industrial wastewater sources.

Globally, extensive efforts have been initiated for the conservation of the fresh water resources, mitigation of the pollution using various sustainable strategies and water resources management. Around 2 million ton sewage, agricultural and industrial wastes are drained into water bodies per day (United Nations World Water Assessment Programme 2003), which corresponds to the mass of the entire human population. According to the United Nations report, annually about 1500 km^3 wastewaters are produced this is likely to be 6 times higher than the water present in the rivers around the globe (United Nations World Water Assessment Programme 2003). Inadequate sanitary practices have influenced 2.5 billion lives and deteriorated the qualities of the water bodies (United Nations Children's Fund 2009).

Three key riverine bodies of India (Indus, Ganga and Brahmaputra) have been alarmingly contaminated from the both point and non-point sources of pollution. Central Pollution Control Board has highlighted that many polluted river stretches and rivers from the 31 States and Union Territories of India are not meeting the water quality standards (Central Pollution Control Board 2018b). Reports from National River Water Quality Laboratory, Central Water Commission, New Delhi has declared many heavy metal polluted river sites throughout the India. Data collected by Central Water Commission from the water quality monitoring stations located throughout the Indian river basins have shown that 25 rivers contaminated with cadmium, samples from 21 rivers containing chromium, 10 rivers were showing presence of copper, 137 rivers have been polluted with iron, 69 rivers contaminated with lead, and nickel was found in 25 river samples (Ministry of Water Resource 2018).

Eco-remediation of rivers deals with the restoring the damages caused by anthropogenic inputs to the entire river dynamics and diversity of the ecosystem through various biological remedies, for instances plants and bacterial systems. Advantages of eco-remediation include cost effectiveness, environment friendly and green remedies for repairing the damaged river ecosystems compared to various physico-chemical remediation technologies many of which are environment disrupting and form secondary pollutants during treatments. Ecologists, strategy planners, officials, public health specialists and researchers have raised their concerns for the riverine pollution. The main initiatives to remediate the water bodies is detecting the source of pollution and groups of contaminants to avoid further decline in water qualities and take preventive measures.

10.2 Occurrence of Pollutants, Emerging Contaminants and Their Riverine Fates

Deterioration of aquatic bodies is mediated due to presence of organic and inorganic pollutants causing adverse alterations in physico-chemical properties of water that affects the flora and fauna of water bodies along with terrestrial organisms consuming such contaminated waters. There are different types of pollution sources based on their nature and origins that are categorised into natural and anthropogenic furthermore, point and defused sources. Ranges of natural phenomenon that deteriorate the water bodies are the changes in geographical landscape, geo-morphological features of the location, hydrological properties and biological interactions. Natural processes like surface integrated composites run-off through rain water, bed rock weathering and settlement of the atmospheric matters brings about alterations in normal status of the water bodies. Moreover, the chief anthropogenic and point sources such as household and industrial wastewaters, pesticides and fertilizers containing agronomic drains significantly impact the qualities and quantities of surface waters.

Industrialized and urbanized processes generate enormous amount of liquid and solid wastes which deteriorate water bodies through surface runoff and dumping (Khatri and Tyagi 2015). According to the investigations conducted by Pure Earth Black Smith Institute, untreated wastewater generated from the ore and mining sites that is being discharged directly into water bodies contains enormous amount of heavy metals and tailing contaminants. Tanneries are another mediator of surface water contamination that generate large amounts of effluent containing chromium, basic, acidic and coloured contaminants affecting the health of almost 1.5 million people (Pure Earth and Green Cross 2016). Textile industries are among the top most sectors utilizing large amount of water, eventually releasing toxic dyes into water bodies (Rathour et al. 2019a). About 17–20% of the water pollution is driven by textile industries, putting 1 million at risk (Pure Earth and Green Cross 2016). Petrochemical industries and refineries produce wastewater composed of toxic pollutants such as, crude oil, cyanides, ammonia, heavy metals, phenols and aliphatic hydrocarbons particularly toxic carcinogenic polyaromatic hydrocarbons which contribute to surface water contamination (Mitra et al. 2019; Rehman et al. 2019; Kleindienst and Joye 2019).

Recently, central pollution control board, India reported that 30,042 million litres per day of domestic sewage is discharged into rivers (Central Pollution Control Board 2018a). The chief sources of pharmaceuticals discharges into water matrices are wastewater treatment plants and direct release (Li et al. 2014). Many recent studies have drawn attention to the concentrations of pharmaceutical compounds in Indian rivers (Mutiyar and Mittal 2014; Shanmugam et al. 2014; Balakrishna et al. 2017; Archana et al. 2016). Sharma et al. (2019) reported the occurrence and distribution of 15 pharmaceuticals, personal care products and 5 artificial sweeteners in the river at numerous sites along the Ganga River. Recent research studies and developments in analytical chemistry have revealed that enormous amount of active pharmaceutical ingredients, endocrine active chemicals, polychlorinated biphenyls, polyaromatic hydrocarbons and other emerging pollutants are widely found in contaminated Indian water bodies (Philip et al. 2018). Apart from various sources of river pollution as described above, the spent water emanating from power plants has been reported to result in thermal pollution affecting river ecosystems (Verones et al. 2010; Hester and Doyle 2011).

Nonpoint sources are dispersed over catchment regions which drain through thin reels, canals, rain storm drains, and flow into water bodies. Run-off waters from defused agricultural and urban sources are the instances of nonpoint sources. Eutrophication of water bodies is the possible outcome of nonpoint sources as they contain substantial amount of organic compounds, nitrogen, and phosphorus besides agronomic chemicals. Due to its long range distribution, appropriate controlling of nonpoint sources is found to be challenging (Cestti et al. 2003). Availability of massive amounts of inorganic phosphorus and nitrogen through range of human activities leads to encouragement of phytoplankton growth and results into the recurrent incidence of harmful algal blooms (Wang et al. 2019). Bacteriological agents of human faeces origin can also drain into surface waters through sewage wastewater for instances, Hamner et al. (2007) have detected highly pathogenic *Escherichia coli* serotype O157:H7 in the Ganga river which poses a serious threat to public health.

Once contaminants penetrate into aquatic ecosystem they undergo the hydrological progression and resulting into numerous chemical modifications. Depending on the composition of water such alteration brings about more lethal forms of pollutants into water bodies. In order to keep an eye on water pollution, World Health Organization has established various drinking water standards (World Health Organization 2011). Thus, it is important to gauge the wide range of pollutants present in a given river ecosystem, for designing effective eco-remediation technologies.

10.3 Hazardous Effects of Water Contaminants on Aquatic and Terrestrial Biota

Water holds prime importance for all the biotic entities on earth. Therefore, any sort of contamination of water resources by hazardous wastes impacts all life forms. The quality and quantity of water resources are important to consider with regards to sustenance of the ecosystems, welfare and health of human populations. Improper sanitary practices as well as water scarcity have huge impact on the surface water and drinking water contamination leading to several diarrheal, hepatic, enteroviral and parasitic infectious diseases (World Health Organization 2011).

Various research groups have undertaken the health risk assessment of the Ganga River waters (Siddiqui et al. 2019; Mitra et al. 2019; Philip et al. 2018). Enormous amounts of carcinogenic and teratogenic pollutants have been discharged into Ganga River, India and were reported to cause disease, infections and abnormalities in surrounding communities (Dwivedi et al. 2018; Paul 2017). Major leather tanneries are situated in the state of Uttar Pradesh, India near Ganga River mostly engage with chrome-tanning processes producing million litres of wastewater per day. Health risk assessment survey conducted on the residents of communities near Kanpur leather tanning operations suggests higher rates of gastrointestinal, dermatological and haematological abnormalities owing to high concentration of metals in waterbodies (Chaudhary et al. 2017; Chaudhary and Walker 2019).

Maurya et al. (2019) and Siddiqui et al. (2019) have recently undertaken research studies concerning human health through the consumption of heavy metal contaminated fishes from Ganga River and have shown risk of kidney and skeletal damages, neurological disorders, endocrine disruption, cardiovascular dysfunction, and carcinogenic effects. Another research group, Mitra et al. (2019) investigated the risks of various organic pollutants mainly polyaromatic and chlorinated organic contaminants on human health through the estuaries arising from the Hooghly River, distributaries of the Ganges river. Findings of this research indicate high risks of carcinogenic polyaromatic hydrocarbons impacting the ecology of Hooghly River. As per the world health organization report, globally around, two billion individuals consume faeces contaminated water and nearly 829,000 humans are subjected to death owing to intake of the contaminated drinking water, improper sanitary practices (World Health Organization 2019).

Large numbers of pollutants persist in water matrices and ultimately lead to accumulation into both autotrophic and heterotrophic entities at different levels of food chain. The concentration of these pollutants increases from lower to higher trophic level and affects all the life forms. All sorts of anthropogenic activities that lead to water pollution are detrimental to freshwater biota (Lake et al. 2000; Revenga et al. 2005) due to their habitat loss, degradation, over exploitation, flow alterations and foreign species invasions (Dudgeon et al. 2006; Malmqvist and Rundle 2002) that contribute to quantitative and qualitative reductions of freshwater matrices. According to the research studies, globally more than 50% of the fresh water fish species and one-third of amphibians are at risk of extinction (Viéet et al. 2009).

Various research studies have shown that many fish species are at a risk of extinction owing to high levels of organochlorides and metals in their tissues (Kafilzadeh 2015; Rajeshkumar and Li 2018). Pesticides and herbicides through agricultural runoff accumulate in fish tissue which affects the metabolic and reproductive functions of fishes (Priyadarshani 2009). Rivers are among the major fresh water sources so, the presence of various contaminants toxic in rivers posing a threat to human health are of particular concern. Therefore, currently, major research focus is on developing eco-remediation strategies to mitigate river pollution problems.

10.4 Historic Concepts of River Bioremediation

Concept of the river restoration initiated from Europe and America, where most of the river restoration projects were conducted on-site. Results of the previous projects have concluded that the success of restoration relies on consideration of indigenous state, involvement of multi-disciplinary research, directions from administration and the combination of ecological and engineered restoration systems (Porta et al. 1993). Ordinarily used practises for the treatment of polluted rivers all over the globe are physico-chemical and bioecological approaches. Physical and chemical practices have their own hindrances and are expensive. Hence, biological approaches are presently the utmost acceptable eco-remediation processes for regulation of deteriorated rivers.

Previous research studies have revealed that the ecological restoration and river pollution abatement is restricted to a small-scale river restoration (Xiao et al. 2016; Liu et al. 2016; Bu and Xu 2013). The river ecology is susceptible to influences from surroundings near river banks, together with anthropogenic inputs and natural weathering (Yang et al. 2005). Thus, large-scale ecological restoration practices should be conducted on a water shed scale, that combine treatment of riverine and terrestrial ecosystems (Bohn and Kershner 2002; Holl et al. 2003; Wohl et al. 2005). Eco-remediation schemes have to recover the river ecosystem entirely instead of aiming only at water quality improvement.

10.5 Physico-chemical River Remediation Methods

For restoring polluted rivers a range of physico-chemical restoration approaches are practiced to deal with pollutions. Physical approaches comprise of sewage diversion, excavation, mechanical separation of algae and water re-routing. Sewage interception and digging deal with the removal of contaminants from the sediments (Zhong et al. 2010). Covering of sediment involve the covering the sediment with plastic films slow down the release nutrients from sediment thereby, improve the transparency of water (Bona et al. 2000). High amount of algal blooms containing river water can be restored by mechanical facilities to remove algae (Pan et al.

2006). The costs of these methods are remarkably higher. Therefore, physical restorations are implemented at small scales and have a limited application for the filed scale restoration projects.

Chemical methods for the river restoration comprise of chemical flocculation, addition of algaecidal compounds, treating water with Calcium hydroxide and on-site chemical treatment. Various chemical algaecides for instances $CuSO_4$, $KMnO_4$, ClO_2, O_3, H_2O_2 and liquefied chlorine can be used to treat the algal polluted rivers (Umphres et al. 2012). To deal with river water acidification lime is added to water bodies (Whitehead and Brown 1989). On-site chemical treatment deals with removal of contaminants like heavy metals through chemical processes such as oxidoreduction, adsorptive, coagulation and precipitation based approaches (Kanan and Nocera 2008). But these methods may introduce secondary pollution of chemicals into the river ecosystems.

10.6 Eco-engineered River Water Remediation Technologies

Eco-remediation of polluted river can be defined as the process of repairing deteriorated water bodies through the biotechnological approaches such as plants and microbial processes. It deals with restoring the overall ecosystem of the rivers and dynamics of flora and fauna. Bioecological approaches like microbial enhanced strategies, biofilters, constructed wetlands, periphyton remediation, floating island and beds, eco-tanks, micro-nano bubble technology and bio-rack, these systems do not form secondary pollution (Liu et al. 2016; Brix 1997; Webb and Erskine 2003; Cao et al. 2012; Chang et al. 2019; Sun et al. 2018; Xiao et al. 2016; Wang et al. 2012). Therefore, bioecological approaches are prudent choice for improvement and regulation of contaminated rivers. Based on the system design and their implementation, eco-remediation technologies are further mainly divided into two categories; plant and microorganisms based river remediation systems.

10.6.1 Plant Based River Remediation Systems

Pollutants removal is the main objective of all restoration practices. Hydrophytes are well researched for their ability to remove metalloids, nutritive loads, organic and inorganic pollutants from aquatic matrices. Aquatic macrophytes can mitigate eutrophication through uptake of N, P and heavy metals; furthermore, heterotrophs residing in the root systems have ability to eliminate contaminants by assimilative and catabolic processes (Webb and Erskine 2003). Depending on the growth pattern of vegetation, there are three main types of hydrophytes: emergent, floating-leaved, and submerged hydrophytes.

For the implementation of these approaches, the level of nutrients must be narrowed down firstly; or else, the restored hydrophytes will unable to reach steady phase (Pan et al. 2016). Plant dependent remediation strategies have gained attention since long period of time. Ranges of plants have proved to be a prudent choice for mitigating the environmental contaminant. Many different plant based systems have been used for river eco-remediation as described below, such as constructed wetlands, floating beds, floating island, floating, bio-racks and eco-tanks.

10.6.1.1 Constructed Wetlands

Constructed wetlands are considered as an ecofriendly approach for sustainable wastewater treatment (Rathour et al. 2019b). Constructed wetlands are considered as “black boxes” that treat the wastewater effectively within considerable time regime (Langergraber et al. 2009). Constructed wetlands have long been implemented for the treatment of various wastewaters for instances, agricultural, household, and industrial wastewater. On the basis of hydrodynamic patterns certain wetland designs are available such as surface flow and subsurface flow constructed wetlands (Wu et al. 2015). Both the constructed wetlands are additionally grouped into horizontal and vertical flow due to their mode of water flow. As the names suggest in horizontal flow wetlands water flows from sides whereas, in vertical flow wetlands, water moves from top to bottom through the hollow cylindrical systems.

There are various factors to be considered while designing the constructed wetlands remediation systems such as substrate selection, hydraulic loading rate, hydraulic retention time, plant species selection, wetland hydrodynamics and surface area of wetland. There are different types of substratums which can be selected as a packing material of constructed wetlands such as pebbles, soil, grit, organic substratum, slag, fly ash, charcoal, and sludge. These packing materials provide growth platform to plants, encourage chemical and biological conversion of pollutants along with control water flow (Kadlec and Wallace 2009).

In the field of river bioremediation certain lab scale models of constructed wetlands have been well investigated by many researchers, wetlands constructed with various materials are described in (Table 10.1). Cao et al. (2016) developed a lab scale cubical floating wetland system for efficient removal of nitrogen pollution containing riverine water. In this study, rice straws and light ceramsite were used as substrates for biofilm development in constructed wetlands planted with *Canna indica*. Rice straws as a substratum achieved 78.2%, 62.1%, 81.2% removal efficiencies for total nitrogen, nitrate and ammonium respectively. Likewise, light ceramsite as substratums were found to be less efficient achieving 65.5%, 42.2%, 71.6% removal efficiencies for total nitrogen, nitrate and ammonium, respectively upon 7 days of treatment. Furthermore, certain on-site constructed wetland systems (Table 10.2) have also proved to be efficient for the treatment of river contaminants.

Zheng et al. (2014) demonstrated on-site constructed wetlands with surface and subsurface-flow cells near the Xi’an River, China. System configuration was made with pebbles and grit as supporting platform planted with *P. australis* and *T. orientalis*. The on-site pump was fitted into systems for water inflow. Average surface

Table 10.1 Lab scale treatment technologies for river bioremediation

Sr. no.	Types of systems	Components of the systems	References
1.	Tidal-operated biofilters	Biofilter carrier: Clay ceramsite, lava rock, fibrous carriers and biological ball	Chang et al. (2019)
2.	Bio-rack wetlands	Plant species: *Thalia dealbata*, *Acorus calamus*, *Zizania latifolia* and *Iris sibirica*	Wang et al. (2012)
3.	Floating constructed wetlands	Biofilm carrier: Rice straw and light ceramsite	Cao et al. (2016)
		Plant species: *Canna indica*	
4.	Integrated ecological floating-bed	Biofilm carrier: Artificial semi-soft assembly medium Plant species: *Ipomoea aquatic, Corbicula fluminea*	Li et al. (2010)
5.	Hybrid floating treatment bed	Periphyton biofilm community: Cyanobacteria, Proteobacteria, Bacteroidetes, Planctomycetes, Firmicutes, Actinobacteria, Chlorobi and Acidobacteria	Liu et al. (2016)
		Plant species: *Ipomoea aquatic*	
6.	Biofilm technology	Biofilm carrier: Carbon fibre grasses and artificial aeration	Pan et al. (2016)
7.	Double-layer biofilter	Bio-filter carrier: Ceramic granules fly ash and coal	Jing et al. (2012)
8.	Biofilms technology	Biofilm carrier: Filamentous bamboo and suspended activated sludge	Cao et al. (2012)
9.	Biofilms technology	Biofilm carrier: Elastic filler and AquaMats® ecobase	Xu et al. (2012)
10.	Eco-tank system	Biofilm carrier: Carbon fibre ecological grass	Xiao et al. (2016)
		Plant species: *Myriophyllum aquaticum*, *Hydrocotyle leucocephala*, *Alternanthera Philoxeroides* (Mart.), Griseb and *Ludwigia peploides* (Kunth)	
11.	Constructed floating islands	Plant species: *Canna generalis, Scirpus validus, Alternanthera philoxeroides, Cyperus alternifolius* and *Thalia geniculate*	Zhang et al. (2014)
12.	Biofilter technology	Biofilter carrier: Activated carbon filter	Gao et al. (2010)
13.	Floating bed	Plant species: *Canna indica, Accords calamus, Cyperus alternifolius* and *Vetiveria zizanioides*	Bu and Xu (2013)
14.	Floating treatment wetlands	Microorganisms: Rhizospheric and endophytic bacterial strains, *Bacillus cereus*, *Aeromonas salmonicida* and *Pseudomonas gessardii*	Shahid et al. (2018)
		Plant species: *Typha domingenis* and *Leptochloa fusca*	

loading of 0.053 $m^3/(m^2$. day) was maintained. Zheng et al. (2014) constructed in-situ series of five constructed wetlands for achieving highest treatment efficiency, which were composed of five free-surface flow wetlands and four horizontal subsurface flow wetlands planted with *P. australis* and *T. orientalis* covering the surface area of around 8000 m^2. Results have shown good efficiencies in terms of performance.

Table 10.2 *In situ* treatment technologies for the river bioremediation

Sr. no.	Types of the systems	System components	Treatment site	References
1.	Surface-flow constructed wetland	Plant species: *Phragmites australis* and *Typha orientalis*	Zaohe River, China	Dzakpasu et al. (2015)
2.	Constructed wetland	Plant species: *Canna indica*, *Iris pseudacorus* and *Acorus calamus*	Nanfeihe River, China	Guo et al. (2014)
3.	Hybrid constructed wetlands	Plant species: *Phragmites australis* and *Typha orientalis*	Zaohe River to Weihe River, China	Zheng et al. (2014)
4.	Integrated eco-engineered system	Physical treatment: Dredging, Multi-pond constructed wetland Plant species: *Eichhornia crassipes*, *Hydrocharis dubia*, *Vallisneria natans*, *Hydrilla verticillata, Canna indica* L., *Arundodonax* var. *versicolor, Iris pseudacorus* L., *Cyperus alternifolius* L., *Phragmites australis, Nelumbo nucifera* Gaertn and *Lythrum salicaria* L.	The Shuangqiao River, China	Fang et al. (2016)
5.	Combined eco-engineered system	Physical treatment: Artificial aeration Ecological floating beds: Plant species: Candocks and *Ipomoea aquatic* Forsk Microorganisms: Photosynthetic bacterial reagents and *Bacillus subtilis* powder, biological aerated filtration: Biofilm carrier: Slag and coal cinder Artificial biofilms: Biofilm carrier (Beier film)	The Dihe River, China	Sheng et al. (2013)
6.	*In-situ* treatment pods	Plant species: *Eichhorni acrassipes*	Northern Hemisphere river	Jones et al. (2018)
7.	Submerged resin floating bed and micro-nano bubble technology	Physical treatment: Artificial aeration Biofilms	Urban rivers, China	Sun et al. (2018)
8.	Micro-nano bubble technology	Physical treatment: Artificial aeration Biofilms	Urban river, China	Wu et al. (2019)
9.	Microbial technology	Microbial agent: HP-RPe-3	Chengnan River, China	Gao et al. (2018)
10.	Surface-flow constructed wetland	Plant species: *Typha latifolia, Phragmites australis, Colocasia esculenta, Polygonum hydropiper, Alternanthera sessilis* and *Pistia stratoites*	Ganga River, India	Rai et al. (2013)

Dzakpasu et al. (2015) configured two floating wetland cells in series, each with a length of 45 m, a width of 20 m and a height of 0.6 m. Pump was fitted into tank systems for water inflow with hydraulic retention time of 4 h. The system was planted with *Phragmites australis* and *Typha oriental.* In another study, on-site treatment system was developed by Guo et al. (2014) where they have fabricated integrated constructed wetland systems comprised of an up-down and horizontal subsurface flowing systems. The systems were planted with *Canna indica*, *Iris pseudacorus* and *Acorus calamus*. Systems were filled with slags and zeolites in the upper level of the down-flow bed and the up-flow bed respectively. *In situ* constructed wetlands configurations shown in various research studies were focused on the engineering aspects and the systems construction according to the level of pollution present and the structure of systems depending on the hydrology of the water bodies.

10.6.1.2 Ecological Floating Wetlands, Beds and Islands

Ecological floating beds, wetlands and islands are the plant based systems which are constructed with few differences in system configuration. A floating treatment wetland consists of floating mats and linked ecosystem communities, such as macrophytes, macro invertebrates, zooplankton, and biofilms (Hubbard et al. 2004; Kato et al. 2009). For the treatment enhancement of polluted river water various biofilm carriers were added to floating wetlands (Zhang et al. 2016). Whereas, the ecological floating bed systems are constructed from free floating plants that lack a substratum as a packing material in the system. Root systems of the floating plants offer surface for the microbial assemblage where they entrap the suspended solids and mediate the breakdown of organic pollutants (Sun et al. 2017).

Furthermore, floating island consists of a broad floating organic mat as a supporter of plants. The top layer of the mat is the root zone made up of tangled plant roots. Lower layer made up of peat and decaying plant material (Lu et al. 2015). Range of lab scale models of all of these systems have been demonstrated by several researchers as described in (Table 10.1), Shahid et al. (2018) have investigated the floating wetland systems to reduce pollution load from Ravi river water. The wetland was constructed of polyethylene foam and floating mat was prepared and planted with *Typha domingensis* and *Leptochloa fusca.* In addition to that rhizospheric and endophytic bacterial strains were isolated and augmented for treatment enhancement.

Bu and Xu (2013) have reported construction of the parallel four floating bed integrated with identical dimensions (2.7 m long, 2.3 m wide and 1.0 m deep with a water depth of 0.8 m) planted with *C. indica*, *A. calamus*, *C. alternifolius*, and *V. zizanioides*. Polluted river was fed into these systems using polyvinyl chloride pipes with valves to control the flow. This system showed the 15.3–38.4, 29.9–88.1 25.4–48.4 and 16.1–42.1% chemical oxygen demand, Chlorophyll a, combined nitrogen and phosphorus reduction efficiencies respectively. While, Zhang and coworkers developed a lab scale floating island fabricated from polyethylene foam planted with *Canna generalis, Scirpus validus, Alternanthera philoxeroides, Cyperus alternifolius* and *Thalia geniculate* which showed better efficiency in removal of biochemical oxygen demand, total nitrogen, total phosphorus from polluted river waters (Zhang et al. 2014).

10.6.1.3 Eco-tanks

Eco-tank systems are constructed using aquatic plants for the remediation of contaminated riverine water as described in (Table 10.1). Xiao et al. (2013) fabricated sequential eco-tank system for the treatment of the contaminated riverine waters. Five quadrangular tanks constructed from polyvinyl chloride that were consecutively connected and contained floating aquatic plants *P. stratiotes, H. leucocephala*, *M. aquaticum* and *P. crispus*. The entire configuration was installed in greenhouse assembly to mimic the polluted riverine environment. The pollutants removal effectiveness of this approach, for chemical oxygen demand, ammonium and overall phosphorus were found to be 71.95%, 97.96% and 97.84%, respectively.

Previous research studies also showed the applicability of lab scale models for the remediation of N,N-dimethylformamide contaminated riverine matrices. Construction of the system was carried out by four hydrophytes namely, *M. aquaticum*, *H. leucocephala*, *A. philoxeroides* (Mart.) Griseb and *L. peploides* (Kunth) Kaven subsp. The eco-tank was found efficient in complete removal of the N,N-dimethylformamide and total organic carbon reduction effectiveness of these models under hydraulic retention time of 10, 7, and 5 d were 72.2, 64.7 and 63.0%, separately while the ammonium concentrations were 2.58, 3.41 and 5.85 mg L^{-1} under hydraulic retention time of 10, 7 and 5 d individually (Xiao et al. 2016).

10.6.1.4 Bio-racks

Bio-rack systems are an emerging approach for treatment of deteriorated river waters. System fabrication contained more than 150 plants per m^2 which showed better efficiency in terms of pollutants removal compared to conventional constructed wetlands (Wang et al. 2012). The biorack system also showed enhanced root zones, which provided more surface area for microbial colonization. However, the bio-rack systems were implemented for the treatment of domestic wastewaters only. Additionally, few research studies have also shown the applicability of the biorack systems to combat lower river pollution.

As described in the (Table 10.1), Wang et al. (2012) constructed bio-rack systems for the treatment of river water contaminated with low pollution loads in terms of total nitrogen, phosphorus, biochemical and chemical oxygen demands. This system was constructed with polyvinyl chloride pipes and planted with four different plant species *Iris sibirica*, *Thalia dealbata*, *Thalia dealbata*, *Acorus calamus* and *Zizania latifolia*. This biorack system achieved removal 62.05 to 74.81% of total phosphorus removal and 34.9 to 43.81% nitrogen removal form the river water. It was suggested in this study that bio-rack systems are applicable to river waters with lower pollution load.

10.6.2 Microorganisms Based River Remediation Systems

Microorganisms based eco-engineered systems utilize the potential of bacteria to degrade a range of contaminants efficiently in a cost effective manner. Furthermore, the microbial treatment technologies do not produce secondary metabolites so; practically it is feasible option for the field scale studies. This section covers most of the microbial biofilms and periphyton based eco-engineered technologies used for river bioremediation.

10.6.2.1 Biofilm Based Eco-engineered Treatment Systems

The biofilm based approaches comprised of bio-membrane adhered to riverine matrices and micro-transporter for the movement of the contaminants present into water through sorption, degradation and purification under the influence of aeration or dissolved oxygen. Biofilm technology utilizes intensive microbial collaborative structure emended in extracellular polymeric substances that keeps biofilm hydrated. A wide range of microorganisms have functional roles to play in the biofilm communities. Few research studies have shown that biofilms have ability to transform the nitrogen efficiently, which has found application in the river bioremediation (Ribot et al. 2012). Furthermore, biofilms have superiority in providing the contaminant degradation at field as well as lab scale in river remediation technologies (Gao et al. 2018; Cao et al. 2012; Xu et al. 2012).

Cao and co-workers have designed the biofilm based systems using filamentous bamboo which showed better chemical oxygen demand reduction compared to control systems. Pollution removal efficiencies were found 11.2–74.3%, 2.2–56.1%, 20–100% for permanganate index, ammonia nitrogen, turbidity, and total bacteria respectively. Xu et al. (2012) have developed various lab scale biofilm based system for river bioremediation. The systems were developed using various bio-filler such as Elastic filler and AquaMats® ecobase. In terms of pollution load removal were found 84.41–94.21% and 69.66–76.60% for ammonia nitrogen and permanganate index respectively. As stated in the Tables 10.1 and 10.2, range of lab and field scale microbial treatment technologies have gain particular attention in river bioremediation processes that are based on biofilms such as bio-filters and periphyton based remediation technologies.

10.6.2.1.1 Bio-filters in River Bioremediation

Bio-filters are the static bed biofilms packed with different substrates which find their application for the remediation of different effluents (Qiu et al. 2010; Loupasaki and Diamadopoulos 2013). Several research findings have suggested the use of bio-filters for the river bioremediation (Jing et al. 2012; Gao et al. 2010; Chang et al. 2019). Bio-filters provide higher surface platform for the microbial interactions and nutrient load reduction (Qiu et al. 2010; Jing et al. 2012). Substrate selection is the important aspect for the efficient treatment system in bio-filter technologies (Liu et al. 2014; Yang et al. 2018). Microbial communities are the key mediator of contaminants removal in biofilters (Faulwetter et al. 2009; Du et al. 2018).

Recent research studies have developed various optimized biofilters as mentioned in the (Table 10.1). Chang et al. (2019) have constructed tidal-operated biofilters with optimization of the biofilm carriers. They have utilized Ceramsite, magma rock, stringy carriers and biological sphere as biofilm carriers. These systems have shown efficient result in ammonium and phosphorus reduction. Systems constructed from ceramsite and lava rock proved efficient in ammonium and phosphorus removal. However, fibrous carrier-packed biofilters gained improved overall nitrogen reduction.

Gao et al. (2010) developed lab scale immobilized biofilters for the bioremediation of Songhua River, China. They have utilized activated carbon filter as the biofilm support material. It was concluded in this study that the major microbial community found on filters were safe for its application in drinking water treatment processes. Likewise, Jing et al. (2012) developed double-layer biofilters as an emerging design in biofilters. These systems were filled with coal fly ash and ceramic granules, the systems achieved more than 80% of chemical oxygen demand, 85% of ammonium and 60% of total nitrogen removal efficiency in treatment of highly polluted river water having high total nitrogen, phosphorus, biochemical and chemical oxygen demands values.

10.6.2.2 Periphyton Based Technologies

Periphytons are the group of aquatic organisms such as algae, microbes, protozoans, metazoan and epiphytes which have ability to colonize under submerged conditions into various surface water matrices (Azim 2009; Wu et al. 2014). Periphyton assemblages have higher affinity towards inorganic N and P (Kangas and Mulbry 2014), metal ions (Soldo and Behra 2000) and organic complexes (Shangguan et al. 2015; Wu et al. 2010). Furthermore, they have ability to withstand range of abiotic ecological factors which prevail in flowing rivers such as variations in temperature, availability of oxygen and nutrients (Shangguan et al. 2015; Liu et al. 2016). Due to these properties, periphyton finds its application in various bioremediation technologies.

Wu et al. (2014) have reviewed various *in situ* treatment technologies for the surface water bioremediation using periphytons. As depicted in (Table 10.1), Liu and co-researchers have developed hybrid floating treatment bed where interactive periphyton communities have assembled with floating beds exhibiting better treatment efficiencies in lab-scale systems.

10.7 *In Situ* Emerging Integrated Systems for the River Bioremediation

Most of the river bioremediation techniques are limited to the lab scale due to various environmental challenges and other factors affecting their application for on-site river remediation. Remediation technologies which are solely dependent on either plants or microorganisms alone have limited application at river sites having higher pollution loads. Therefore, the emerging technologies must have to focus on the integrated approaches for remediation of actual polluted river sites. These integrated techniques have supremacies in upholding the constancy and durability of the remediation efficiency, and should be designed to have less treatment period, space along with costs. However, there have been only a few reports concerning the application of integrated eco-engineering in remediation of polluted rivers.

In terms of integration, various physical and chemical approaches are also integrated as a pre-treatment for remediation of the heavily polluted rivers sites for instances, artificial aeration and dredging (Fang et al. 2016; Sheng et al. 2013). Polluted rivers are deficient in dissolved oxygen content. Artificial aeration is prudent choice to oxygenate the polluted river artificially for the growth enhancement of aerobic microorganisms for river restoration and purification (Liu et al. 2019; Dong et al. 2012; Wu et al. 2019; Gao et al. 2018). Various case-studies of on-site river bioremediation technologies have conducted by various research groups as described in (Table 10.2).

Sheng et al. (2013) constructed on-site eco-engineered integrated systems on the Dihe River, China. In this study, ecological floating beds were planted with can-docks and *Ipomoea aquatic Forsk.* For the microbial growth enhancement and improvement of water quality, photosynthetic bacterial reagents and *Bacillus subtilis* powder were used. In addition to that biological aerated filters were combined with the treatment process, biofilms were developed on slag and coal cinder. Furthermore, artificial aeration was selected for microbial growth enhancement. This eco-engineered system has proved to be applicable for onsite river water treatment in terms of efficiency and stability.

Fang and co-researchers have integrated the plant based systems with dredging as a pre-treatment for heavily eutrophicated the Shuangqiao River, China. They have designed on-site multi-pond constructed wetlands planted with range of plant species for instances, submerged hydrophytes, floating-leaved plants and emergent plants for bank site treatment of various wastewaters shown enhanced treatment effectiveness (Fang et al. 2016). Jones and co-workers have investigated In-situ phytoremediation potential of Water hyacinth (*Eichhornia crassipes*) of highly polluted British river (Nant-Y Fendrod, a tributary of the River Tawe).

Bank-side study using an *in situ* treatment pods was carried out within the dynamic environment of the Nant-Y Fendrod River itself intended to evaluate the heavy metal removal proficiency of the real field scale system. The treatment system was fabricated with two 1000 litre bulk vessels. Each treatment vessels were affixed with 50 plants. Data indicated that the removal of around 21 heavy metals together with antimony for the first time, in a single experiment was reported. Data indicated reliable results for heavy metal removal from the actual river site (Jones et al. 2018).

Microbial nano-bubble systems are currently emerging technologies for river bioremediation (Sun et al. 2018; Wu et al. 2019) as depicted in (Table 10.2). In these systems, artificial aeration in form of the micro-nano bubble can produce minor bubbles with diameters in micrometres and nanometres which have ability of self-sustenance and lesser rising time compared to ordinary aeration proved to be efficient for an on-site river remediation technology.

In an another study for on-site river bioremediation, the Council of Scientific and Industrial Research-National Botanical Research Institute designed and engineered a subsurface-flow constructed wetlands systems near Haridwar, India, in order to combating urban drains that is being discharged into Ganga directly (Rai et al. 2013, 2015). These wetland systems encompass a surface area of nearly 79.17 m^2 and are composed of two compartments; a four-sided planted sector having length, width and diameter around 57.8 m, 56.65 m and 51.8 m respectively. While a settling reservoir has 57.8 m length, 53.5 m width and 51.8 m diameter. The packing materials of constructed wetlands utilized were gravels (0.75 m thickness) of variable dimensions extending from 6 to 25 millimetres thickness. Selection of configuration was done on the basis of pollutants load and hydrodynamics of 0.065 million of litres per day urban runoffs (Rai et al. 2013, 2015). The movement of wastewater from the settling tank was mediated 15 cm below the pebbly layer using hollow tubes. The flow rate was regulated by inlet valve. The macrophytes utilized in wetland configuration are, *C. esculenta, P. australis, T. latifolia, A. sessilis, P. hydropiper,* and *P. stratoites.* These systems are doing well in terms of overall biochemical and chemical oxygen demands, total nitrogen and total phosphorus removal for on-site river water treatment.

10.8 Concluding Remarks

Large numbers of treatment methods are available in the field of river bioremediation, but for the proper method selection, it is very crucial to do an advance analysis of the contaminated riverine environments and the types of pollutants present at such sites. It is significant to integrate eco-engineered bioremediation technologies in order to develop better river restoration systems. Single eco-engineering practises are limited to the lab scale applications, whereas, *in situ* applications would require working with several approaches simultaneously. Integrated remediation technologies have advantages in upholding the steadiness and durability of the remediation effectiveness. Bacteria and plants assisted remediation can be superior option for the specific contaminated site having comparatively low pollution loads. Various eco-based technologies such as constructed wetlands, biofilters, periphyton, islands, floating beds, microalgal, ecotanks, micro-nano bubble technology and bio-rack based remediation technologies account for an ecofriendly and sustainable approach for the restoration of polluted river ecosystems.

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Chapter 11
Ballast Water Definition, Components, Aquatic Invasive Species, Control and Management and Treatment Technologies

Mohamed A. Hassaan and Ahmed El Nemr

Abstract Ballast water releases from ships can have undesirable effects on the marine environment. Invasive amphibian species released from ballast water is a standout amongst the most basic issues presented these days in the marine ecology. This work surveys the accessible treatment approaches utilized for ballast water which can be ship or port-based, with the first being less demanding. On-board treatment approaches, named mechanical, physical and chemical techniques, were given particular importance. The effectiveness of these systems, along with component of ballast water, biological invasion, ballast water treatment standards and treatment technologies were compiled and presented in this chapter.

Keywords Ballast water · Biological invasions · International Maritime Organization · Treatment technologies · Disinfection · Ozone · Electrochlorination and ultrasound

11.1 Introduction

The term “balance” refers to the manner in which old shipowners have been trying to refrain from using ballast since time immemorial (CETS 1996). Balance is characterized as: “Any object operated for the equilibrium and weight of an item” (IMO 2004). A model is the sandbags kept on customary tourist balloon, which can be disposed of to ease the inflatables burden, enabling it to climb. In this way, ballast water is the water conveyed by boats to guarantee trim, steadiness and basic trustworthiness. In the time of old cruising boats, stones and rocks were regularly

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utilized as ballasting materials and remainders of deballasting actions, for example, foreign flora can be discovered in many areas around the globe (İnmeler 2009).

Ships use ballast water to keep up their parity permitting adjustment for variations in bunker oil and cargo-weight. Present day shipping can't work without ballast water, which gives stability and dependability to empty boats. Boats that are even completely loaded down with payload should have ballast for stability or will utilize ballast to modify stability through harsh oceans. A possibly severe ecological concern, along these lines, emerges when the released ballast water contains oceanic animals. There are a huge number of sea-going species that might be transported in ballast water, which incorporates microorganisms, micro-algae, seaweeds, eggs, small invertebrates, seeds, spores, larvae and cysts of different aquatic animals and plants species (Bailey et al. 2004; Brickman and Smith 2007; Burkholder et al. 2007; Doelle et al. 2007; Eames et al. 2008; Gavand et al. 2007; Gray et al. 2005, 2006; Gregg and Hallegraeff 2007; Holm et al. 2008; Hua and Liu 2007; De Lafontaine et al. 2008; McGee et al. 2006; Quilez-Badia et al. 2008; Smit et al. 2008; Tamburri and Ruiz 2005; Gonçalves and Gagnon 2012; Veldhuis et al. 2006) Fig. 11.1. The advancement of bigger, quicker ships finishing their voyages in ever shorter periods, joined with quickly expanding global trade, indicates that the distribution of species over the seas are diminished.

Regarding the significance of this area, the main objectives of this chapter were to: (1) identify the components of ballast water; (2) distinguish the significance of

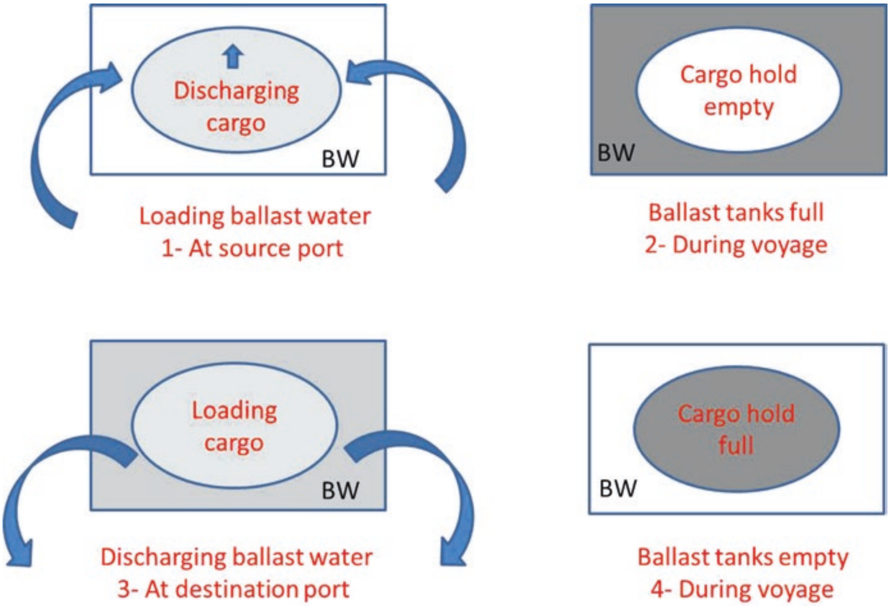


Fig. 11.1 Schematic indicating potential exchange of oceanic invasive species from one area to another via ballast water (BW). (Modified after Bircher 2016)

the bio invasion released from ballast water and its effects on marine environment; (3) studying the ballast water management options; (4) list the different ballast water treatment techniques.

11.2 Component of Ballast Water

Ballast water, in a basic clarification, is seawater. Analysis of the chemical and physical structure of seawater suggests, investigating of ballast water (Inmeler 2009). For limiting marine species transport from one environment to another by means of ballast water is conceivable just by pulverizing these marine life forms through the exchange. Now, the treatment techniques undertake a vital role. Table 11.1; demonstrate the chemical, physical and oceanographic parameters of seawater which progressed toward becoming determinants in the development of the treatment frameworks (İnmeler 2009).

A portion of the ballast water treatment techniques created with the utilization of seawater qualities are; destroying of creatures by method for expanding the saltiness proportion or the pH degree. Seawater is described as "a mixture solution of dissolved salts, mineral and elements" and it comprises the majority of the recognized constant components and elements in different concentrations (İnmeler 2009). The proportion between different elements is constant (Beer 1983).

Table 11.2, demonstrates the compositions of ions in seawater. The world oceans have distinctive characteristics. The profiles of Living creatures in oceans fluctuate as indicated by various salinity levels, pH degrees, temperatures, nutrient densities and current factors. Ballast water management plans intend to be dependent on these changes of chemical and physical factors of seawater will undertake a crucial part in giving the performance and economy in practice (İnmeler 2009).

Table 11.1 Seawater characteristics in the worldwide seas and oceans

pH	Between 7.5 and 8.4.
Salinity	Between 3.1% and 3.8% (based on the river flow, evaporation, river runoff etc.).
Freezing point	−2 °C (increasing with decreasing salinity).
Density	From 1020 to 1029 kg/m^3 (based on the temperature and salinity).
Dissolved gases	O_2 comprises 21% of atmospheric gases, N_2 comprises 78% of the atmosphere and CO_2 comprises 0.03% of the atmosphere. (Sea surface waves ventilate the water and dissolve atmospheric gases into it).
Nutrients	C, O, N and P available in solution as dissolved HCO_3^-, PO_4^{-3} and NO_3^-.

Modified after İnmeler (2009) and Wikipedia (2007)

Table 11.2 Ionic compositions (by weight) in seawater

Ion	Symbol	Seawater %
Chloride	Cl^-	55.04
Sodium	Na^+	30.62
Sulphate	SO_4^{--}	7.68
Magnesium	Mg^{++}	3.69
Calcium	Ca^{++}	1.15
Potassium	K^+	1.10
Bicarbonate	HCO_3^-	0.41

Modified after Beer (1983, p. 86) and İnmeler (2009)

11.3 Aquatic Invasive Species

Ballast water discharge at the present comprises one of the essential trajectories for the worldwide spreading of aquatic invasive species (Gonçalves and Gagnon 2012). The human-interceded transport of dangerous life forms by means of shipping, particularly through ballast water exchange, prompting the loss of biodiversity, change of environments, negative effects on human well-being and in a few areas financial misfortune, has brought wide consideration particularly up in the most recent decade (Barry et al. 2008; Bolch and Salas 2007; Brickman and Smith 2007; Burkholder et al. 2007; David and Perkovič 2004; Doelle et al. 2007; Eames et al. 2008; Endresen et al. 2004; Flagella et al. 2007; Gavand et al. 2007; Gray et al. 2006; Herwig et al. 2006; Holm et al. 2008; Jones and Corona 2008; Jones et al. 2006; McCollin et al. 2007, 2008; McGee et al. 2006; Murphy et al. 2006; Murphy et al. 2008; Niimi 2004; Oemcke and van Leeuwen 2004, 2005; Perrins et al. 2006a, b; Roberts and Tsamenyi 2008; Sano et al. 2005; Smit et al. 2008; Tang et al. 2006a, b; Veldhuis et al. 2006; Wright et al. 2007a, b; Gonçalves and Gagnon 2012). Examples of some aquatic invasive species with their impacts on ecosystem are presented in Table 11.3 (Gonçalves and Gagnon 2012; IMO 2004).

11.4 The International Convention for the Control and Management of Ships Ballast Water and Sediments

The aim of the convention is to limit the possible serious impacts that may arise from the distribution of dangerous oceanic creatures transported by vessels. Ballast water was embraced by IMO at a global meeting organized (IMO 2004). The Convention forces vessels to create Ballast Water and Sediments Management Plan. Vessels should have a ballast water record book and will be prerequisite to complete ballast water performance standards that satisfy a particular guideline (Sassi et al. 2005).

Table 11.3 Examples of aquatic bio-invasions

Name	Introduced to	Native to	Impacts
Cholera *Vibrio cholerae* (numerous strains)	Gulf of Mexico, South America and other regions	Numerous strains with broad ranges	Certain cholera epidemics seem to be completely linked with ballast water
Mitten Crab *Eiocheir sinensis*	Western Coast of North America, Western Europe, and Baltic Sea	Northern Asia	Experiences mass movements for regenerative purposes.
			Tunnels into stream banks and dykes causing disintegration and siltation. Preys on local fish and invertebrate species, causing nearby extinctions during population outbreaks. Overlapping with the activities of fishing
Cladoceran Water Flea *Cercopagis pengoi*	Baltic Sea	Caspian and Black Seas	Reproduces to make exceptionally expansive inhabitants that overwhelm the zooplankton network and clog trawls and fishing nets, with related financial effects
Toxic Algae (Red/Brown/Green Tides)	Numerous organisms have been relocated to another regions in ship's ballast water	Several species with broad ranges	Can create Dangerous Algal Blooms. According to the species, can create massive kills of marine life through oxygen exhaustion, poisons release and or potentially bodily mucus. Can foul shorelines and effect on the recreation and tourism. A few animal varieties may pollute filter-feeding shellfish.
			Furthermore, lead to fisheries shutting. Utilization of infected shellfish by people may produce extreme sickness and then death
North American Comb Jelly *Mnemiopsis leidyi*	Caspian, Azov and Black Seas	Eastern Seaboard of the Americas	Reproduces quickly (self-fertilizing-hermaphrodite) under desirable environments. Extremely feeding on zooplankton. Reduces zooplankton stocks; changing Food-web and ecosystem task. Added considerably to downfall of Black and Azov Sea fisheries in 1990s, with great social and economic social influence. Currently threatens comparable effect in Caspian Sea.
Round Goby *Neogobius melanostomus*	North America and Baltic Sea	Caspian, Azov and Black Seas	Extremely adjustable and invasive. Rises in numbers and Distribute rapidly. Habitat and food competitive with local fishes containing commercially significant species, and kills their eggs and young. Reproduce many times per season and stay alive even in bad water quality

(continued)

Table 11.3 (continued)

Name	Introduced to	Native to	Impacts
Zebra Mussel *Dreissena polymorpha*	Baltic Sea; eastern half of North America, Western and northern Europe, including Ireland	Eastern Europe (Black Sea)	Fouls all accessible hard surfaces in mass numbers. Dislodges local oceanic life. Changes natural surroundings, biological community.
			Furthermore, food-web. Leads to serious fouling issues on foundation and ships. Close water consumption pipes, floodgates and water system trench. Financial expenses to US alone around $750 million to $1 billion between 1989 and 2000
North Pacific Seastar *Asterias amurensis*	Southern Australia	North of the Pacific	Reproduce in enormous amounts, achieving 'plague'.
			Extents quickly in invaded ecosystems. Easts shellfish, containing monetarily commercially scallop, shellfish and mollusk species
European Green Crab *Carcinus maenus*	South Africa, Southern Australia, Japan and USA	European Atlantic Coast	Exceptionally versatile and invasive. Impervious to predation due to their hard shell. Contends with and uproots local crabs what's more, turns into an overwhelming animal types in invaded zones. Expends and drains wide scope of prey organisms. Changes inter-tidal rocky shore environment.
Asian Kelp *Undaria pinnatifida*	West Coast of the US, Europe, Argentina, Southern Australia and New Zealand	Northern Asia	Develops and spreads quickly, both vegetative and through dispersal of spores. Uproots local algae and marine life. Changes environment, biological system and food web. May influence commercial shellfish stocks through space competition and change of environment

Modified after IMO (2004) and Gonçalves and Gagnon (2012)

The International convention for the control and management of ships ballast water and sediments entered into force a year after ratification by 30 countries, demonstrating about 35% of the world's trader shipping capacity. Vessels built before 2009 with a ballast water limit of 1500–5000 m^3 must perform ballast water management that, in any event, meets the ballast water exchange standards or ballast water performance standards until 2014, at which point it should in any case meet the ballast water performance standards (Sassi et al. 2005).

Ships built before 2009 with a ballast water limit of ≤ 1500 or ≥ 5000 m^3 must direct ballast water management that, at any rate, come across the ballast water exchange standards or the ballast water performance standards until 2016, at which point it should in any event meet the ballast water performance standards (Sassi et al. 2005).

Ships built in or after 2009 with ballast water limit $\leq$5000 m^3 must lead ballast water management that, in any event, meets the ballast water performance standards. Boats developed in or after 2009 however before 2012, with ballast water limit $\geq$5000 m^3 must running ballast water management that, at any rate, meets the ballast water performance standards. Ships built in or after 2012, with a ballast water limit $\geq$5000 m^3 must running ballast water management that at any rate meets ballast water performance standards (Sassi et al. 2005).

Different strategies for Ballast water management may likewise be acknowledged as options in contrast to the ballast water exchange standards and ballast water performance standards, gave that such techniques guarantee in any event a similar degree of assurance to the earth, Health of human, property or assets, and are endorsed on a fundamental level by Marine Environment Protection Committee (IMO 2005a, b).

11.5 IMO Standards for Ballast Water Quality

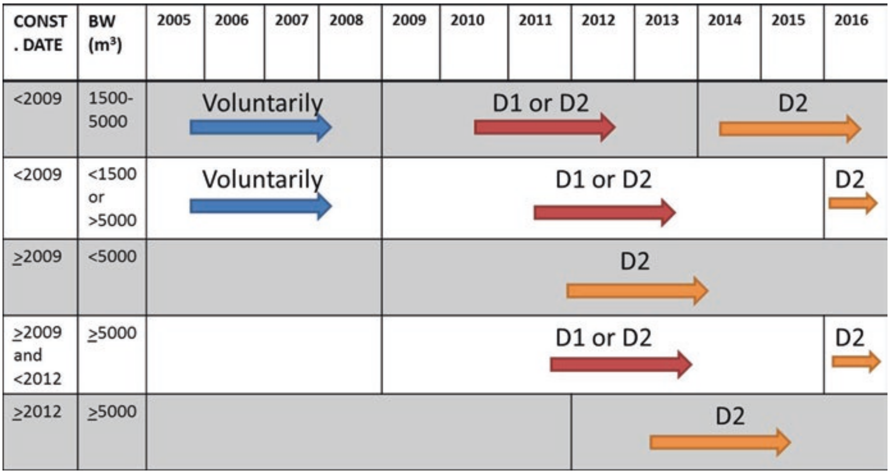
The International convention for the control and management of ships ballast water and sediments states two principal of ballast water management standards: (Vorkapić et al. 2018**).**

D1 – ballast water exchange standards, requiring the exchange of 95% of the amount of ballast water utilizing either the flow technique or the sequential flow or dilution technique (Vorkapić et al. 2018), and

D2 – ballast water performance standards, requiring ballast water treatment coming about with;

1. <10 living organisms per m^3, sized $\geq$50μm,
2. As well as <10 living organisms per ml of water, sized <50μm and $\geq$ 10μm, with a predetermined number of indicator microorganisms (microscopic organisms) (Vorkapić et al. 2018). Furthermore, a ballast water discharge of pointer microbes should not exceed the following identified concentrations;
   1. Toxicogenic Vibrio cholerae (O1 and O139) < 1 cfu per 100 mL (cfu) is colony-forming unit or less than 1 cfu per 1 gram (wet weight) zooplankton samples,
   2. Escherichia coli <250 cfu per 100 mL and Intestinal Enterococci <100 cfu per 100 mL. (Vorkapić et al. 2018; Tsolaki and Diamadopoulos 2010; https://maritimecyprus.com/2018/07/31/maritime-regulations-guidance-control-and-management-of-ballast-water/).

As per the Regulation D-2 ballast water performance standards, releases of ships performing ballast water management will follow to the particular guidelines (Tsolaki and Diamadopoulos 2010). As per the Convention, vessels ought to build



CONST. DATE	BW (m³)	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016
<2009	1500-5000	Voluntarily				D1 or D2					D2		
<2009	<1500 or >5000	Voluntarily				D1 or D2							D2
≥2009	<5000					D2							
≥2009 and <2012	≥5000					D1 or D2							D2
≥2012	≥5000								D2				

Fig. 11.2 Timeline for the implementation of the International convention for the control and management of ships ballast water and sediments. (Modified after Gollasch 2004 and Sassi et al. 2005)

up a ballast water management system somewhere in the range of 2009 and 2016. The timeline plan (Fig. 11.2) relies upon the time of ship establishment and the volume of ballast water (Tsolaki and Diamadopoulos 2010).

At that point each ship will have a ballast water treatment system installed that could be fit for ballast water treatment before releasing it into the marine ecology (Tsolaki and Diamadopoulos 2010). Figure 11.2 (received after Gollasch 2004 and Sassi et al. 2005) presents the ballast water management implementation timeline.

11.6 Management Options of Ballast Water

A portion of the set standards are: direct of ballast water exchange by the ship outside of exclusive economic zone, statement of the location of ballast water filling, etc. (İnmeler 2009).

The situation of the Australian Quarantine and Inspection Service (AQIS 2008) can be refereed to for instance. AQIS categorized the ballast water as high-hazard or low-hazard ballast as per the spot of filling, and chooses whether the release of ballast water is to be allowed in Australian regional waters. After the reception of the International convention for the control and management of ships ballast water and sediments, several technological and scientists were possessed and suggested management options. The essential headings of ballast water management options can be shown in Fig. 11.3.

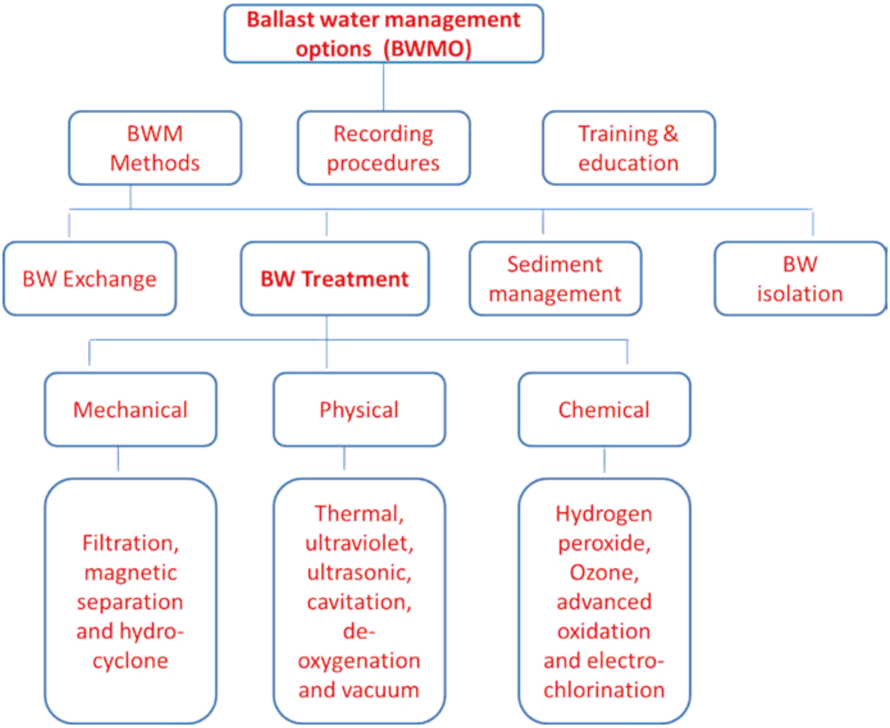


Fig. 11.3 Ballast water management options (BWMO) including ballast water treatment technologies. (Modified after the Guide for Ballast Water Treatment 2016)

11.7 Ballast Water Treatment Technologies

The Present technologies of ballast water treatment always utilize 2 steps treatment approach (Stehouwer et al. 2015). The point of the primary treatment is to decrease the marine living organism's quantities. Thus, it extensively expands the effectiveness of secondary treatment, which at that point decreases the levels of organic compounds below the required standards (Briski et al. 2014).

11.7.1 Mechanical Treatment

The primary treatment techniques being used are filtration and hydrocyclone. In the filtration, ballast water is separated by going throughout a semi-porous filter (membrane), expelling sediments, zooplankton, and phytoplankton >50µm (Vorkapić et al. 2018). The hydrocyclone isolates solids (oceanic organisms) from fluids (for this situation, ballast water), utilizing centrifugal powers. Because the effectiveness of the hydrocyclone significantly relies upon the mass and thickness of the particles, this technique is to some degree insufficient in the removal of smallest organisms from ballast water (Vorkapić et al. 2018).

11.7.2 Physical Treatment

Secondary Treatment techniques include several of chemical and physical techniques, applied both individually or in combination (Tsolaki and Diamadopoulos 2010; Wu et al. 2011). The most ordinarily applied physical techniques incorporate ultraviolet (UV) irradiation, ultrasound, thermal and magnetic and electrical water treatment (Vorkapić et al. 2018).

11.7.2.1 Ultrasound and Cavitation

Sonication or ultrasound (US) innovation can be utilized as a secondary treatment alternative (Tsolaki and Diamadopoulos 2010). Systems that utilize ultrasound are likewise powerful in organism evacuation (Vorkapić et al. 2016). Gavand et al. analyzed a sonicator instrument working at 1.4 kHz. The research was done on two different organisms; the brine shrimp (Artemia salina) and the green algae (Dunaliella tertiolecta) in 3 development stages (adults, larvae and cysts). Green algae expulsion was 40% for a living arrangement after 20s (Tsolaki and Diamadopoulos 2010). The inactivation was much higher for Artemia salina under similar conditions. The most elevated expulsion (100%) happened for the larvae stage, then adult stage (85%) and at long last by cysts (60%). Cavitation is utilized as an extra treatment strategy in different systems, however challenges are conceivable when water is siphoned at a flow rate > 5000 m^3/h.

11.7.3 Chemical Treatment

The chemical approaches in use include ozone (O_3), biocides, Electrochlorination, chlorine dioxide (ClO_2), chlorine (Cl), and other chemicals.

11.7.3.1 Ozone

O_3 is an extremely strong oxidizing agent which pulverizes viruses and bacteria, plus spores when utilized as a disinfectant in water treatment factories (Reynolds et al. 1989; Tsolaki and Diamadopoulos 2010; Hassaan et al. 2017a, b; El Nemr et al. 2018a, b; Hassaan et al. 2020a, b). Since the late 1800s O_3 has been utilized as a disinfectant, O_3 is utilized generally in Europe and US in the treatment of drinking water (Hoigné 1998). The chemistry of O_3 in seawater varies from that in freshwater as a result of the nearness of Br^- (Oemcke and van Leeuwen 1998, 2003; Hassaan et al. 2016, 2017b, 2019; Hassaan 2016; Hassaan and El Nemr 2017).

Oemcke et al. analyzed the possibility of disinfection effect of O_3 on boats ballast water utilizing the spores of Bacillus subtilis as marker organisms and reached the conclusion that O_3 isn't reasonable for the regulation of spore-forming organisms in ballast water. They utilized O_3 dosages of 9 mg L^{-1} at pH 7 and 14 mg L^{-1} at pH 8.2 and accomplished 4-log inactivation of the spores of Bacillus subtilis. Oemcke and van Leeuwen (2005) examined the possibility of O_3 to expel the marine dinoflagellate alga Amphidinium sp. Also, thought about that the elimination of alga Amphidinium sp. from ballast water demands higher doses of O_3. During this trial they utilized O_3 dosages between 5–11 mgL^{-1} and the exposure time was 6 h and accomplished a 4-log inactivation of these species.

11.7.3.2 Electrochlorination

Electrochlorination is a procedure of making reactive Cl compounds by passing electric pulse across ballast water with higher salts content (Vorkapić et al. 2018). The effectiveness of these techniques is very high. A destruction of 99% of zooplankton, phytoplankton and bacteria was recorded by electrochlorination techniques (Matousek et al. 2006). Beside the concentration of Cl in the water, the proficiency of the procedure additionally relies upon the time of reaction, temperature and the remaining Cl and its compounds. Moreover, this kind of ballast water treatment reduce the problem of making the supposed 'disinfection byproducts', the most hazardous of which are compounds coming due to the reaction of Cl with natural organic matter, for example, trichloronitromethane, dichloroacetic, trichloroacetic acid and chloroform ($CHCl_3$). It is in this way, its obligatory before releasing ballast water to treat it by electrochlorination, to kill 'disinfection byproducts' by addition of sodium bisulfite or sodium sulfite (Balaji and Yaakob 2011; Werschkun et al. 2014).

11.8 Conclusions

Ballast water releases from ships have unfavorable Impacts on marine environment. Ballast water, in a basic clarification, is seawater. Ships use ballast water to keep up their parity permitting adjustment for variations in bunker oil and cargo-weight. Present day shipping can't work without ballast water, which gives stability and dependability to empty boats. Ballast water discharge comprises the essential trajectories for the worldwide spreading of aquatic invasive species. The Present technologies of ballast water treatment always utilize 2 steps treatment approach. The point of the primary treatment is to decrease the marine living organism's quantities. Thus, it extensively expands the effectiveness of secondary treatment, which at that point decreases the levels of organic compounds below the required standards. Many modern approaches are utilized in ballast water treatment among of them; O_3, electrochlorination, ClO_2, Cl, UV and US. Right now, the most widely recognized ballast water treatment systems is 2-step electrochlorination for high-capacity system and UV for low-capacity system, both joined with filtration or cyclonic separation for the important primary treatment.

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Chapter 12
Source, Pollution and Remediation of Carcinogenic Hexavalent Chromium from Industrial, Mining Effluents

Aliya Naz, Abhiroop Chowdhury, and Brijesh Kumar Mishra

Abstract Chromium, a transition metal found in earth crust, is a major pollutant impacting air, surface water, groundwater, soil and plants. It is naturally found in high concentration only in serpentine soils originating from weathering of mafic and ultra-mafic rock structures rich in iron loving siderophile. Anthropogenic sources of chromium apart from chromite mining activities are industries like iron and steel, ferrochrome ore processing units, electroplating and tannery. Amongst the two stable species of chromium, hexavalent chromium is classified as group 'A' carcinogen, due to its mutagenic properties while trivalent species is relatively safe in terms of ecotoxicity as well as human health hazards and considered as a micronutrient. The range of hexavalent chromium in the groundwater is reported upto 115 mgL^{-1} worldwide.

Though there are different conventional methods for removal or immobilization of hexavalent chromium from effluent, but selection of a particular method in terms of economic feasibility and removal efficiency is a major point of academic as well as technological debate. Popular hexavalent chromium removal methods from water are; chemical and electrochemical, ion exchange along with membrane separation, adsorption, biosorption, nanozerovalent iron adsorption and microbial remediation. Among all these techniques, microbe based technologies shows comparatively good Cr^{6+} removal in context of feasibility, limited operational constrains and cost effectiveness.

Keywords Hexavalent chromium · Bioavailability · Cancer risk · Chemical reduction · Groundwater · Surface water · Microbial remediation · Toxicity · Technology

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12.1 Introduction

French chemist Louis Nicolas Vauquelin discovered a metal with ability to form coloured compounds in 1797 and named chromium after Greek word Chroma, meaning colour. This transition metal have various uses in modern world mainly because of its industrial application. Chromium was first introduced in steel plants during 1865 and its use became prominent in leather industries since 1884. The main source of chromium was ferrochrome ore whose mining has started in India and South Africa around 1906. Start of 1920, has seen the advent of electroplating industries which also started relying on chromium for chrome-plating. This ever increasing demand of chromium has lead to more mining and processing of ore, hence contaminating the air, water and soil in the process.

There are two stable form of chromium found in environment, i.e. trivalent and hexavalent chromium. Hexavalent chromium, amongst them is carcinogenic. According to Indian Standard (IS:10500) the acceptable limit of hexavalent chromium in drinking water need to be less than 0.05 mg L^{-1} to minimize its negative health impacts on population. Since last two decades consciousness has been rising on saving the environment as well as humans from exposure to deleterious and toxic chemicals spewing out of major industries like iron and steel, thermal power plants, tannery, ore processing, mining and allied heavy industries. But recent studies on extent of chromium- pollution from industrial and mining sources has proved that more stringent environmental regulations are required for the sustenance and existence of biota including human. The removal and remediation of Cr from the environment has been a challenge and the major research focus amongst industries and scientists alike.

12.2 Sources of Chromium

Chromium ranks 21st amongst abundant metal in term of its overall concentration in the earth's crust. The average concentration of chromium is about 120 ppm and it is the sixth most abundant transition metal (Emsley 2001). Chromiunm concentration in soil ranges between 1–3000 mg kg^{-1} (Alloway 2012). Mafic and ultramafic rock type is an igneous rock formation and chromium rich minerals are generally found along with such rock formations. In vicinity of such rock structures chromium concentration can be staggeringly high. Near mafic and ultramafic igneous rocks (basic) the Cr concentration can vary more than 3000 mg kg^{-1}. However, the acidic sedimentary and igneous rocks have 5–120 mg kg^{-1} of Cr concentration (Oze 2003). Apart from these cases chromium concentrations above general average values is only reported in areas affected by industrial, mining activities or impacted by atmospheric fallouts (Naz et al. 2018). Chromium is observed to have the potential to get bioaccumulated in the native plant species growing in regions polluted due to influx of industrial effluent or mining fall outs (Naz et al. 2020; Chowdhury et al. 2021).

12.2.1 Natural Sources of Chromium

Weathering of parent materials is the major natural source of chromium in soil. Serpentine soils originated from weathering of ultramafic rock with strong enrichment of Fe- loving siderophile elements like chromium and Nickel. Presence of these metallic ions, is responsible for easy substitution of minerals like pyroxene, olivine, and biotite which are principal mineral constituent of these rocks and these have high concentration of magnesium. In natural conditions without anthropogenic impacts, chromium concentrations in aquifer, soil is low (Table 12.1). As an exception, in few areas comparatively high concentrations of dissolved chromium have been reported because of their association with soluble chromate species even without anthropogenic impacts (Vengosh et al. 2016).

12.2.2 Anthropogenic Sources

Industrial activities like mining, electroplating, tanning, manufacture of stainless steel, paint and dye, chemical, and glass manufacturing are the major anthropogenic source of Chromium (Naz et al. 2016a). The largest producers of chromium ores are South Africa, Kazakhstan, India, Turkey, Russia, Oman, Zimbabwe, and Finland (Shanker and Venkateswarlu 2011). Around 14 million tons of chromite ore is produced per year globally, having a reserve of around one billion tones with potential unexplored deposits in Greenland, Canada and USA (Shanker and Venkateswarlu 2011). India rank 3rd in chromite ore production worldwide and 97% of that production of India comes from a group of mines operating at a place called Sukinda, at Jajpur district in the state of Odisha (IBM 2012).

12.3 Chromium Chemistry and its Bio-availability

Chromium can have different oxidation states varying between −2 and +6. But only hexavalent and trivalent chromium are the stable forms and usually found in the aquatic systems, while other forms of Chromium are rare (Oze 2003). The speciation of Chromium is generally dependent on pH of the medium. At pH range between 0 and 4, trivalent chromium tends to be associated with hexa-coordinate complexes with ligands (for example H_2O, NH_3, SO_4^{-2}, CH_4N_2O, and organic acids). Between pH 4 and 6, trivalent chromium are present as hydrolysis products like $Cr(OH)^{2+}$, $Cr(OH)^{2+}$, and $Cr(OH)_3$. However, at pH more than 6, trivalent chromium forms stable solid precipitates of hydroxides mostly in forms of Cr^{3+}, and at alkaline condition, (pH more than 9), this precipitate formed a complex of $Cr(OH)^{4-}$ which have better solubility than the previous forms (Unceta et al. 2010).

Table 12.1 Chromium content in the groundwater (GW) and surface water (SW) in different areas of globe, where TCr and Cr^{+6} are 'total chromium concentration' and 'hexavalent chromium' respectively, and BDL is 'below detection limit'

Country	Locations	Source	Type	TCr (mgL^{-1})	Cr^{+6} (mgL^{-1})	References
Mexico	Leon Valley	Natural	GW (Wells of eastern area)	4.38	0.0057	Armienta et al. (1993)
		Anthropogenic	GW (Wells of central area)	96.52	0.0123	
		Anthropogenic	GW (Wells of western area)	200.73	0.0021	
		Natural	GW	0.0097	0.004	Robles-Camacho and Armienta (2000)
Haiti	Port-au-Prince	Anthropogenic	GW	0.326	0.007	Emmanuel et al. (2009)
Italy	La-Spezia Province	Natural	GW	0.0113	0.01	Fantoni et al. (2002)
California	Sheep Creek fan	Natural	GW (Recharge area, apex and Midfan areas, and deep aquifer)	0.013	0.0123	Izbicki (2008)
	Sheep Creek fan	Natural	GW ('Perched' aquifer)	0.017	0.026	
	Surprise Spring area		GW (upper aquifer)	0.0084	0.009	
	Surprise Spring area		GW (lower aquifer)	0.01166	0.015	
	Other areas in the western Mojave Desert	Natural	SW (Deadman Lake area)	0.0099	0.0095	
Greece	Anthemountas River basin	Natural	GW (shallow porous aquifer)	0.02	0.015	Kazakis et al. (2015)
			GW (deep porous aquifer)	0.00085	BDL	
			GW (Ophiolitic)	0.011	0.011	
			SW	0.00212	0.0004	
Italy	Cecina Coastal area, Tuscany	Natural	GW	–	0.0005–0.047	Lelli et al. (2014)

(continued)

Table 12.1 (continued)

Country	Locations	Source	Type	TCr (mgL^{-1})	Cr^{+6} (mgL^{-1})	References
India	Chrompet industrial area, Chennai	Anthropogenic	GW	0.078	0.055	Kumar and Riyazuddin (2010)
	Ranipet industrial area, Tamilnadu			0.247	0.01–28	Gowd and Govil (2008)
	Sukinda chromite mine Odisha			0.049–0.25	0.02–1.15	Naz et al. (2016b)
	Rania			–	<0.005–34.8	Matern et al. (2017)
	Chhiwali			–	<0.005–115	
	Godhrauli			–	<0.005–2.0	
Saudi Arabia	Drinking water cooler of School (Riyad)	Anthropogenic	Drinking water	0.5–3.76	–	Al-Saleh (1996)

Chromium species such as trivalent and hexavalent have different impact on health. Trivalent chromium is an essential micronutrient for biota unlike toxic hexavalent (Wang et al. 2013). Trivalent chromium is an essential mineral and worked as a micro nutrient at low concentration, which found in drinking water, grains, meats and vegetables (Lee et al. 2012). This form of chromium is essential for glucose and lipid metabolism as it binds with the insulin receptors, which increase the efficiency of this major blood sugar regulating hormone.

Bioaccessibility of chromium and its compounds can be defined as the concentration of the target element or compound available to be absorbed in the digestive system out of the total amount of the ingested material. While bioavailability is the concentration of chromium compounds that can pass through cellular membrane and hence is available to the target tissues. Bioavailability can be defines as cellular uptake amount of chromium in elemental or compound form out of the total exposed concentration.

12.3.1 Hexavalent Chromium Toxicity and Regulation Strategies

Hexavalent chromium is highly carcinogenic via ingestion pathway (Stern 2010). Cohen et al. (1993) reviewed toxicity and carcinogenicity of chromium and concluded that it can cause skin tumors in rodents by chronic exposure along with solar ultraviolet light. This work represented a new animal model for Chromium- induced cancers through exposure to hexavalent species contaminated drinking water. Hence, it also shed light into the possibility of its carcinogenicity on human cell lines. Hexavalent chromium species passes through membrane sulfate transport channel and it interacts with glutathione and ascorbate motifs, ultimately making a complex with, nuclear protein, and deoxyribonucleic acid which eventually interrupt the entire cellular metabolism. Hexavalent Chromium generally get reduced after entering the cytosol and processes Reactive Oxygen Species (ROS) in the process. Deoxyribonucleic acid (DNA) get damaged due to strand break, chromosomal instability, alteration in sister chromatid exchange or epigenetic changes (Nigam et al. 2014). Generally, DNA repair mechanism is responsible for restoring this deleterious modification. But due to repeated genotoxicity, this repair mechanism can fail resulting in programmed cell death (apoptosis) or mutation resulting in carcinogenic malignancy in cell line.

Exposure of hexavalent chromium can result in impairment in human reproductive potential in both genders, and it not only cause reproductive problems but it can also cross over the placental barrier and interfere with the fetal development process, hence can be classified as teratogen (Marouani et al. 2015; Naz et al. 2016a). Because of these harmful impact of this chromium species via consumption, Environmental protection agency of California has set 0.02μgL^{-1} concentration for it in drinking water in their report named 'public health goal' (PHG 2009).

12.3.2 Health Risk Assessment of Hexavalent Chromium

United State of Environmental Protection Agency (USEPA 2005), proposed cancer and non-cancer risk models to quantify toxic substance exposure induced health hazards. Direct experimentation is difficult in cancer research because of ethical constrains. To overcome this constrain, empirical equations are generally employed to estimate the multi-pathway health risk. Epidemiological studies highlights carcinogenic effect of hexavalent chromium in upper respiratory track and atrophy due to inhalation of hexavalent chromium (Das and Singh 2011). On the basis of carcinogenicity of it, United State of Environmental Protection Agency conducted a dose response assessment study in 1998 with the title "Toxicological review of Hexavalent Chromium" (USEPA 1998). This study concluded that there is data regarding the occupational exposure of chromic acid mists is uncertain compared to direct exposures to this toxic form of chromium. But it fails to determine a dose response assessment for hexavalent chromium by oral route of exposure. In this regards agency again conducted a dose response assessment to estimate health hazard through oral pathways (USEPA 2012) and drafted "Toxicological review of Hexavalent Chromium 2010" (Nathanail 2013). This draft concluded that the potency of cancer due to hexavalent chromium and derived the factor for estimating cancer slope around 0.5 (mg per kg-day)$^{-1}$. Different studies have been done on the assessment of probable health risk of chromium on human beings (Naz et al. 2016a, b).

12.4 Treatment Methodologies for Removal of Carcinogenic Hexavalent Chromium from Water

Many procedures have been tested over the years in order to eliminate hexavalent chromium from aqueous systems. The most commonly used methods are adsorption, chemical precipitation, membrane separation, ion exchange, reverse osmosis, and electro dialysis (Barakat 2011). Every method has its own limitations according to the local conditions and economic status of the area. Some of treatability studies are discussed as follows.

12.4.1 Chemical Reduction Followed by Precipitation

The chemical reduction and precipitation process is widely used in different industries. This is because of the process of reduction involves Fe^{2+} and S^{2-} ions. The chemical reduction of CrO^{2-} by Fe^{2+} is >100 times faster than the efficiency of biological reduction processes (Madhavi et al. 2013). Chemical precipitation generally follows four major steps namely, (i) reduction of hexavalent chromium to less toxic and less soluble trivalent form (Cr^{3+}), (ii) precipitation of Cr^{3+} ions in form of Chromium (+3) hydroxide at alkaline pH range, and (iii) disposal of precipitated sludge containing insoluble metal hydroxides. Chemical precipitation includes OH^-, S^{2-}, $CO_3{}^{2-}$ and $PO_4{}^{3-}$ precipitation. Two types of remediation methods commonly used in industries are sulfide and hydroxide precipitation. The S^{2-} precipitation process is more useful in most of the industries in comparison to OH^- precipitation because metal- S^{2-} precipitation is less soluble than metal-OH^- precipitation, and thus it can be easily separated out from water.

Chemical reduction through sulfide precipitation mainly takes place in acidic conditions, usually at pH below 3. As this process consumes protons, it becomes essential to provide more acid to maintain a low pH condition. In most of the industries widely used reductants are gaseous SO_2, Na_2SO_3, $Na_2S_2O_5$, $FeSO_4$, $BaSO_3$. Among above mainly $FeSO_4.7H_2O(s)$ used as the reducing agent. When $FeSO_4.7H_2O(s)$ is added to the synthetic Cr^{+6} solution to change the Cr oxidation state following general reaction takes place:

$$3Fe^{2+}{}_{(aq)} + Cr^{6+} \rightarrow 3Fe^{3+} + Cr^{3+}{}_{(aq)}$$

In this method $FeSO_4$ $.7H_2O(s)$ (150 and 200% in excess quantity) was mixed in water then stir to promote above reaction and then to remove chromium and iron from the aqueous phase. To maintain pH, 1 M $Ca(OH)_2$ was added (Bruzzone et al. 1992). Maximum insolubility for Fe^{3+} and Cr^{+6} hydroxide species was reached under these conditions. After the solid phase (sludge) are formed, separation from the aqueous media followed by filtering.

Chemical reduction of hexavalent chromium can also be done by hydroxide precipitation. Limestone and CaO are used as precipitant agents. However, it is shown that this method required excess addition of the reductant, and generate a large amount of sludge. Consequently, management and final disposal of this residue is quite difficult and proved to be expensive. Colin and Gazbar (1995), stated that the disposal cost of the generated sludge be equal to 50% of the total operational cost of a wastewater plant. Hydroxide precipitation processes also generate a large volumes of sludge, which creates disposal problems. Few hydroxides of metal, used in this process may be very active and it can react either acid or base, and these mixed metals can create difficulty in this process. This method is also not suitable for the effluents containing complexing agents, as these compounds can inhibit the process. Therefore, the costs of management and final disposal of sludge must, of necessity, be taken into account in designing a wastewater treatment process.

12.4.2 Electrochemical Precipitation

Researchers emphasised that the electrochemical option, provides a significant chromium removal by generating very low amount of sludge, i.e. about 50% less in comparison with the chemical reduction process (Zhao et al. 2018; Peng et al. 2019). In an electro chemical precipitation, an electrolytic cell works, which consists an anode (−ve charged) and a cathode (+ve charged), and the metallic ions attracted toward its opposite charge (Kurniawan et al. 2006). This process is effective for the removal of metal ions at very low concentration, while other methods like chemical reduction and precipitation and ion exchange are not effective. Various conductive materials in this process are vitreous carbon, carbon aerogel, stainless steel, graphite (Rana et al. 2004; Rana-Madaria et al. 2005; Park et al. 2007; Ruotolo and Gubulin 2009).

Although electro chemical precipitation process is cost effective but, this process is largely dependent on various parameters, like type of effluents, its pH, current input, electrolytes concentration and the presence of other salts in effluents (Liu et al. 2011). Further, this process requires costly electrodes and electrolytes, and also generate of sludge containing hazardous elements, which create the disposal problem make the process not economical.

12.4.3 Ion Exchange and Membrane Filtration

In this process ions of a given chemical are exchanged from an insoluble material (resins) in solution. In which, the metal containing effluents passes through the resin bed, where it is adsorbed by resins, and metal free water will be collected. The column is need to be backwashed after a particular interval, in order to take out trapped materials in the resins and before regenerated. Different resins have been used for hexavalent chromium removal, in which Synthetic Dowex 2-X4, Ambersep 132, resin are commonly used to treat industrial wastewater and chrome recovery (Lin and Kiang 2003; Liu et al. 2019).

Ion exchange resins are very selective for various metals which is the main disadvantage of this process for industrial use. Only selective resin can be selectively removed the hexavalent chromium from contaminated water. Further, the equipment used in ion exchange is expensive and that can be incapable in complete removal of the chromium from the effluent. Additionally, this process is extremely sensitive to the pH and it required appropriate pre-treatment before the operation.

Membrane filtration technique consists semi permeable membrane to separate metallic ions from the contaminated water. Semi permeable membranes commonly used to remove hexavalent chromium are polymeric, inorganic and liquid membranes (Pugazhenthi et al. 2005). The major drawback of ion exchange and membrane filtration methods are they required high energy, expensive and toxic chemical reductants and they are not appropriate for the removal of metallic ions from low chromium contaminated water (Kurniawan et al. 2006).

12.4.4 Adsorption and Biosorption

Adsorption is the demanding process in order to remove metallic contamination from industrial effluents due to its remarkable advantages like availability, effectiveness, easy operation, feasibility and comparatively good efficiency, than other conventional methods. Raw materials like clay, flyash, sawdust, shells of nuts and coconut are found effective for the adsorption of hexavalent chromium (Mohan and Pittman 2006). Researchers have used several adsorbents like activated carbons derived from nus of *Terminalia arjuna* (chemical activation with zinc), and Sutcliffe Carbon prepared from a bituminous coal for the adsorption hexavalent species of chromium. These derived adsorbents worked very well, however, the adsorption capacity of an adsorbent is largely dependent on the physicochemical property of the effluents, for e.g. pH, and presence of alkali metals (Owlad et al. 2010).

Biosorption is the process of adsorption of metallic ins by a variety of non-living biomass like tree bark, dried grasses, tree bark, leaves, lignin and peanut hulls, coconut shells and from living biomass like fungi (Park et al. 2005), bacteria (Dey and Paul 2014), *Syzygium cumini* bark (Hashem et al. 2019). The hexavalent chromium is significantly adsorbed through agricultural waste and it can be a feasible method for the treatment of contaminated aqueous systems (Gardea-Torresdey et al. 2004; Bansal et al. 2009). Major drawback of this process is the frequent desorption, dependency on adsorbent amount, regeneration and recovery of adsorption column and the further treatment of the backwash water. These processes increase the complexity and cost of treatment by adsorption technology.

12.4.5 Nanozero Valent Iron and Nanozero Valent Metal Technique

Nano Zero Valent metal is emerging as new option for the treatment of metallic ions from the contaminated soil, surface water and groundwater. Zero-valent iron and nickel particles are commonly applied to removal of metals from contaminated water Gillham and O'Hannesin (1994).

The oxidation of these nano zero particles slightly changes the pH, which provides effective surfaces for sorption of metallic ions in the media (cations and anions). Srivastava et al. (2014) have used nanozero NiO particles (0.1–1.0 g) in 500 ml solution of 10–100 mgL^{-1} of hexavalent chromium contaminated water and found these nano-particles are effective to reduce it to trivalent chromium. Further, Sun et al. (2014) have used SBA-15 rods and removed hexavalent chromium from contaminated groundwater at different pH, and found maximum reduction efficiency at pH 5.5 (i.e. 99.7%), The main drawback of using nano zero valent iron method is that it is not cost effective and the method is very complicated.

12.4.6 Microbial Remediation of Hexavalent Chromium

Microbial treatment of wastewater containing metal ions, has shown a good efficiency for hexavalent chromium removal at low capital and maintenance cost, eco-friendly, and broad source. The ability of microbial cells to remove heavy metals is widely demonstrated by researchers and various bacterial strains identified as hexavalent chromium reducer (Table 12.2). A flourishing microbial remediation method depends on the microbial populations capable to tolerate and remove hexavalent chromium from contaminated water.

Table 12.2 Microbial population capable in hexavalent chromium reduction and their removal efficiencies

Microorganisms	Chromium concentration (mgL^{-1})	Time (h)	Efficiency	Environmental condition	References
Ochrobacterium spp.	200	48	100%	Aerobic	He et al. (2009)
Bacillus cereus S-6	500	96	100%	Aerobic	Faisal and Hasnain (2004)
Pseudomonas C-171	1500	96	75%	Aerobic	Rahman et al. (2007)
Corynebacterium paurometabolum	104	240	92%	Aerobic	Viamajalaa et al. (2007)
Desulfovibrio spp.	20.8	1	100%	Anaerobic	Klonowska et al. (2008)

At present the main barrier for commercialization of this technique is lack of knowledge about suitable growth conditions, metal reducing pathways, minimum inhibitory concentration and efficiencies of microbes.

12.4.7 Selection of Suitable Technique for Hexavalent Chromium Removal from Water

Studies showed that physiochemical methods for chromium removal from the water, have some drawbacks like high installation and operational cost, requirement of costly chemicals, disposal of huge amount of toxic sludge. Microbial remediation mildly depends on the temperature and pH, and it is eco-friendly, economic, easy operative, green practice for the reduction as well as removal of hexavalent chromium from the water. Various microbial strain have proven to be efficient and shows maximum chromium removal at neutral pH in normal-high temperature range (Table 12.3). Average temperature of tropical countries like India is about 20–40 °C. At this temperature microbes would work properly, and there are no any requirements of costly chemicals, membranes, complex equipment and electrodes which make this process more economical.

12.5 Conclusion

Studies showed that chromium is abundant in natural environment but anthropogenic activities is responsible for chromium pollution, and increasing it's bioavailability in soil, water, plants and organisms. Hexavalent chromium is bioavailable and is toxic to biota due to its potential to act as a carcinogen by hampering with the intercellular functions as well as metabolism. Hence, removal of hexavalent chromium by reduction, adsorption, absorption and bioremediation is necessary to make the environment clean and decontaminated. In India, Sukinda in Odisha and Kanpur in Uttar Pradesh, showed the higher hexavalent chromium contamination in both surface and groundwater, because of mining along with unrestrained overburden dump at Sukinda, India. Non-green dumping of tannery effluents and allied industrial waste is the cause of chromium contamination at the Leon valley, Mexico. There is need to identify economically viable, and efficient hexavalent chromium removal technique from contaminated environment with a large-scale applicability. Investigations stated that, microbial treatment may prove efficient for removal of this toxic form of chromium contaminated water. Though, microbial remediation mildly depends on the temperature and pH, but it is eco-friendly, economic, easy operative and a green practice.

Table 12.3 Comparison of different remediation techniques for hexavalent chromium (Cr^{+6})

Techniques	pH range	Advantage	Disadvantage
Chemical reduction followed by precipitation	Works on varied pH (3–10)	Require less time and suitable for high Cr^{+6} Concentrated water.	Consume large amounts of costly chemicals.
		99% efficient to reduce Cr^{+6}	Produce large amount of low density sludge.
Membrane filtration	pH dependent (pH more than 7)	Can treat high Cr^{+6} concentrations.	Ineffective in removal of low level of Cr^{+6}.
		Can be operating in different environmental conditions.	Require expensive and toxic chemical.
		Less time consuming and no sludge generation.	Generate secondary toxic wastes and high operational cost.
Adsorption and biosorption	Limited tolerant (varied according to adsorbent and biosorbent nature)	Low cost adsorbent proven efficient and economical.	Complex process affected by many factors.
		Can remove highly concentrated Cr^{+6} from water.	Process lies in its frequent desorption and regeneration.
		Easy to operate.	Recovery of the adsorption increases the complexity and cost of treatment.
Microbial remediation	Maximum microbial strains work at neutral pH (limited tolerant)	Require fewer amounts of chemicals, less operational and maintenance cost and easy to operate.	Slow process as compare to other methods.
		Eco friendly and techno-economically feasible.	Depends on the environmental parameters such as pH, temperature
		No much sludge generation as compared to chemical processes.	Cannot effective to remove high concentrated Cr^{+6}

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Chapter 13
Pesticides in Drinking Water and Removal Techniques

Jagvir Singh and Anuradha

Abstract Aldrin, dieldrin, dichlorodiphenyltrichloroethane, polycyclic aromatic hydrocarbons, benzene hexachloride, polychlorinated biphenyls and many other pesticides are used as agrochemicals to increase the harvest production and these have also believable power to the contaminant. The resulting, these organic and inorganic substituents have posed a threat for health depends on its toxicity, exposure and how much quantity are present in water. World health organization has set the maximum pesticides residue limit in drinking water of 0.1 micrograms/liter. The monitoring of contaminated water and their regulation, supply is working under the United State Environmental Protection Agency and Federal Country safe drinking water Act (1979).

Excessive use of pesticides has led to health problems and fatal incidents worldwide. Pesticides have acute, carcinogenicity, and mutagenicity or causing aesthetic problems and chronic toxic risk to children. Since the health data available so far are limited to estimate the global health effects of such dangerous chemicals, some diseases such as birth defects, fetal toxicity, blood defects, genetic mutations, reproduction, benign or malignant tumors, nerve defects and endocrine disruption the effects of strength become difficult to assess. In this chapter, we have discussed the removal techniques such as membrane filtration, Ion exchange treatment technology, activated carbon, electrochemical treatment, phytoremediation, bioaugmentation and electrocoagulation for such type's pollutants.

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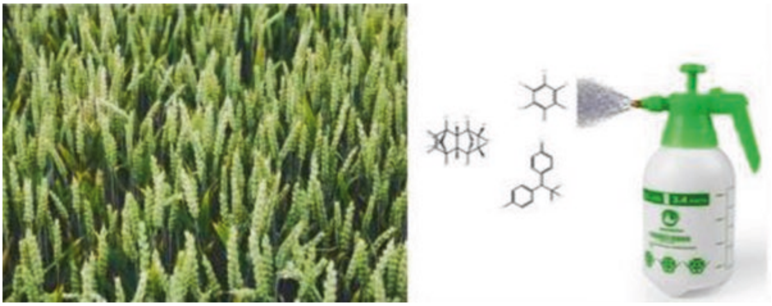

Keywords Organochlorine pesticides · Clinical effect · Membrane filtration · Ion exchange treatment technology · Activated carbon · Electrochemical treatment · Phytoremediation · Bioaugmentation · Electrocoagulation · Pesticide transportation

13.1 Introduction

Pesticides are being used globally as a fungal weed. These chemicals allow crops to flourish vigorously in use time, thereby increasing global production rapidly (Rosa et al. 2019; Aly et al. 2019; Yihan et al. 2018). These substances predominantly enter ground water through water sources and leaching through drift and agricultural runoff due to one or more substances being active. Diseases caused by water pollution through insect mites, weed contaminated surface water leaks, improper disposal (Arne et al. 2019; Eduard et al. 2019; Hicham et al. 2008) and even waste material injected into wells, crop be it a developed nation or a developing nation, both harmful to pesticides and causing economic damage. The problem of water pollution by pesticides in India is so severe that 50% urban and 80% of rural people were getting badly affected. Insecticides may contain weeds, fish, birds, molluscs, nematodes, plant pathogens, and a pesticide chemical substance that may be a biological agent, disinfectant, or any device that forces economic power (Xiaochu et al. 2019; Tawfeek et al. 2019; Gangesh et al. 2006; Wangyang 2017) by using them.

The use of pesticide chemicals started after 1940 to protect crops, increase yields. Along with protecting crops, plants and increasing crop production, their use is also increasing in defense of organisms. Their use is constantly increasing in every production filed. Organochlorine pesticide (Adgate et al. 2000; Ankley et al. 2010) usage has increased substantially since World War II. The article by Rachel Carson in "Silent Spring" was published in 1962, in which shows the excessive use of pesticides in agriculture and due this sources of water are at peak of dangerous point, these dangerous chemicals cause eating disorders and at the same time their negative effects on the environment can be described in detail. Research records of the researcher obtained suggest that people in ancient Mesopotamia had already used pesticides to protect their crops about 4500 years ago, and primary sulfur dusting has been the first known used pesticide (Arena and Sgolastra 2014, Arias et al. 2008).

If we talk about water, then after air, it has been like the most important part of nature here for the creatures on earth. Only 3% of the water as fresh-water resources exists on earth. These water resources are very important for daily use water, ecosystem, energy industry, health of animals and other water-dependent subjects. Developing countries are still struggling with this kind of problem compared to other developed countries (Epstein and Bassein 2003; Epstein and Zhang 2014). Industrialization and increased population are fully responsible for this. Due to the quality of its illiteracy, they are also causing financial problems in the environment along with the problem of water pollution. If we talk about the last 20 years, it is seen that the use of some pesticides has increased to a very high percentage, which makes water (Zijian and Aaron 2018; Arisekar et al. 2019) resource of polluted. Due to their poisonous effects, these chemicals are poisonous for the life of our earth.

The pesticide-rich water source is a major concern all over the world because many deadly diseases start with such water pollution. 18,000 or more people die every day due to pesticide pollutants. If we compare this kind of problem (Mourabit and Boulaid 2019; Rani and Kumaraguru 2014; Rasul and Thapa 2003; Abarikwu and Adesiyan 2009) with the developed countries, then we find that it is a very terrible problem in developing countries. In addition to pesticides, water pollution can also be natural in which storms, earthquakes, volcanoes, algae blooms and ecosystems can occur. Molluscicides, plant growth regulators, fungicides, herbicides, nematicides, rodents are all types of pesticides. Before 1900, organochlorine, a pesticide, was used to control many deadly diseases such as malaria and typhus, which was later banned in most countries (Williamson 2007; Westbom et al. 2008).

Such agrochemicals are polluting the life of humans with viruses. The arrival of organophosphates, carbamates, herbs and pyrethroids in the decade of 1970–1960 gave a new direction to agriculture and its production. Although a pesticide should be lethal only for its target, it has been observed that it has proved to be very deadly for non-target species, even humans. This has created a controversy over the use and non-use of pesticides (Baker and Wilkenson 1990; Bohmont 1997). In 1952, with the production of Benzene Hexachloride, the use of pesticides took birth in India and its use started on a large scale. After India, China is the second largest agrochemical producing country in Asia and ranked twelfth globally. These pesticides in drinking water remain a health concern even after years. It is a very small part or quantity of pesticides that reach drinking water from various sources which enters the human body with drinking water and causes adverse health effects.

Every country uses pesticides in agriculture, residential gardens and commercial areas. Due to their exposure, these natural waters reach the human body through source, breath and dermal contact. Organophosphorus insecticides (Salam et al. 2015) have been used in agriculture since the ban on organochlorine pesticides, which has created dangerous health problems. Pollution of ground water by pesticides has become a national problem because more than 50% of the people here depend on ground water. In countries or places where these chemicals are used more or say that agricultural areas are more affected because their life depends on ground water. Before 1970 it was thought that the soil, like a filter, prevents pesticides from going into this ground water (Sattar and Rahman 1987; Satyavardhan 2013). New research tells us that these dreaded chemicals do not get filtered and go to ground water through leaching from agricultural land, which is a huge source of such type water pollution. The problem of pesticide pollution also arises through the disposal of waste material, improper disposal, leakage of contaminated surface water, accidental spills and leakage.

13.2 Dispersal of Water on Earth

So far it has been possible to see life only on Earth, the reason for this is the presence of water only on this planet. Which covers 71% of it. Table 13.1 shows the different sources of water and available water on the earth.

13.3 Historical Perspectives

The history of pesticides is very old, the whole world has been using such chemicals in agriculture for centuries. People started using them in the nineteenth to the twentieth century by using synthetic pesticides. By mixing the right proportion of pesticides, we got rid of undesirable pests, weeds and gave the agricultural world a chance to flourish (Sharmin et al. 2015; Bolognesi 2003).

Table 13.1 Distribution of water on our earth planet. Quantity and their percentage indicate that all most water quantity is useless for household purposes with as drinking (Michael Gross 2015)

Sources of water	Quantity in ppm	Percentage	Area in Km.
Fresh ground water	7600	0.76	10,530,000
Saline ground water	9400	0.94	12,870,000
Ice form	17,400	1.74	24,064,000
Biological water	1	0.0001	1120
Atmospheric	10	0.001	12,900
Swamp water	8	0.0008	11,470
Rivers	2	0.0002	21,200
Saline Lakes	60	0.006	85,400
Oceans like water	965,000	96.5	1,338,000,000
Ground ice &Permafrost	220	0.22	300,000
Soil moisture	10	0.001	16,500
Fresh Lakes	70	0.007	91,000

In the agriculture farm, and other places, these chemicals pesticide named Paris Green was the first chemical pesticides have been starting to use in United States nation since the year of beginning 1867. The rise of synthetic pesticides in the nineteenth century led to Paris Green being discharged with pesticides containing calcium arsenate, nicotine sulfate and sulfur (Bolognesi and Merlo 2011; Cerejeira et al. 2003). Initially, the Romans used to control weeds with nonmetallic salt and sulfur which is have many anti properties against pets, fungus, bacteria, used to control them and both are the same work as done by pesticides or other herbicides, fungicides. In the 1600 century, the mixture of honey and arsenic compounds in a fixed proportion has been used to control ants and such others. Pyrethrin compound containing pesticides that very hazardous chemicals were used to control various types of insects and hellebore to control plant lice. Dichlorodiphenyltrichloroethane (Fig. 13.1) was the first synthetic pesticide of the time to establish a new identity with its use in the whole world (WWF 1998). The reason for its popularity was its use against mosquitoes and conquered the disease like malaria. Along with utility, it also gave birth to its derivatives.

It created a revolution in the world by giving birth to a new era with the availability of agriculture and domestic applications. Along with the utility, these pesticide chemicals have also given rise to their dangerous and deadly derivatives. Dichlorodiphenyltrichloroethane became very famous due to its multiple utility in agriculture but unfortunately the persistence of its properties made it almost nonexistent after World War II. After this, some more pesticides started to be used in agriculture, in which aldrin, Benzene hexachloride, andrine, dyedrin are some of the major chemicals (Shi et al. 2011; Siddika et al. 2012). These pesticides became popular with being effective, cheap. Rachel Carson, through her research, in her book 'Silent Spring in 1962', presented a harsh picture of people's understanding of the environmental risks of pesticides.

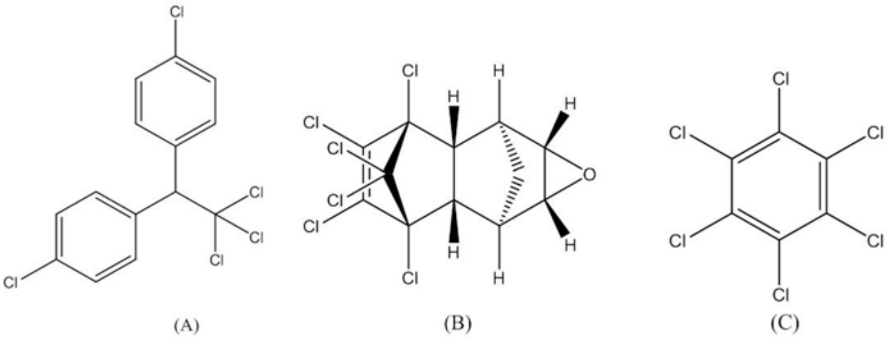

Fig. 13.1 Dichlorodiphenyltrichloroethane (**a**), dieldrin (**b**) and Benzene hexachloride (**c**) was the starting the chemicals that used as pesticides but now-a-days banned. These belong to highly persistent organochlorine insecticide. (WWF 1998)

13.4 Pesticide Classification

The term pesticide is a group of some dangerous, contaminated and negatively impacted chemicals (Jing et al. 2016; Schipper and Marc 2008). They are mainly divided into two classes natural and artificial or manmade. The main basis of classification is based on their chemical composition, properties, size, target as shown Fig. 13.2.

The classification has also been made by the World Health Organization based on the potential health risks and toxicity of pesticide chemicals as following-.

Class 1 a: Extremely dangerous
Class 1b: Extremely Dangerous
Class 2: moderately dangerous
Class 3: a little dangerous
Class 4: In general use, it is unlikely to present acute hazards

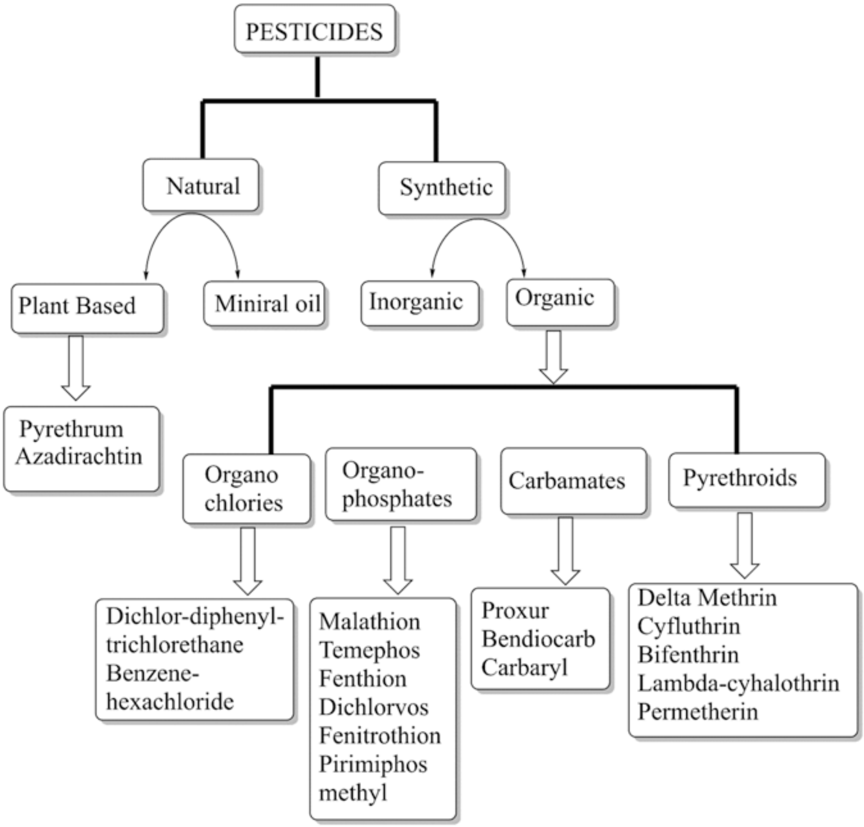

Fig. 13.2 This diagram shows the general classification of pesticides. The proposed classification is mainly based on the nature, character of insecticides and their specific targets. (Jing et al. 2016)

These insecticides are based on functions such as orchards, wood preservatives, domestic germ-ants, fungicides, herbicides and rodents. Many pesticides are increasing their amounts in the environment based on their special properties and their specific targets and water solubility (Alavanja et al. 2004; Arinaitwe et al. 2016). Manmade chemical pollutants can be classified into subclasses based on their varying physicochemical properties.

13.4.1 Mode of Action

Mode of action is the class of pesticides in which the chemical or pesticide affects its target. Such chemicals or insecticides fall under the mode of action. After this, they are classified into non-systemic and systemic category. Systemic insecticides exhibit their effects by moving into the target's vascular system while externally displaying their effects by not entering non-systemic target tissues (Bertolote et al. 2006).

13.4.2 Target Insect

The target insect class includes insecticides or chemicals that are classified based on the organism of the target insect. This is the most familiar category. In this category, pesticides are named because of their unique properties (Devleesschauwer et al. 2014). At the end of their names, the Latin word cide (dyeing) is used which is used as a suffix as a victim. For example, insecticides target plants with pests and herbicides, while mollicides for rodents, fungicides for fungus, bactericides for bacteria, insecticides for insects are affected.

13.4.3 Chemical Composition

As we know that insecticide is a type of chemical compound. Chemical composition class as it is known by the name that they are classified on the basis of their chemical nature and active elements. This category is also very important from the point of view of research in the field of pesticides and environment (Uddin et al. 2012; Ullah et al. 2014; Van Brink 2013).

Depending on the chemical properties, it can then be divided into seven subclasses, organochlorines, organophosphorus, carbamates, pyrethroids, organochlorins, organophosphorus, agotic heterocyclics, amides, and anilines. Organochlorine pesticides have five or more chlorine atoms. It was the first synthetic organic pesticide to be used in agriculture, in which the chemical composition is stable and keeps accumulating in the atmosphere. The first target of this pesticide is the nervous system, which, under control, leads to the goal of paralysis or death convulsions (Drechsel et al. 2010; Dufour et al. 2012). It causes severe endocrine disorders in aquatic animals and birds, so it was banned for the use of agriculture.

Organophosphates containing phosphate group are very toxic pesticides. From the point of view of the user, it was occupied by 48.6%. Organophosphates were used as a war material in World War II. This pesticide has also established records of its utility in industries, cosmetics, medicine, agriculture. In humans and some other species this compound prevents acetylcholine from being formed in the nervous system by the acetylcholinesterase enzyme formed in the hydrolyze process. The residue of this pesticide is dangerous for both ecosystems and food industries due to acute toxicity (Eerkes et al. 2015; Epstein 2015). Based on annual reports, three million cases of its acute poisoning have led to the death of 250–370,000 people annually, so this pesticide was also banned worldwide.

Carbamate is an organic compound and this compound's derived from carbamic acid (NH_2COOH) which is highly toxic pesticide. This pesticide is completely different from reversible, cholinesterase inhibition and organophosphates and inactivates the acetylcholinesterase enzyme. Pyrethroids, aniline, amides and abiotic heterocyclic insecticides are toxic compared to the above.

13.5 Sources of Pesticide Pollutants

Pesticides reach different sources of water and contaminate it. Examples of mediums such as air flow, water flow, soil (through leaching) can be found, even directly, the evidence of contamination of water is fair. These pollutants originate from agriculture itself, which are the source of pesticide polluted water (Accra et al. 2008; WWF 1998). Excessive use of agrochemicals has created competition for their food, habitat for vegetation risks as well as wildlife living there (Austin 1999).

These pollutants originate from agriculture itself, which are the source of pesticide polluted water. Excessive use of agrochemicals has created competition for their food, habitat for vegetation risks as well as wildlife living there. When these agrochemicals are used in the fields, as a result of improper formatting, the emission of these pesticides pollutes ground water through surface water or air flow and drinking water sources and leaching (Agricultural Chemical Regulations 2006).

If some amount of these pesticides gets deposited on the tree plants through the air, then by damaging them, it gets deposited through rain water in the source of these water, where it also becomes a target for humans and animals as well. They give birth to terrible diseases and end of life. Pesticides persist for a long time in water bodies due to their physical and chemical properties such as deposition rate, partition coefficient, degradation rate (Erlanger et al. 2005). According to the study, its percentage is different in different regions of India is graphically shown in Fig. 13.3.

Due to the physical and chemical properties of the pesticide such as partition coefficient, erosion rate, deposition rate, etc., persist for a long time in water bodies

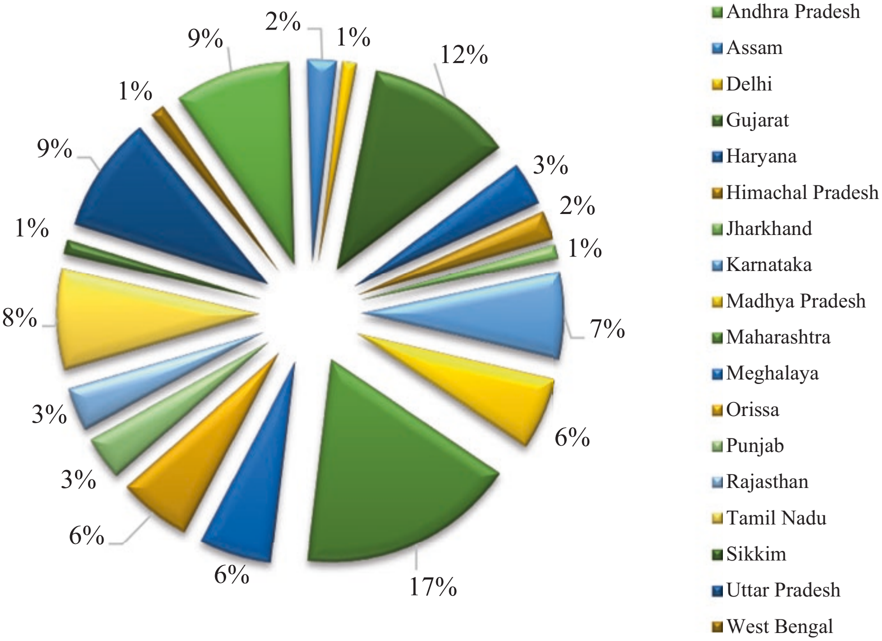

Fig. 13.3 This picture represents the pesticides pollution in water different percentage in Indian states. This graph showed that Andhra Pradesh has higher these sites. (WWF 1998)

and the environment. During these properties, their importance has also been seen in climate change.

13.5.1 Pesticides Water Pollution

In the American Geographic Survey, it has been found that out of 76 pesticides, seven pesticides were found which were broken down and converted into other products. In a subsequent research, researchers found in 90% water streams and 50% wells research findings that every water source had at least one pesticide presence (WHO 2009). Carbamate pesticide is found most often in ground water or drinking water. Aldicarb pesticides have been found in more than two thousand wells in some states along the island of India. Due to the different nature of these chemicals, their quantity in drinking water is different and given in Table 13.2.

"Our water is our world" is a motto for public awareness of water pollution. Given the risks of pesticides, water pollution prevention becomes very important. Through awareness campaigns, schools, colleges, news-papers, internet etc., their use and poisoning can be prevented with life consciousness.

In this way, by managing their, control strategies, information, scientific studies and tests, you can save the environment and its organism. In their research paper

Table 13.2 The nature and polluted concentrations of various chemicals that behave like pesticides are tabulated. (WHO 2009)

Pesticides	Nature	Fouling concentration (μg/L)
Carbofuran	Nematicide	40
Dalapon	Herbicide	200
Dibromochloropropane	Nematocide	0.2
Dinoseb	Insecticide	7
Dioxin	Herbicide	0.0003
Diquat	Herbicide	20
Endothall	Algicide	100
Ethylene dibromide	Insecticide	0.5
Glyphosate	Herbicide	700
Methoxychlor	Insecticide	40
Oxamyl	Insecticide	200
Pentachlorophenol	Fungicide	1
Picloram	Herbicide	500
Simazine	Herbicid	3
Toxaphene	Insecticide	4

low-cost alternatives like biomass such as wood, coconut shell, chitosan fiber such as bio-sorbents have been used to reduce pesticides from drinking water. In mg/liter to microgram/liter amounts of pesticides, they are very effective in disturbing the environment and life to a large extent.

Along with pesticides to pollute our drinking water, we are also responsible to a great extent because the population of the earth has grown very fast in the last few decades (Richa and Shilpi 2018), due to which the use of these pesticides in agriculture for food reimbursement is very high (Fig. 13.4).

As a result, the amount of these pesticide pollutants in the water has also increased, which has serious consequences for the environment as well as human health.

13.6 Pesticide Properties

Adsorption, evaporation, firmness and solubility are the properties of pesticides that reflect the eccentricity of leach or runoff. Through these processes, these chemicals get adjusted to ground water.

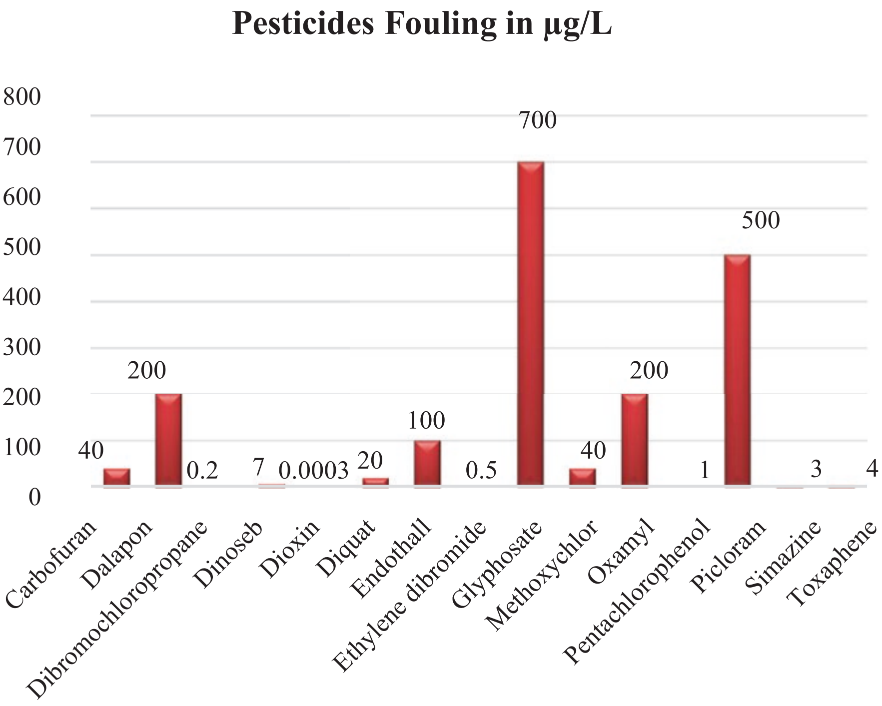

Fig. 13.4 This bar graph plotted between the different types of pesticides chemicals versus their fouling concentration in µg/L. Glyphosate is herbicide showed the maximum concentration to contaminant. (WHO 2009)

13.6.1 Adsorption

In this process, the pesticide gets stuck by the particles on the upper surface of the agricultural land while using chemicals, this is called the process of adsorption. Etrazine, paraquat which is an herbicide. The adsorption strength of paraquat is higher than atrazine. This action also depends on the adsorption properties of the soil.

13.6.2 Solubility

This property depends on the solubility characteristic of the pesticide chemical and can be written in milligrams per liter (mg/L) or in parts per million. If this characteristic is too much of a chemical, if the amount of a pesticide chemical is more than 1.0 parts per million, then it reaches the various sources of ground water and water very fast through the above medium.

13.6.3 Firmness

The term literally means how often a pesticide chemical is decomposed. This pesticide is the specific property of the chemical that can control the environment stagnation and its loss or for how long. Some other factors such as microbial action, chemical reactions, half-life and photodegradation also have their effect on this specificity.

13.6.4 Evaporation

As we all know that in the evaporation process, the pesticide chemical solid or liquid differs at different temperatures which is converted into a gas state. Pesticides at this stage are less polluting the environment. The risk of pesticides increasing in the water environment increases due to rain. In this manner, mainly the amount of pesticides is very low.

13.7 Pesticide Transportation

The transportation of pesticide may mainly consist of air and water. Air is a type of transport method in which it picks up pesticide chemicals and reaches other sources, such as fields, water reserves. If this chemical is absorbed by the surface of the ground, then it contaminates both ground water and ground water.

13.7.1 Surface Runoff and Erosion

Runoff is a type of action that involves water, soil and pesticide chemicals. It is found mainly where staircase is cultivated. When water is given in the fields, it overflows along with soil erosion and pesticide chemicals along with it goes through these steps and goes to these water sources. The amount of runoff depends on its slope, soil texture, moisture.

13.7.2 Diffuse Source

This pollution is caused by various activities without any particular point. This type of transport brings a series of such pollutants that water alone does not have any effect on the environment, but these insecticides by capturing these have specific effects. It is also governed by the spread of pesticides in agriculture. Apart from this, forestry, rural housing, atmospheric deposition, urban land can also be a source of diffuse.

13.7.3 Spray Drift

In this, the inadvertent spread of pesticides and their negative effects are mainly described. In this transport, the spray of these pesticides with spray, runoff from the soil is also polluted off-target, which severely affects property, environment and human health. Including off-target contamination due to spray runoff as well as runoff from plants or soil.

13.7.4 Leaching Processes

This transportation provides a medium for pesticides to reach ground water through such means. This is called leaching. Leaching solubility, soil types such as sandy, rain after some time of spraying succeeded in increasing leaching. Such moments help to maintain its properties to a great extent on pesticides and soil physicochemical properties, vapor pressure, dependence, solubility.

13.7.5 Overland Flow

In this, water flows on earth from rain, snow or other sources, which also plays a major role in the water cycle. The surface runoff before reaching a source is called surface runoff/overland flow. It also corrupts soil.

Total runoff = Surface runoff + groundwater Baseflow

After the ice melts, the river merges with water from various sources. Which then overflows and causes great harm to the atmosphere. The overflow flows downstream from the top surface to the hydrographic network due to gravity. Another way of overflow can also be that it works to uplift the source of water, after that when this level exceeds the maximum level, then it starts to flow from the water. Which also takes pesticide contaminants along with them and mix them in the source of clean water. When this water is used, the presence of pesticides shows its opposite effect.

13.8 Pesticide Poisoning

Pesticide chemicals are very toxic in nature. Those act like sweet poison in our food and which are constantly being served in front of us. These are being included in grains, vegetables and fruits through irrigation water and pesticides or in every food item of agricultural production. Continuous use of pesticide chemicals has increased fertility, quality and toxicity of agricultural land.

The sources of water like ponds, rivers etc. make the water there poisonous, causing great harm to humans as well as animals, birds and environment. Excessive spraying of pesticide chemicals leads to very serious fatal diseases. Their toxicity results in increased incidence of diseases such as ingestion, inhalation or cutaneous ab-sorption, neurological, psychological and behavioral disorders, hormonal imbalances, leading to infertility, breast pain.

13.8.1 Organophosphates

Organophosphate pesticides were created in the year 1940 after the tetraethylepro-phosphate pesticide was synthesized. Organophosphate poisoning is a type of pollution caused by pesticides containing organophosphate. Organophosphate chemical affects the nervous system. Some fatal diseases of this pesticide such as increase in saliva, tears, diarrhea, vomiting, red marks in the eyes, sweating, body swelling and confusion occur. The initial symptoms of which may take a few minutes, seven weeks or even months.

In developing nations, it has been observed that patients with organophosphate poisoning suffer from these pesticides in such a way that they are forced to commit suicide attempts. This toxicity is also increased by drinking water, breathing and skin. Its basic process is similar to inhibition of acetylcholinesterase. Which later becomes cetylcholine. Its confirmation is based on its symptoms. Butyryl cholinesterase has its activity in the blood after confirmation.

13.8.2 Chlorpyrifos

Chlorpyrifos is a versatile insecticide. Since its use has been banned in today’s date. It is a type of organophosphate insecticide. This pesticide affects termites, grubs, flies, lice, fire ants, cockroaches and corn root worms. Chlorpyrifos acts primarily as a poison (Jing et al. 2016). Its presence was found in some fruits specimen responsible for dangerous damage to the liver, lungs, kidneys, eyes and central nervous system. Its presence in some of the well-known brands of milk stored here also damages carcinogenic and sensory systems.

13.8.3 Dichlorodiphenyltrichloroethane

It is a well-known pesticide with a low soluble tendency in water. Whereas fats and organic oils dissolve easily. After their use, it is seen that it kills the surrounding aquatic and flora by its use. Their decaying dead parts accumulate in living creatures and flora which are then added to the food chain by organisms and flora. Since solubility in Dichlorodiphenyltrichloroethane vasa, it dissolves in the vasa of the body which increases concentration and toxicity (WHO 2003).

The molecules of these pesticides do not decompose over a long period of time and lying in the ecosystem it effects all the ecosystem factors. Once used, they are present in the soil and environment for a long time, such as Dichlorodiphenyltrichloroethane for 5 years, lindane for 7 years and arsenic molecules for an indefinite period of time (Michael et al. 2018). Exist in nature. Thus, insecticides are active all the time to destroy our nature.

13.8.4 Aldrin and Dieldrin

Since the 1940s, aldrin and dieldrin have started to use pesticide chemicals. These pesticides fall under the organochlorine class until 1970 it was used in crops, and in 1987 it started being used for termite control. Their high concentration in water affects dopaminergic and monoaminergic neurons, increasing the likelihood of diseases like Parkinson's and Alzheimer's (Honeycutt and Shirley 2014). Neurotoxicity is the result of these pesticides that aim to block the central nervous system of vertebrates. Headache, nausea, vomiting, spasms and coma are some of such physical onset symptoms.

The World Health Organization has determined body weight and is 100 ng per kilogram. 0.5 micrograms of dieldrin contains (WHO 1995) our food directly from various sources including food (Atreya 2006), water, and air, daily research has shown that in the United States (Pengfei et al. 2011; Alan 2014).

In the body of mankind, these pesticide chemicals live a half-life of 300 days. In the body of mankind, these pesticide chemicals live a half-life of 300 days. Dieldrin pesticide in tap water has a maximum limit of 0.001μg/ liter and river water maximum are 0.002μg/ liter.

13.9 Pesticide Treatment Technologies

Pesticide chemicals have been used continuously in botany for the past several decades. They have been used in the prevention of pests, weeds and plant diseases. The use of these pesticides by the agricultural world has opened up new dimensions in the economic world. Along with this, these chemicals have created a crisis in front of his life by contaminating the environment to a great extent. If we talk about our drinking water in the environment, then these chemicals have also contaminated the groundwater with these sources.

The presence of these chemicals has become a concern in human society. In view of the above problems, it is absolutely necessary to remove these chemicals from the source of drinking water or to negligible its effect.

13.9.1 Membrane Technology

In the early 1990s, it was in the form of membrane filtration that began to remove a wide spectrum of contaminants from the growing wastes. The membrane separation process is basis on its pore size and the range from 0.03–10μm (1μm = 0.0001 millimeter). The two class of this technology, material science and membrane fabrication technology as well as increasing demand due to inferior quality have increased the usefulness of this technology (Shin-ichi 1994; Lilane et al. 2019). This technology has emerged as a very useful option due to clean and safe drinking water.

Some of its features are as follows.

(i) It is technically applicable at any ambient temperature without changing the state.
(ii) When used, there is no accumulation of substances in it, which makes it volatile. For example, in the ion-exchange resin process.
(iii) It does not include any chemical additives when removing the membrane. Which proves helpful in enhancing the environment and water quality.
(iv) In technology, this technology is very simple and traditional separation.
(v) These membranes made with the use of polymer chemistry or at low pressure also prove to be very suitable. Like new technology, these membranes or very less foam.
(vi) Also gives very important features like low energy, low cost operation, cleanliness and long life.

13.9.2 Reverse Osmosis

The methodology of this technique is based on high pressure. It is used in wastewater treatment technology. it is a very popular technique throughout the world (Endre 2019; Simon 2019). The contaminated water is passed through an impermeable membrane. By this, almost all inorganic ions, turbidity, bacteria, solids and organic matter present in water can be separated from the water (Haidari et al. 2019).

Advantages

1. Removes contaminants and most soluble chemicals.
2. These technologies work without break-in period.
3. Low flow concentrations possible,
4. In addition to pesticide, it is helpful in removing bacteria and other contaminated particles.
5. Along with this small reverse osmosis system, this technique can be operational simplicity and automation its applications.
6. It has high capital and high cost of starting
7. Along with pollutants, it is also suitable in removing salinity of water.
8. Produces the most waste water (25–50% of feed water)

13.9.2.1 Microfiltration

Microfiltration technique can be used to separate particles and bacteria of size up to 0.04–1.0-micrometer from water. It is available as a filter cartridge in the form of a tubular, disc plate, spiral or hollow fiber. This technique is not applicable to remove the smaller particles that ultrafiltration and nanofiltration but it is effective in eliminating bacteria, colloids, pyroxenes, Suspended Solids with high atomic weight 0.05–0.10 micrometers and used in domestic water recycling systems.

13.9.2.2 Ultrafiltration

The ultrafiltration technique mainly uses this method in the removal of high-molecular-weight compounds of 0.5–0.10 micrometers, colloids, pyroxenes, bacteria and suspended solids by ultra-filtration. An ultrafilter is used as a membrane or filter tubular, disc plate, spiral and hollow fiber.

Advantages

1. The biggest advantage of this technique is that this technique does not require any chemicals.
2. Useful in silt filtration of its cavity
3. Important role in the removal of contaminated particles and microbials of certain size
4. Simple automation and
5. Process and plant compactness

13.9.2.3 Nanofiltration

Nanofiltration technology uses nano filters with holes up to 0.6–5 nanometers. Nanofiltration technology is multifunctional, clean water that separates contaminants from ions, microorganisms, and suspended solids, etc., which is free from these contaminants. In nanofiltration, monovalent ions cannot be separated from the water. Nanofiltration technology is also used to remove membrane alkalinity, hardness.

13.9.3 Ion Exchange Resins

The presence of contaminated water in water through ion exchange resins is the separation of many heavy metals. Along with this, the hardness of water also goes away by this means. This method (Alexandratos 2009) is also used for the separation of dyes in contaminated water.

Contaminated water from various industries is treated according to its nature. Combined contaminated water treatment plants can be set up to treat contaminated water from industrial units installed in industrial areas or clusters. It is also possible to treat contaminated water discharge of two different forms by mixing them together. For example, contaminated water of acidic and alkaline nature can be mixed and neutralized. Similarly, many metallic pollutants are precipitated by mixing them together.

After proper treatment of contaminated water (Deepti et al. 2016; Liang et al. 2018; Irina et al. 2018) they can be recycled under process. It is also possible to be used in plantations etc. as required. Classification of this type resins is as follows.

- Strong acid cation- R-S(=O)$_2$-OH group containing species are strong acid cation.
- Strong base ion- That have negative ions, called anion exchange resins.
- Weak acid cation- H-ions lover species are weak acid cation.
- Weak base ion- These species are more stable than strong base as used for removal of mineral acids, organic acids and other organic materials.

13.9.4 Activated Carbon

Activated carbon is a technique in which pesticides separate pollutants from polluted water, resulting in clean water. Along with the elimination of pesticides from water, this technique is a very effective method in the pesticide manufacturing industry (Atkins 1972; Kobylinski et al. 1984). It is used as a cleaning method in these factories. The carbon adsorption treatment method consists of a prefilter or alum flocculation chamber made of sand when the contaminated water containing these effluents passes through these chambers or these profiles, the carbon has strong adsorption so that it is absorbed. As a result, clean, sterile water is obtained by this mechanism.

It has been found in some researches that the presence of some pesticides such as chlorpyrifos, malathione, dioxanone, dimethoate and propoxur insecticides have been observed in the rinsing water. Thus, this method of adsorption has efficiently absorbed the waste and pollutants arising from the water. Many researchers have used this technique for remove or separate of pesticides. (Dennis and Kobylinski 1983; Nye 1984) these techniques have also proved very useful.

13.9.5 Phytoremediation

This technique is an environmentally friendly technique. In this technique, plants are mainly used to remove pollutants such as pesticides from ground water. In this way, money, time can be avoided with any other water cleaning technique (Nele et al. 2017; Prabakaran et al. 2019). Aquatic vegetation can also be prevented from getting dirty by absorbing pollutants of this type from its source. Coat and Anderson, in their research study and found a reduction of about 45% in the presence of pesticides such as atrazine, metolachlor, and trifluene, indicating that phytoremediation is a very effective emerging technique. But the above aquatic plants recorded the presence of these pollutants up to 2–50%. Phytoremediation techniques have proved very helpful in removing pesticide pollutants.

13.9.6 Bioaugmentation

Bioaugmentation is a technique in which pesticide pollutants are isolated with the help of bacteria-microbes and all the process they have play an important role. These germs convert these dangerous lethal pesticide chemicals into low toxicity products through aerobic and anaerobic processes through metabolic activity and pure water is obtained. Some bacterial strains that are the only nutrient or carbon source of these are degraded (Mariusz et al. 2017). As the carbon monoxide is released during metabolism, it is released during this process with a large amount of carbon monoxide, which causes these reactions to be known as minerals.

Bacteria - micro-organisms in their metabolic process, secretes some enzymes in which these pesticides are consumed as food, which reduces the pollutants present in the environment. They can be easily used as a result of bacteria-microbe found everywhere. They always exist in the environment and serve as nature and maintain life cycle while serving nature (Do et al. 2015).

Microorganisms use this energy to complete this process, from the energy generated by the breakdown of pesticides to the energy used to increase their number or biomass. The breakdown of the bond and the taking of electrons from the contaminants receive energy and more and more new cells are produced.

Now it comes that depending on which cars these pesticides are destroyed by the environment or water source. This type is as follows.

1. Types of bacteria or microbes
2. Pesticide Chemical Type
3. Geological composition and presence of chemicals on contaminated water and water bodies

These factors greatly influence the result of this technique. Overall, it is concluded that this technology or organism used in this technology converts harmful compounds present in water and environment into other such products which are less harmful.

13.9.7 Electrocoagulation

Nowadays electrocoagulation technology is being used on a large scale in wastewater treatment. Among the classical physico-chemical treatment processes, this technique is a reaction based on an advanced electrochemical technique. In this process, water is treated as a medium and is used to remove hazardous pesticide chemicals by electrifying them in various types of anodes and cathodes. These can be in the form of anode and cathode with rods, fluidized bed shells, plates, tubes, balls and wire mesh. In this, metal salts polymer and polyelectrolyte can be used to break the emulsion and suspension (Nuno et al. 2019; Miguel et al. 2019; Rabiatuladawiyah et al. 2019). Polymers which are highly charged used to remove water contamination through pesticides or other such as colloidal solids, soluble inorganic and metals from aqueous media.

13.10 Conclusion

From the above study, it is concluded that insecticide, which is a deadly chemical, is affected by both the fauna and flora. Its bigger source is mainly agricultural where these pesticides are used the most. Some pesticides form as complex with organic compounds and these compounds have carcinogenic properties. If these chemicals sprayed on the surface of plants by spraying methods, during rainy days when the plants are watered, these chemicals dissolve in water, or form colloidal solution with it. In both the states, they come out in the water source and they contaminate it and make it harmful.

Most pesticides or biocides are chlorinated hydrocarbons. These pesticides are non-biodegradable i.e. why their extreme effects are on water bodies and aquatic life. So, it is need to remove them from our water system. Many modern technologies are using to remove them. The bioaugmentation method is the best method for treatment of pesticides contaminants. It is green and very significant method.

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Chapter 14
Opportunities and Challenges in Heavy Metal Removal from Water

Mriganka Sekhar Manna and Chanchal Bhaumik

Abstract Heavy metals such as cadmium, chromium, lead, mercury, arsenic, nickel, zinc, and copper are critical pollutants of freshwater reservoirs due to their toxic, non-biodegradable characteristics and persistent nature. The rapid industrialization is the major cause for the contamination of heavy metals into the water body. Heavy metals are easily absorbed by flora like smaller plants and fauna like fishes of the aquatic system and higher plants also owing to their high solubility in water. The accumulation of heavy metals in the human body is persistent through the food chain.

The existing techniques for the removal of heavy metals include ion-exchange, membrane filtration, adsorption, electrochemical chemical precipitation. The more advanced processes include nanotechnology assisted treatments, membrane adsorption, and advanced oxidation processes. Invariably, each method is burdened with one or other issues and challenges. The issues and challenges of a particular process depend upon multiple factors like the quantity of pollutant, concentration level of pollutant, management of secondary pollutant, global removal facility, the requirement of the limit of concentration in the treated water and cost of treatment. The opportunities for employment of various techniques to remove the hazardous heavy metals from water in general and challenges therein have been enunciated in this chapter.

Keywords Wastewater · Contamination · Heavy metal · Remediation · Conventional technique · Sludge · Global management · Challenge · Advance technique · Cost-effectiveness · Nanomaterial · Bio-adsorbent · Future trend

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14.1 Introduction

The ever increasing industrialization and rising of societal living standards of mankind influence the available water sources. The discharge of heavy metals through the industrial effluent to the aquatic environment has to be controlled. The removal of toxic heavy metals from aqueous solutions has become a challenge for the twenty-first century. Substantial amounts of hazardous heavy metal ions from the development activities in various industries such as chemical manufacturing, mining, metallurgical, and nuclear energy are discharged into the natural water environment. This discharge causes severe intimidation to the water environments (Vilardi et al. 2018; Yin et al. 2018). Owing to the high permeability, hazardous metal ions are accumulated in the cells of the human body through a slow but continuous process. The persistent accumulation of the heavy metals into cells of human and other species causes long-term damage to their body (Wang et al. 2015; Wang et al. 2018).

Heavy metals are likely to be accumulated in living organisms as they are not biodegradable and are highly soluble in water. The persistent accumulation of these obnoxious metal ions in the body of human causes the disease and disorder therein. Therefore, they are to be removed from the industrial effluents before they are discharged into the aquatic environment. Environmental regulations have become stricter in recent time. Hence, the practiced techniques for the removal of heavy metals are required to be revamped for producing a superior standard of treated water in the effluent. The techniques with cost-effectiveness and environmentally benignity are required to treat the water-bearing heavy metals. The increasing awareness and concern about the environment at the beginning of the twenty-first century motivated the research communities to develop alternative technologies for the treatment of water-bearing heavy metals inexpensively. The widely used treatment processes for heavy metal ions from water include ion exchange, distillation, electrodialysis, reverse osmosis, chemical precipitation assisted with coagulation and flocculation (Azimi et al. 2017). The conventional technologies for heavy metals removal from the industrial effluents are not adequate for the stricter regulation imposed by the regulatory authorities. The generation of secondary pollutants i.e. metal bearing sludge almost in every case creates the secondary problem. Globally disposal of this metal bearing sludge is extremely difficult. No single technique can precipitate the heavy metals to low levels of solubility without processing by another technique and using additional reagents. The use of additional steps significantly increases the volume of sludge.

There are conventional techniques (Fu and Wang 2011) which are being used for the removal of heavy metals. Various researchers have worked with the conventional techniques including chemical precipitation (Wang et al. 2005), adsorption (Srivastava et al. 2011; Zamboulis et al. 2011), ion exchange (Motsi et al. 2009; Ostroski et al. 2009), membrane filtration (Ersahin et al. 2012), reverse osmosis (Bódalo-Santoyo et al. 2003), coagulation and flocculation (Zhang et al. 2003), flotation and extraction (Rykowska et al. 2008), irradiation (Batley and Farrar 1978), electrochemical treatment techniques (Walsh and Reade 1994), advanced oxidation processes and bio-adsorption processes (Dave et al. 2010; Kavamura and Esposito 2010). The chemical precipitation technique is widely used by the utilization of the chemical reaction of respective chemicals with target heavy metals to form the precipitates. The chemical reagents are categorized into three classes such as inorganic, organic chelating reagents and organic polymers (Pan et al. 2009).

Lime precipitation is reported as the most effective conventional means for removal of heavy metals with a metal concentration higher than 1000 mg/L (Barakat 2011). The adsorption with new modified adsorbents and membrane filtration are also extensively used to treat these contaminations. On the other hand, photocatalysis is a more recent and promising process to obtain cleaner water but is more expensive in comparison to other processes. Many other techniques can be used for the treatment of heavy metals from wastewater. The choice of the best technique for this purpose depends on factors such as pH, the concentration of metals in the wastewater, the possibility of ultimate performance in comparison with alternative processes, impact on the surrounding area after its employment as well as economic obligations viz. the cost of both investment and operation. Moreover, appropriateness of the application, simplicity of the process, and cost-effectiveness are the salient issues that contribute in the selection of the most appropriate technology for the treatment of heavy metals from industrial wastewater and surface water. Global management of the sludge containing concentrated heavy metals is the most critical challenge to be addressed. Novel nanomaterials having outstanding adsorption capacities, environment friendly performance and serene stability have emerged as a very important advancement in the removal techniques of heavy metal ions (Savage and Diallo 2005). Consequently, the promising nanotechnology with the exploration of very specific properties of nanomaterials has recently emerged for the treatment of wastewater (Lu and Astruc 2018). The cost, efficiency, and toxicity to the eco-system are to be combined to estimate the economic viability of nanotechnology for this purpose.

Another, very advanced process for the capturing of heavy metal ions is involved with the synthesis and use of metal-organic frameworks. The coordination chemistry between various inorganic metals (as precursors) and organic ligands helps in the synthesis of metal-organic frameworks. The inorganic precursors include various transition and heavy metals such as titanium(III), iron(III), copper(II), zirconium(IV), cobalt(II), cadmium(II), aluminium(III), zinc(II) and magnesium(II). On the other hand, various functional groups of organic compounds such as imidazole, *p*-phthalic acid, amines, benzoic acid, pyridine, sulfonates, phosphates, and carboxylates are used as organic ligands for the preparation of metal-organic frameworks (Wu et al. 2018). The capacity of metal-organic frameworks for the adsorption of heavy metals is likely to be higher in comparison to the other adsorbents due to some unique properties of them. The well-defined and diversified structures of metal-organic frameworks provide the high porosity, large surface area, the required characteristics of a novel adsorbent (Ricco et al. 2015; Yang and Yin 2017).

Recently, biological treatments are considered as an environmentally benign technology for the remediation of hazardous heavy metals. Extracellular polysaccharides produced during microalgal growth have emerged as the biological adsorbents for toxic components. The polysaccharides containing various positive and negative functional groups that facilitate the binding of metal cations or anionic metal radicals present in the wastewater based on the pH level of it. E.S. Priya et al. reported that the aquatic macrophytes provide very interesting results in the field of phytoremediation (Sanmuga Priya and Senthamil Selvan 2017). They have great potential for the accumulation of hazardous heavy metals inside their cellular structures up to 100,000 times greater than the amount present in the general water bodies. So, they are used for the removal of heavy metals from a variety of sources (Mishra and Tripathi 2008). Water hyacinth is one of the most commonly used macrophytes because of its fast growth rate and large uptake of nutrients and heavy metals (Rai 2009). The dried roots and the whole plant are used as the bio-adsorbent for removal of heavy metals. Other plant tissues were used by various researchers for the removal of heavy metals (Jadia and Fulekar 2009). The principles of various conventional and comparatively more advanced techniques are discussed in this chapter. Several opportunities and challenges for application of these techniques are elaborated.

14.2 The Available Techniques

Wastewater effluents from various industries, such as metal-plating processes, mining operations, tanneries, pulp, and paper industries are contaminated by heavy metals. The prevalent metals that are discharged to the aquatic environment from these activities include mercury, nickel, cadmium, iron, chromium, and lead. The existing physicochemical methods like various types of filtration by membranes, chemical precipitation, ion exchange, adsorption, and electrochemical processes are presently used for the heavy metals remediation. Each of the methods is limited by one or more drawbacks such as the production of a large amount of sludge, difficulty in removal of sludge, use of an excessive quantity of hazardous chemicals and technical constraints. Many of the methods are widely used in large scale for the decades with certain merits and demerits and termed as the conventional methods. Others methods which are employed in the developed countries and still are required to be researched for the cost-effectiveness and better yield are termed as the advanced techniques. The basic principle, procedural details, and applicability to a particular type of heavy metal contamination and cost-effectiveness of both the conventional and advanced techniques are discussed in the following sub-sections and depicted in Fig. 14.1.

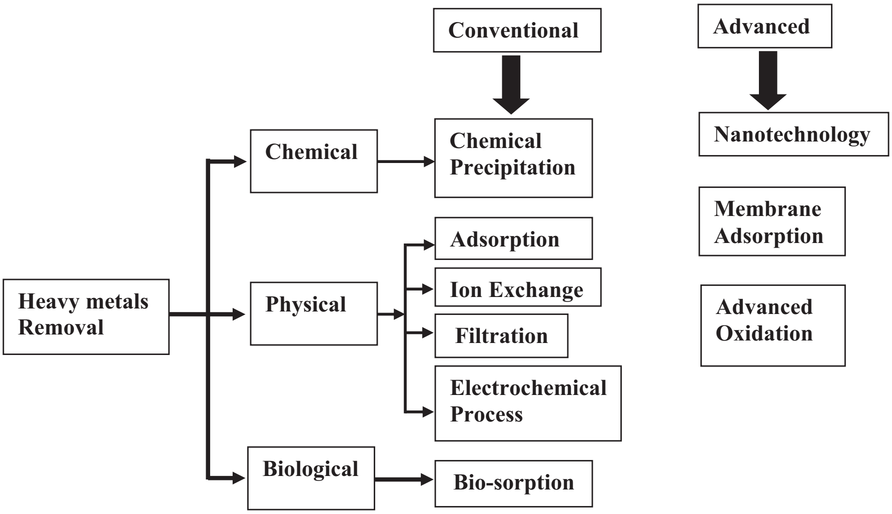

Fig. 14.1 Various conventional and comparatively advanced processes for the removal of heavy metals from contaminated water

14.2.1 The Conventional Techniques

The conventional techniques for the removal of heavy metals from water are the techniques that have been widely used for the past several decades. The techniques are characterized by low cost but less efficiency and generation of a larger amount of secondary pollutants. The global management of secondary pollutant is an added problem. The conventional techniques are well experimented and limited by the further improvement. Some of the conventional methods are elaborated in the following sub-sections:

14.2.1.1 Chemical Precipitation

Chemical precipitation is a chemical process by which heavy metal ions soluble in surface water or industrial wastewater are separated. The undesired soluble ions of heavy metals present in water are converted to insoluble ions in the aqueous medium, settled down as precipitation and discarded. Therefore, the heavy metal ions are coagulated to tiny solid particles. The ionic state of the heavy metal ions is changed by the chemical reaction with the help of appropriate chemicals. The solubility of heavy metal ions is reduced by the addition of counter-ions supplied by the chemicals. The technique involves the shifting of the ionic equilibrium to produce insoluble precipitates before sedimentation. It is mostly used for the removal of heavy metals as cations. It is mostly applicable to the wastewater that contains also phosphorous compounds, hardness and organic hazards such as aromatic amines and phenols (Atlow et al. 1984). The conversion to insoluble ions is always followed by one or more unit operations to separate the coagulated ions into solids. The unit operation such as coagulation, flocculation, sedimentation, and filtration are quite often used to assist the chemical precipitation. Sometimes the metal ions are reduced by the use of chemicals so that they can be transformed to the ionic state for precipitation (Wang et al. 2005).

The heavy metals are discharged in large quantity in the wastewater from the metal plating industry. The soluble salts of various heavy metals like cadmium, chromium, copper, nickel, lead, zinc and others are present in the wastewater in higher concentrations. Chemical precipitation technique is the most inexpensive for removal of high concentration of heavy metals ions and therefore widely used for this purpose. The alternative processes for high concentrated heavy metals removal are ion exchange, electro-precipitation and reverse osmosis. But the capital cost is higher for all three alternatives. Operational energy cost is very high for both the electro-precipitation and reverse osmosis. But, advantages of theses alternative processes remain in their capacity to be better adapted to metal recovery and recycling of metals. On the other hand, chemical precipitation is simple in operation and the investment cost is low. The major issues of chemical precipitation are its operating costs arising from a large expense on a high amount of chemical utilization and the disposal cost of the precipitated sludge.

The chemicals used for precipitation are hydroxides, sulfide and carbonate salts of sodium and potassium. The heavy metals to be removed must be either reduced or oxidized to a state of valence that can then be insoluble and precipitated accordingly. The precipitation of tiny insoluble ions is facilitated by coagulation and flocculation. The concentration of flocculent, coagulant and pH of water have major influence on the precipitation. Ferric chloride has a strong capacity to form larger flocs leading to the removal of metals. Contrary, polyaluminium chloride is generally used as an agent for the neutralization of charge of ions (Zhang et al. 2003).

14.2.1.2 Membrane Filtration

Membrane filtration is considered as another conventional technique to remove inorganic heavy metals from water streams. The membrane filtration used for simultaneous removal of suspended solids, organic compounds along with heavy metals. Based on the working principle and size of the membrane pores, membrane filtration is classified as ultrafiltration, nanofiltration and reverse osmosis. Each of the types of filtration process is used depending upon the characteristics of wastewater containing heavy metals. The various membrane filtration processes are classified with regard to sizes of both the pores of the membrane and that of the particles of the solute. The pore size of the ultrafiltration membrane is in the range of 5–20 nm and it is used for the separation of coagulated heavy metals ions from water solution. The particles in the size range of 1000–100,000 Da can be separated by the ultrafiltration technique (Vigneswaran et al. 2004). Various ultrafiltration membranes are also used for the removal of metals when their concentrations remain in the range of 10–112 ppm. The operational pressure for ultrafiltration ranges from 2 to 5 bar. The advantages of ultrafiltration include the requirement of a lower pumping cost due to lower resistance to water permeation and a smaller footprint as the packing density of membrane fibers is high.

The ultrafiltration technique has been enhanced by the employment of polymers in the fabrication of membrane materials. Polymer-supported ultrafiltration technique uses polymeric ligands that are water-soluble. The binding of metal ions to membrane materials is facilitated by the formation of macromolecular complexes (Rether and Schuster 2003). The requirement of energy for the ultrafiltration becomes lower by the use of polymer-supported ultrafiltration. The reaction kinetic becomes faster and metal selectivity increases. The ultrafiltration assisted with water-soluble metal-binding polymers is a hybrid approach with higher selectivity for the recovery of heavy metals from the water. The other modification of ultrafiltration technique with the same advantages as that in polymer-supported ultrafiltration is the complexation-ultrafiltration. In this approach, the heavy metal cations are first complexed with a macro-ligand for enlargement of the metal ions to a size which is larger than the size of the membrane pores (Petrov and Nenov 2004; Trivunac and Stevanovic 2006). The polymeric ligands are water-soluble and make powerful complex to remove trace amount of heavy metals from surface water and industrial wastewater using the membrane processes. Nanofiltration is useful for the separation of the smaller particle size (nano size) of heavy metals ions. The pressure drop is larger compared to ultrafiltration and hence, the cost of separation is more. The membrane fouling problem is bigger in nanofiltration.

Semi-permeable membranes are used in reverse osmosis. The heavy metal ions are retained and the water is passed through the semi-permeable membrane with the application of high pressure. The particles of the heavy metals ions that are even smaller than the size of nano-levels are separated in reverse osmosis. The membrane is semi-permeable that permits the passage of water but not that of metal ions. The technique is used to separate different kinds of ions, molecules, even the microorganism like bacteria along with heavy metal ions from water solution. The principle of reverse osmosis is like diffusion operation and the separation efficiency depends upon the variables such as the concentration of metal ions, trans-membrane pressure, and flux of water.

14.2.1.3 Ion-Exchange

The cations and anions of heavy metals present in the water can be removed by the technique of ion exchange. The exchangers are made of a polymeric substance by cross-linking the chains of one or more monomers. The polymeric chains are so entangled that they form a solid matrix with the attachment of various functional groups by covalent bonds. They consist of a cross-linked polymer matrix (resin) in which various charged functional groups are attached by covalent bonds (C. Sherrington 1998). The exchanger resins are so hard that they are insoluble not only in water but also in various organic solvents. The exchangers with functional groups containing cations and anions as counter-ions are known as cation exchangers and anion exchangers, respectively. One of the widely used polymer matrices is polystyrene where 3–8% of divinylbenzene is incorporated with polymer matrix of polystyrene to get the strong structural stability (Kunin et al. 1962). The incorporation of more proportion (12–16%) of divinylbenzene in the polystyrene matrix provides a more stable and harder grade of ion-exchange resin that can be employed for remediation of contaminants present even in an adverse environment. They are capable to resist their degradation against the strongest oxidizing agents like ozone and chlorine. The physical stability of highly cross-linked ion exchangers is also higher. The ion-exchangers for the separation of anions form cations are fabricated with a particle size of 20–50 mesh. The smaller particles of resins (200–400 mesh) are advantageous in the affinity-based separation of heavy metal ions. The particle size of 50–100 mesh is adequate while separation by ion-exchange is facilitated with complexation of target ions by suitable complexing agents.

Ion exchange resins are classified as acidic, basic and neutral considering the attached functional groups to the polymer matrix. The various functional groups are sulphonate for strongly acidic, carboxylate for weakly acidic, quaternary ammonium for strongly basic and secondary and tertiary amines for weakly basic ion exchangers. The acidic exchangers easily dissociate over a wide range of pH and consequently, they are the best type of exchangers. The weak acidic exchangers have more capacity when the pH of water is in the alkaline region. Some amphoteric exchangers can work as both cationic and anionic exchangers depending upon the pH of the water. The amphoteric exchangers are also called as zwitterionic ion exchangers (Nesterenko and Haddad 2000). The amino-carboxylic exchangers and the carboxylic cation exchanger with a carboxylic functional group have been recently used for separation of nickel(II) from the mixture of nickel(II) and manganese(II) in aqueous solution (Kononowa et al. 2000). The heavy metal ions in the water and wastewater are separated based on the difference in their affinity to the ion exchange resin. Moreover, types of the ionic species attached to the polymeric resin decide the effectiveness of the ion exchange technique (Fritz 2005). The affinity series is the decisive factor in the formation of the types of ion-exchangers and are considered for the selection of ion exchangers for a particular heavy metal ion to be separated.

14.2.1.4 Adsorption

Adsorption is a solid-liquid or a solid-gas interaction with the objective of separation of target component from either the liquid or gas phase. The target solute present in either liquid or gas phase is adsorbed to the solid surface of the adsorbent and separated from the liquid or gas stream, respectively. Adsorption is a surface phenomenon which is limited to distance of one molecule deep on the adsorbent surface. The extent of adsorption depends upon the nature of both adsorbent and the target molecule known as the adsorbate. It also depends on the available surface. Hence, the size of the adsorbent particles is important. The smaller is the size of adsorbent, the more is the available surface area and hence, the higher rate of adsorption. Activated charcoal is the most widely used chemical adsorbent. The adsorbents of the nanoparticle size of different inorganic substances are synthesized and used as the modified adsorbent. On the other hand, some adsorbents are synthesized from organic bio-sources. Adsorption is a reversible process and the temperature has a significant role in the equilibrium. The solute molecules are adsorbed on the surface of the adsorbent and are oriented in a definite manner. The de-sorption technique is used to remove the solute from the surface of the adsorbent so that adsorbent can be reused and solute can be recovered. Adsorbents may be classified as inorganic or bio-adsorbent based on their sources.

14.2.1.4.1 Inorganic Adsorbent

Zeolites are the most effective and widely used inorganic adsorbents and ion-exchange media for removal of heavy metal ions. Commercially known NaP1 zeolites (Na_6Al_6 $Si_{10}O_{32}$, $12H_2O$) contains enormous sites of Na^+ to exchange various cations of water. The zeolites are synthesized inexpensively by the process of hydrothermal activation. The fly ash containing silicon and aluminum is mixed with the caustic soda solution of 1–2 M (Moreno et al. 2001). Alvarez-Ayuso et al. used synthesized NaP1 zeolites to remove various heavy metals like copper(II), chromium(III), zinc(II), nickel(II) and cadmium(II) from wastewater of electroplating industries (Álvarez-Ayuso et al. 2003). The single layers of zeolites are assembled on the supports of mesoporous characteristic to fabricate the effective inorganic adsorbent, NaP1 (Yantasee et al. 2003). The support ceramics are prepared in the templated synthesis using the surfactants. The nanoporous ceramic oxides are formed. The adsorbent so formed is characterized by the large active surface ($1000\ m^2.g^{-1}$) and numerous adsorption sites. The sites are functionalized accordingly to enhance selectivity to the heavy metals that are targeted. Savage and Diallo reported that the diphenyl dithiocarbamate is another important inorganic adsorbent for capturing the heavy metals (Savage and Diallo 2005). It is more efficient and provides higher capacity in comparison with widely used activated carbon. It is more applicable to the polluted water contaminated by multiple heavy metals (Savage and Diallo 2005). The efficacy of diphenyl dithiocarbamate as an adsorbent for the treatment of four common heavy metals in different operational conditions is summarized in Table 14.1.

Several research works are going on for the modification of inorganic adsorbents. The modification is based on the inclusion of magnetic property, the inclusion of polymeric property, size and shape of the adsorbent particles. The sizes of the particles are maintained in the nanoscale so that the available surface area for adsorption is very high. The examples of such modified nano-adsorbents are magnetic multi-wall carbon nanotubes, magnetic zeolite-polymer composite, graphene nanosheets, nanocrystalline titanium dioxide, and others. The removal efficiencies for various heavy metals by using these modified nano-adsorbents at various operational conditions are depicted in Table 14.2.

Table 14.1 The metal removal efficiency of diphenyl dithiocarbamate (Abu-El-Halawa and Zabin 2017)

Metal	Initial concentration (ppm)	pH	Remaining concentration (ppm)	Removal efficiency (%)
Cadmium	4	3 5.30 7.30	4.00 0.531 1.372	0.00 86.72 65.70
Lead	5	3.0 5.30 7.30	0.559 2.703 2.441	88.82 45.94 51.18
Zinc	5	3.0 5.30 7.30	1.240 2.493 1.477	75.20 50.14 70.46
Copper	5	3.0 5.30 7.30	0.100 0.229 0.079	98.00 95.42 98.42

Table 14.2 The efficiency of various nano-adsorbents for the removal of heavy metals in wastewater (Barakat 2011)

Nano-adsorbents	Heavy metals	Experimental conditions			Removal (%)
		pH	Contact time (min.)	Adsorbent dose (g/L)	
Magnetic multi-wall carbon nanotubes	Chromium(VI)	3	600	0.1	100
Magnetic zeolite-polymer composite	Vanadium	4–5	1440	0.15	73
ZIF-8 nanoparticles	Arsenic (III)	7	240–420	0.20, 0.05	60.03
Zinc sulfide nanocrystals	Mercury (II)	1–6	510	–	99.99
Modified magnetite nanocomposite	Copper (II)	6.5	15	0.19	99
Graphene nanosheets/d-MnO_2	Nickel (II)	5.5	20	5	77.04
Nanocrystalline titanium dioxide	Arsenic (III)	9.5	10	0.2	98
	Arsenic (III)	7	10	1	99.9
Magnetic nano-particles coated zeolite	Arsenic (III)	2.5	15	0.5	95.6
Zeolite materials obtained from fly ash	Lead(II)	6–7.5	90	6	>80
Magnetic nano-adsorbent	Lead(II)	6	10	20	80
Magnetic nano-adsorbent	Zinc(II)	5.5	90	2.5	95

14.2.1.4.2 Bio-adsorbent

Both the dead and live cells of organisms are employed as bio-adsorbents to remove heavy metals from wastewater. The bio-sorbents are loaded with the positive and negative functional groups that facilitate the binding of heavy metal ions in different electronic states. The various functional groups are hydroxyl, carboxyl, amine, sulfate and phosphate ions. The currently practiced technologies for the remediation heavy metals are precipitation, adsorption, reduction, coagulation, and membrane filtration. However, they have several limitations. They are not applicable very well in treating heavy metals with high concentrations with the exception of chemical precipitation. The bio-sorbents which are wastes in the agricultural sector and various industries are used at present for removal of heavy metals. Regeneration of metal-treated bio-adsorbent and reuse of it is an important matter for the cost-effectiveness of this technique. Desorption of metals from adsorbed biomaterials is usually accomplished by eluting with different stripping agents such as water, acid, and base in different concentrations.

Agricultural wastes, especially algal biomass and activated carbon produced from such waste are used as low-cost adsorbents (Babel and Kurniawan 2003; Ahalya et al. 2005; Vijayaraghavan et al. 2005). Various functional groups such as carboxylic, sulfonic and hydroxyl groups in the extracellular polysaccharides produced from marine algae is observed to be responsible for impressive metal uptake (McKay et al. 1999; Davis et al. 2003). Javadian et al. proposed wet algal biomass as bio-adsorbent in the separation of metal ions from water (Javadian et al. 2013). On the other hand, S. Zakhama et al. used dried algal biomass for this purpose in batch and continuous reactors (Zakhama et al. 2011). El-Sikaily et al. used algal biomass to remove hexavalent chromium from wastewater (El-Sikaily et al. 2011). Soltmann et al. studied the biosorption of heavy metals with immobilized or encapsulated algal biomass, macro (*Fucus*) and microalgae (*Spirulina* etc.) in the three different silica sols for the removal of copper, nickel, chromium, and lead in drinking water (Soltmann et al. 2010). Daniel et al. reported the bio-adsorption of heavy metals (cadmium and copper) from industrial wastewater by using algal and bacterial biomass (Daniel et al. 2005). The application of live algae and bacteria for the adsorption purpose were found more promising than the immobilization of biomass.

14.2.1.5 Electrochemical Process

Two types of electrochemical processes are generally used in the remediation of heavy metals. In the electroplating process, the soluble heavy metal ions are electroplated on the electrode and thereby separated from the water. The electric potential is applied across the electrodes. On the other hand, an electro-coagulation is an electrochemical technique for remediation of metal ions that are suspended or made suspended by altering the pH of the solutions. An electrical current is passed through the solution and the suspended ions are coagulated so that they can be easily precipitated and removed. The electro-coagulation process is effective for the removal of both the suspended and dissolved heavy metals. The electrochemical technique is currently the most effective process for treating wastewater from metal extraction process industries containing a high concentration of metal ions. The pH of water solution and the current density passing through the water are two important factors. Electrochemical process is considered as a potential technique for its versatility and environmental benignity.

The heavy metal cations are neutralized with ions of negative electrical charge passed through the water solution. As soon as the cations are neutralized in electrocoagulation, they become destabilized and precipitate down. The electrochemical technique is simple, fast, very easy to operate and environmentally benign. The treated water is potable, completely free from heavy metal ions. The amount of sludge generated is very less as no precipitating agent or chemical is added. There is a very minimum chance of secondary contamination of treated water as nothing is added to the water except the electrical current in this technique. Various researchers have reported that the electro-coagulation technique can successfully remove the heavy metals as well as other soluble ionic species (Rincón and Motta 2014; Nouri et al. 2010).

14.2.1.6 Electrodialysis

Electrodialysis technique is an extraction process of heavy metals assisted with electrochemical activity. This technique is considered as a potential method to separate metals from fly ashes. The variables of this process are type and concentration of electrolytes, pH of water, the temperature of operation, and the time of the process. The remediation of heavy metals from contaminated water stream can be achieved with high current efficiencies and reasonable stack resistance (Gering and Scamehorn 1988). Electrodialysis is a combination of membrane separation and electrical potential assisted process in which ionized heavy metal ions in the aqueous solution are transported through an ion-exchange membrane. The driving force for the transportation of metal ions is an electric potential. The thin polymeric membranes with both the anionic or cationic characteristics are used. Water containing metal ions passes through a stack of cation exchange and anion exchange membranes placed in the electrodialysis cell. The anions and the cations travel toward the anode and the cathode, respectively while passing through both types of ion-exchange membranes (Chen 2004). Tzanetakis et al. reported the electrodialysis of two contaminants such as cobalt and nickel (Tzanetakis et al. 2003). Two cation-exchange membranes such as perfluorosulfonic membrane (Nafion 117) and sulfonated polyvinyl difluoride membrane are extensively employed for the separation of heavy metals from surface water and wastewater.

14.2.2 Advanced Techniques

The advanced techniques for the remediation of metal ions from water are referred to the comparatively new processes. The processes are potential but much improvement is required to be efficient concerning cost-effectiveness and efficacy. They are not extensively used for heavy metal removals. Such techniques are discussed in the following sub-sections.

14.2.2.1 Nanotechnology Assisted Treatments

The prospect for the applications of novel-nanomaterials for the removal of heavy metal ions is current research topic to have more efficient practical applications. The novel-nanomaterials with large specific surface area, much more surface-active sites due to the presence of various functional groups, have an excellent capacity for removal of heavy metal ions. They have two unique properties that make them particularly attractive for the purpose (Savage and Diallo 2005). Firstly, they have a much larger surface area per unit mass. Secondly, they are functionalized with various negative and positive functional groups to increase their affinity towards a target heavy metal ion. The research community is exploiting the unique properties of nanoparticles to provide high capacity and selectivity for metal cations and anions. Nanomaterials for heavy metal removal are categorized as inorganic and organic nature. Qi et al. studied the efficiency of chitosan nanoparticles in the size range of 40–100 nm prepared by ionic gelation of chitosan and tripolyphosphate (Qi and Xu 2004). Inorganic nanomaterials are composed of an inorganic core surrounded by small organic or inorganic molecules and polymers. Moreover, magnetic nanomaterials containing magnetic core have the great advantage of easy separation by the use of a magnetic field. Alternatively, the agricultural wastes such as bagasse, rice husk, the shell of the coconut and peanut and mycelial microorganisms such as *Dictyophora indusiata and Bacillus*, fly ash, clay and mineral slag like coal are reported for the synthesis of the nano-organic adsorbents. The bio-material based nano-adsorbent is preferable due to non-toxicity, economical viability and environmental compatibility. The carbon-based nanomaterials like graphene and carbon nanotubes have the limitation for their application due to the high cost for their synthesis. Therefore, the conversion of agricultural waste to carbon-based nanomaterials for the removal of heavy metals is becoming a promising alternative nano adsorbent to activated carbon. Both the agricultural waste-based nanomaterial such as cellulose and chitosan-based nanomaterial offer enormous opportunities for the remediation of heavy metals from water.

14.2.2.2 Advanced Oxidation Process

The inorganic nano-catalysts like semiconductors and metal oxides have gained considerable attention in the remediation of contaminants from wastewater. Nanosize photocatalysts (Dutta et al. 2014) electrocatalysts (Dutta et al. 2014) and Fenton reagents as catalysts (Kurian and Nair 2015) are being used in practical purposes in the developed country for removal of heavy metals through their oxidation (Ma et al. 2015). In a developing country, the advanced oxidation process ate yet to apply in the industrial level as removal of pollutants by this method is expensive. The cost of semiconductor materials and also the cost of energy for excitation of the catalytic materials for the generation of oxidizing species are very high. In recent years, inexpensive solar energy is used for the excitation of the photocatalysts. Although the installation cost for solar energy conversion for the purpose is substantially high. This photocatalytic process has the ability for rapid and efficient breakdown of heavy metal compounds. The interface between catalyst and electrolyte is irradiated by the light (solar) energy greater than that of the bandgap of the semiconductor. The electron-hole pairs (e/h+) are generated in the conduction and the valence band of the semiconductor or photocatalyst, respectively (Herrmann 1999). These charge carriers (electrons and holes) migrate to the surface of the semiconductor and oxidize the compounds of heavy metals in the solution having suitable redox potential. The semiconductors or photocatalysts such as titanium dioxide, zinc oxide, cerium dioxide, cadmium sulfide and zinc sulfide have been extensively explored for the research in this direction. The titanium dioxide has emerged as the best photocatalysts with maximum quantum yields. Zhang et al. have reported the principle and mechanism of photocatalytic reaction using titanium dioxide as catalyst (Zhang and Itoh 2006). The hydroxyl ions (-OH) are used to trap the holes and leads to the generation of strong oxidizing hydroxyl radicals. In contrast, adsorbed oxygen species are likely to trap electrons and leads to the generation of superoxide species (O^{-2}). The superoxide species are very reactive, but they are unstable.

14.2.2.3 Membrane Adsorption

The membrane adsorption technique is the integrated process of two separation techniques such as membrane filtration and adsorption with the synergistic effects. Membrane adsorption technology was developed in the mid-1980s (Avramescu et al. 2003; Avramescu et al. 2008). The polymeric membrane is applied for the adsorption of hazardous pollutants like heavy metal ions. Membranes are used for the dual purposes of membrane filtration and adsorption of contaminants on the active sites incorporated on the surface of the membrane. This technique can be applied for the very effective removal of both the metal cations and anionic species like phosphates and nitrates. The novel nanoparticles are incorporated in the membrane to boost the effectiveness of the membrane filtration. The functional groups on the surface of the nanoparticle adsorbents facilitate in the adsorption of heavy metal cations. The pH of water solution is a key variable for the process efficiency. The solubility of the metal ions in water solution is decisive by the pH. The pH maintains the concentration of the counter-ions on the surface of the adsorbent. Moreover, the extent of ionization of target solute (heavy metals) in the aqueous solution is also maintained by the pH level of the aqueous solution. The adsorbent with functional groups is attached to the surface of the pores of the polymeric membrane. The target heavy metals ions are selectively adsorbed to the appropriate functional groups. The heavy metal ions are bound to the binding sites of adsorbent and thereby are removed from the water stream. The rate of adsorption is substantially high as a very short distance (a distance of a molecule) between the solutes and binding sites of the membrane adsorbents is pertinent for the adsorption process (Zheng et al. 2015).

14.3 Challenges

The remediation of heavy metals is a challenge from the implementation of mainly four considerations such as efficiency, recyclability, environmental benignity and cost (Lu and Astruc 2018). The cost of the treatment of the effluent water containing heavy metals is very expensive for the smaller throughput. The benefits of the regeneration of adsorbent by desorption, recovery of catalyst and recycling of the streams are achieved in lesser amount for smaller installation and the treatment process is not economically viable (Barakat 2011). The existing treatment strategies need costly chemicals. The cost of unit operations for the treatment processes is high. A substantial amount of supervision and maintenance are involved in the existing techniques for heavy metals remediation. The processes like chemical precipitation, electrochemical coagulation have more capacity, are inexpensive but generate a higher amount of sludge. Management of sludge containing heavy metals is very much likely to be unsolvable. On the other hand, processes like electroplating and electro-dialysis produce lower sludge, but the consumption of electricity is higher. Membrane filtration has the drawbacks of membrane fouling and lower flux.

The interaction between metal ions and active sites of biomass is essential for the implementation of adsorption techniques. The use of ion-exchange resins is both effective and convenient. But, it is too expensive to be used by developing countries. On the other hand, reverse osmosis employs tiny organics to generate tri-halomethane during disinfection of water using chlorine. The Environmental Protection Agency strictly confines the allowable limit of compounds like tri-halomethane in drinking water due to possible chronic exposure that causes cancer.

The use of synthetic coagulants that are used for removal of heavy metals is also restricted. The tri-halomethane seriously leads to several issues concerned with the central nervous system of human beings. The application of nanomaterials for the removal of heavy metals from water has certain merits and demerits. The high efficiency is one of the merits, and high cost, potential health risk and generation of a secondary pollutant are some of the demerits. Hence, the search for innovative and highly efficient nanomaterials with lower cost and lesser health hazards is important (Lu and Astruc 2018). Even the novel nanomaterials still face various challenges in their use for separation of heavy metals from contaminated wastewater. The nano-size of novel-nanomaterials is very prone to be clumped leading to the fouling and/or blocking of the membrane in the real applications. The blocking reduces the adsorption capacity very rapidly. Moreover, the nanoparticles may not be used in a packed column as it creates high pressure due to their nano-level sizes. Therefore, they are either implanted in or layered on the surface of support materials. Then the advantages of the nanoparticles are largely reduced. The characteristics of the surface of the promising nanomaterials very often diminish with time and nanomaterial compounds sometimes easily oxidized with the exposure of air and/or water. The production of nanomaterials in industrial scale is limited as they are unstable and proper storage is both difficult and expensive. Therefore, it is necessary to develop in each of the aspects like capacity, efficiency, selectivity, and stability of nanomaterials to separate heavy metal ions from water even under complex environment. It can be accomplished through the optimization of the surface properties and subsequent geometric arrangements of nanoparticles through compatible synthesis scheme.

The desorption techniques are to be more efficient for the recycling of bioadsorbents to achieve cost-effectiveness. The advanced oxidation process is expensive due to the high cost of photocatalyst and irradiation. The challenge for the application of membrane adsorption is to develop a mathematical model for the optimization of the parameters concerning both filtration and adsorption processes (Table 14.3).

Table 14.3 The merits and demerits of various techniques used for the removal of heavy metals from water

Technique	Merit	Demerit
Chemical precipitation (Assisted with coagulation and flocculation)	Low capital cost, Simple operation	Sludge generation is high, extra cost is required for sludge disposal, chemical requirement is high, large amount of sludge management globally is difficult
Ion-exchange	Generation of no sludge, Less time requirement	High capital cost, not all heavy metals can be removed
Membrane filtration	Requirement of footprint is less, generation of no sludge	Membrane fouling, Lower flux at a later time, Pumping cost is high
Adsorption	Cost-effective, Quicker process	Regeneration of adsorbent is difficult, management of secondary pollutant is difficult, Desorption agent is required
Electrochemical process	Effective for removal of very trace amount of heavy metals	The cost of electric energy is high
Electrodialysis	Both anions and cations are simultaneously removed	Energy cost and installation cost is high
Advanced oxidation process	Otherwise very difficult unionized metal compounds can be removed	Costs of photocatalyst and irradiation energy are high, Installation cost is high
Nanotechnology assisted treatments	Very fast process, Capacity is high, Scope of flexibility and selectivity is high	Generation of secondary pollutants, synthesis process requires hazardous chemicals,
Membrane adsorption	The synergistic effect of membrane filtration and adsorption is available	Not much developed, Optimization of various properties are required

14.4 Conclusions

The existing treatment processes of wastewater to eliminate hazardous heavy metals are not substantially potential. The generation of sludge for chemical precipitation, membrane fouling for membrane filtration, consumption of high electricity for both the electrochemical and the electrodialysis, lack of adequate desorption agent and/or technique in case of adsorption are among the problems of conventional processes. No unique method is available for the remediation of the heavy metals in solo step as metals are in different ionic states. In the present stricter environmental obligation, green methods for the preparation of novel-nanomaterials must be explored at length. The nanomaterials have broad application prospects for the separation of heavy metals from aqueous solution. The design of integrated treatment processes for the removal of the heavy metals along with other pollutants will be practicable in principle. Several recently developed novel adsorbents such as nanosheets of porous boron nitride, porous graphene, metal organic framework and carbon nanotubes are to be developed for improving the selectivity, stability, capacity, and regenerability of these adsorbents. The membrane adsorption technique may be useful with the solution of the optimization problem.

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Chapter 15
Modification of Bagasse for Heavy Metal Removal Form Water

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Abstract As the population enlarges, the pressure on the waters of the globe is continually increasing. In a way, human activities embrace inland waters by reducing their quality. In industrial wastewater, heavy metals are regularly differentiated, causing many poisoning effects to water quality, human health, and ecological biodiversity. The treatment of wastewater is a highly challenging issue in a developing country. However; the discharge of agricultural wastes is causing an impact on the environmental, which encourage the researchers to use them as biosorbent in discharge distinctive types of contaminants from waste wastewater. A consultant example of these adsorbents is the sugar cane bagasse or bagasse. Bagasse is the dry tender fibrous residue that stays as a regularly occurring agricultural by-product after sugarcane stems are beaten to put off their juice. The last fibrous residue includes cellulose, hemicellulose, and lignin. The metal adsorption affinity of bagasse in aqueous solution can be associated with carboxyl features. There are many treatments used to modify the adsorption capacity of bagasse by amine, acid, and base to target a definite metal removal.

Keywords Water pollution · Heavy metals · Sugar cane bagasse · Adsorption capability · Carboxyl functions · Hydroxyl groups · Ethylenediaminetetra acetic acid · Succinic acid · Epoxidation reaction · Amination reaction

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15.1 Introduction

Due to the fast industrialization, water pollution by heavy metals has been a significant impact on humans and other organisms (Gupta and Suhas 2009). In industrial wastewaters, chromium, cadmium, zinc, copper, iron, nickel, and lead metal cations are often identified, posing an apparent to water feature, living organisms, and ecosystems (Huidong et al. 2008). At definite concentrations heavy metal ions are not processed in live organisms, resulting in many diseases (Rocha et al. 2015; Pan et al. 2016). They are expected to be having a broad effect on the nerves system, liver, and bones, also they impede with the functions of the different enzyme (Garg et al. 2008; Nagh and Hanafiah 2008). Because of this enhanced risk to environmental pollution, strict domestic and international regulations have been established to generate more study attempts in this region, particularly in finding better and more effective techniques for treating wastewater containing heavy metals (Kadirvelu et al. 2008).

To reduce their influence on the environment, several techniques have been screened for removal of heavy metals from industrial effluents. These techniques include chemical precipitation, exchange of ions, extraction of solvents, inverse osmosis, co-precipitation and adsorption (Tiravanti et al. 1997; Dahbi et al. 1999; Rao et al. 2002).

The adsorption technique was regarded as a strong instrument for heavy metal separation and enrichment (He et al. 2008; Ahmed 2008). The greatest obstacle in the sectors applying this method is the elevated price of adsorbents currently accessible for business use. The cost of the process can be lowered if the adsorbent is cheap and readily accessible.

Cellulosic agricultural waste is a wealthy source of possibly metal-sorbing biomass. These materials may be a cheap replacement for heavy metal loaded wastewater treatment. They are commonly accessible, endless, and cheap material that displays important for target the metal cations. Agricultural biomass consists primarily of lignin, cellulose, hemicellulose and certain proteins (Nagh and Hanafiah 2008; Mohan and Pittman 2006).

One of the most significant agricultural-based sectors is the sugar sector. The sugar cane bagasse (SCB) or bagasse is the dry mushy fibrous residue that stays as a prevalent agricultural by-product after juice extraction. The remaining fibrous residue includes cellulose (45%), hemicellulose (28%) and lignin (18%).

It is either used as a biofuel for heat, power and electricity production, as a raw material for tissue and paper production (Rowell and Keany 1991; Sun et al. 2003). It is blended with tapioca starch and glycerol to generate composite materials; while a mixture of gelatin, starch, and agar generates tableware products; it is capable of partly replacing cement and acting as a pozzolanic additive in concrete manufacturing (Loha et al. 2013).

15.2 Heavy Metal Removal from Wastewater Using Sugar Cane Bagasse

Bioadsorbent based on cellulose has received great attention as one of the promising adsorbents for high surface area and ability to modify the surface, fast adsorption rate and resistance to swelling (Shi et al. 2011; Zhou et al. 2007). Sugarcane bagasse has an abundance of carboxyl features, can capture metal cations heavily in wastewater, allowing sugarcane bagasse to be an economically feasible biosorbent (Aksu and Isoglu 2005). Usually drying the sugarcane bagasse at 30 °C for 1 h is sufficient to low humidity in sugarcane bagasse after the store had withdrawn the sugarcane juice for sale (Liu et al. 2012). However, greater temperatures generally improve the adsorption capacity of metal ions by enhancing the surface area and kinetic energy of biosorbent, but can harm the physical composition of it (Park et al. 2010). Based on the outcomes achieved, the dried biosorbents at 120 and 150 °C was more effective than at other temperatures. The particle size of bisorbents was a fetal factor whereas the particle size decreases the surface area increase which decreases the adsorption time (Volesky 2001). Alomá et al. (2012) simply used sugar cane waste for removal Ni^{+2} ions through washed, dried, and grinded to less than one mm particle size. With a pseudo-second-order kinetic model, the sorption method was described. The maximum sorption capacity was 2 mg/g at 25 °C and pH 5, the data was good fits with Langmuir isotherm, and the thermodynamic calculations showed the spontaneous nature of nickel particle biosorption on sugar can bagasse biomass.

On the other hand, hydroxyl groups of cellulose molecules can be altered with carboxyl group (Gurgel et al. 2008; Zhou et al. 2013), amino group (Zhao et al. 2015), sulfur group (Zhou et al. 2014), and cyclodextrin group (Alsbaiee et al. 2015), to remove the specific pollutants. These treatments displayed better adsorption capacity and effectiveness than indigenous cellulose. Examples of cyclic anhydrides used to modify the surface of cellulosic fibers are succinic, maleic and phthalic (Gurgel et al. 2008; Liu et al. 2007; Liu et al. 2008), lignins (Xiao et al. 2001), and/or hemicelluloses (Sun et al. 2003). To bring chelating skills to lignocellulosic products Ethylenediaminetetra acetic acid (EDTA) was used to introducing carboxylic and amine groups that form a stable complex with target metal in wastewater (Yu et al. 2008).

15.2.1 Amine Treatment

The world health organization has set a threshold of 4 mg/l for copper in drinking water (Dumrul et al. 2011). Tetraethylenepentamine (TEPA) could be used for biosorbent alteration to boost amine groups for metal ion adsorption. TEPA modified bagasse was used to remove copper (II) ions (Xu et al. 2019). The adsorption kinetics was assessed on the modified bagasse in column using 0.5 g sorbent dosage, 12.5 mg/g original copper concentration, and 6.25 mL/min flow rate. The quantity of copper (II) produced in the column at the moment t (q_t) decreased considerably as the adsorption function decreased to the balance, and the saturated adsorbed ions in the column were 0.17 mmol/g.

Different processes used to introduce amine features in washed and dried sugar can bagass treated with succinic anhydride under pyridine reflux, sequentially washed with 1 M of acetic acid solution in dichloromethane (CH_2Cl_2), modified sugar cane (MSB 1), treatment of 1 with saturated sodium bicarbonate ($NaHCO_3$) solution obtained modified sugar cane (MSB 2), also treated with 5 equivalent of 1,3-diisopropyl carbodiimide (DIC) and 6 equivalent of polyamine in anhydrous dimethylformamide (DMF) (Karnitz et al. 2007). The analysis of modified sugar cane (MSB) adsorbate was carried out for each material and three metal ions (copper, lead and cadmium). The three metal ions' adsorption improves in basic media. The maximum removal of Cd^{2+}, Pb^{2+}, and Cu^{+2} was observed above pH 6, 5 and 5.5 respectively, after 30 min using MSBs 2. Similar results have been obtained out using MSBs 5 and 6 for three metal ions. The Q_{max} isotherm parameter of Langmuir shows that MSB 5 has the biggest ability for Cu^{2+} removal, while MSB 6 removes Cd^{2+} and Pb^{2+}. Metal ion adsorption efficiency has been increased as amine function groups increased in the material.

Maity and Ray (2017) prepared many composite hydrogels by acrylamide free radical crosslink polymerization (AM) and acrylic acid (AA) comonomers in the presence of natural polymer gelatin (GT) and sugar cane bagasse (CB). The CB was treated with acid to reduce the lignin, and to improve the adsorption affinity. The tiny quantity of GT and CB is caught in the polyacrylic network during polymerization to create the composite gel. Using Box-Behnken Design (BBD) response surface methodology, the synthesis parameters were optimized to formulate a composite gel effective in the removal of copper ions. The gel was also subjected to copper sorption under different process circumstances. The impact of different process parameters, i.e., hydrogel dose and pH parameter at 100 ppm concentration of copper was assessment. It was noted that the increase of pH from 2 to 5.5 improves the Cu^{+2} removal percentage from 62.3 to 97. Whereas in acidic media, the protons (H^+) compete with Cu^{+2} to bind to the hydrogel's functional groups, leading in low removal or extraction percentage for Cu^{+2} (Zheng et al. 2010). The increasing in the hydrogel dose from 3 to 6 g/L copper ions removal increase from 39% to 97% but another increase in hydrogel dose decreases the metal ion removal percentage. Generally, at a much greater dose of gel in copper solution, the concentration gradient is decreased due to rivalry between the adsorbent and also divided (Wang et al. 2009). The adsorption of copper on the gel obeys second-order kinetics confirming chemisorption mechanism.

A highly competent and environmentally friendly biosorbent sugar cane bagase was prepared by epichlorohydrin, ethylenediamine (EDA) and carbon disulfide (CS_2) (Wang et al. 2017). The biosorbent was prepared as follows: sodium chlorite and potassium hydroxide pretreated the bleached sugarcane bagasse, epoxidation, amination, sulfonation reactions, leading to formation of a hydrogel bioadsorbent (Li et al. 2009). At pH 5, the maximum adsorption values were reached 559, 446 and 363 mg/g for Pb^{2+}, Cu^{2+} and Zn^{2+} ions respectively and the adsorption isotherms followed the Langmuir model in the single-component system. With the competitive Langmuir isotherm model, the binary component scheme was better defined. The excremental demonstrated there is a competition between lead and copper ions where the first metal delays the removal of the second one. Finally, the mechanism of metal ions removal was taking place by coordination, ion exchange, and electrostatic association.

Zinc is commonly used in the galvanizing industry and is an essential component for human enzyme activators and its deficiency results in serious health effects, but it is poisonous at concentrations above 100 mg/day (Senthilkumar et al. 2006). Sugarcane bagasse was chemically treated with ethylenediaminetetraacetic acid (EDTA) dianhydride and used to remove zinc ions from an alkali-zinc electroplating wastewater line in Contagem, Brazil (Pereira et al. 2010). Studies of sorption in basic medium enhanced adsorption of Zn^{2+} in 50 min, and that the Langmuir model described the process very well. The calculated adsorption capacity of Zn^{2+} in single metal ion solution was discovered to be 80 mg/g, while those values decreased to be 47 mg/g for industrial wastewater. These findings stated that for the adsorbent binding locations, other ions mainly calcium (Ca^{2+}) and chloride (Cl^-) present in industrial sewage competed with Zn^{2+}.

15.2.2 Acid Treatment

15.2.2.1 Phthalic Acid

Treatment of sugarcane bagasse with phthalic anhydride (PA) to generate carboxylate-functional sugarcane bagasse (SPA) has been researched as a function of the quantity of PA and the moment of response. Considering SB's altered training expenses with PA (SPA), a 6 h response time and a 6:1 PA–to–SB ratio were selected. The produced SPA has a 77.1% weight gain and 4.76 mmol/g carboxylic acid groups and it was used for removal Co^{2+}, Cu^{2+} and Ni^{2+} ions from mono-and bicomponent aqueous solutions (Ramos et al. 2016). The adsorption rate followed pseudo-second-order kinetics and the adsorption rate of metal ions was ranked as $Co^{2+} > Ni^{2+} > Cu^{2+}$. The Langmuir model portrayed monocomponent information well, while the modified expanded Langmuir and P-Factor models portrayed bicomponent information well. For the Langmuir model, the maximum adsorption capacity (Q_{max}, mono) was 0.561, 0.935, and 0.932 mmol/g for Co^{2+}, Cu^{2+}, and Ni^{2+} respectively. Bicomponent adsorption disclosed that Cu^{2+} suppressed Co^{2+} and Ni^{2+} adsorption, while Ni^{2+} suppressed Co^{2+} adsorption.

15.2.2.2 Sulphuric Acid

Lead is discharged from various sectors like leather industrial and batteries in water; it is non-biodegradable and tends to accumulate in organism through food causing different impact on human health (Hamad et al. 2016; Abbas et al. 2018; Iqbal 2016; Ahmaruzzaman and Gupta 2011). The treatment of SCB with sulphuric acid was run by suspended them for 3 h with 0.5 M H_2SO_4 afterward; the biomass was divided and washed with water until pH 7 and finally dried (Martín-Lara et al. 2010). Typically, 50 mL of 10 g/L lead solutions at 25 °C and pH 5 were approached with 0.5 g of H_2SO_4–SB biomass. The highest sorption capability of q_m for SB and H_2SO_4–SB was 6.366 mg/g and 7.297 mg/g. It was therefore discovered that the sulfuric acid therapy improved the sorption ability of sugarcane bagasse. The experimental results disclosed that the carboxylic groups in SB and H_2SO_4–SB were regarded to be the only responsible for removing lead under natural pH (Martín-Lara et al. 2008). It was discovered that the Langmuir model represents Pb^{2+} sorption on both untreated SB and H_2SO_4-SB biomass (Homagai et al. 2010).

15.2.2.3 Phosphoric Acid

Reformed phosphoric acid bagasse (PA-BS) was prepared using 30 g urea-containing dimethyl formamide (DMF) (Xu et al. 2019; Xiong et al. 2019). Phosphoric acid, which includes hydrogen and phosphate ions, is tribasic. It was dissociated into negatively loaded phosphate ion in aqueous solution at pH 4.5, which had a strong binding capacity with heavy metal ions. Phosphoric acid was noted to be grafted on the surface of bagasse through alcoholysis response by urea, and the inserted phosphoric acid could provide active locations for Pb^{2+} adsorption by exchanging ions with Na^+.

Lead adsorption kinetics exceeding 0.5 g of phosphoric acid treatment bagasse (PA-SCB) with an original lead concentration of 20.8 mg/g and 6.25 mL/min were 0.31 mmol/g (Xu et al. 2019). 0.5 g of PA-BS biomass was used for removal of mono- and bi-heavy metals ions in aqueous solution with 0.5 mmol/L concentration for each metal and pH 5.5 as represented in Table 15.1.

This related to the introduced phosphoric acid offered a fresh active site for the adsorption of metal ions by Na^+ ion-exchange. It was observed in the binary systems

Table 15.1 The adsorption equilibrium quantity (q_e, mg/g) of metal ions over phosphoric acid treatment bagasse (PA-SCB) and sugar cane bagasse (SCB) (Yu et al., 2015; Xu et al. 2019)

(q_e, mg/g)	PA-SCB	SCB
Pb^{2+}	7.65	8.3
Cu^{2+}	23.1	14.6
Zn^{2+}	21.7	6.4
Cd^{2+}	30.3	4.6
Ca^{2+}	17.9	4.0

that q_t of Pb^{2+} steadily increased until equilibrium was achieved, whereas that of the four cations first increased to a maximum and then decreased to the equilibrium value. The adsorption potential of metals in binary system ranked as $Pb^{2+} > Ca^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$. This result is related to electronegativity and radii of hydrated ions of metal in agues solution, whereas the metal has lowest electronegativity and the lowest hydrated ionic radii will poses the greatest adsorption potential (Xiong et al. 2019; Wang et al. 2011; Nightingale Nightingale 1959).

15.2.2.4 Succinic Acid

Treatment with succinic acid may be a promising adsorbent for Cr (VI) suppression. The optimal method conditions for removing Cr (VI) from the simulated alternatives by succinic acid-SB include pH 2; 200 rpm stirring velocity and 20 g/L adsorbent dose (Garg et al. 2009).

15.2.3 Base Treatment

Base treatment of bagasse was achieved with 0.1 N sodium hydroxide (NaOH) and 0.1 N acetic acid (CH_3COOH) (Rao et al. 2002). These low-cost adsorbents have been used to remove the aqueous solution from chromium and nickel. The efficiency of adsorbent products to remove Cr(VI) and Ni(II) were found to be between 56.2% and 96.2% and 83.6% and 100%, at pH 6 and 8 respectively, within 60 min contact time, 1 gm/l sorbent dose, 100 mg/l sorbate concentration, and with adsorbent particle size variability between 0.075 and 4.75 mm. Two adsorbents could be recovered and regenerated securely by burning after drying. Besides, Fe(III) was selectively removed from various natural water specimens such using batch and column methods (Soliman et al. 2011). The optimum application units for Fe(III) suppression was a 100 mg mass SCAB, 100µl Fe(III) concentration within 60 min of contact time at pH 3 and 50 ml iron solution. Its sorption output was well adjusted with the Langmuir model and pseudo-second-order kinetic.

15.3 Conclusion

Bioadsorbent based on cellulose has received great attention as one of the promising adsorbents for high surface area and ability to modify the surface, fast adsorption rate, resistance to swelling, low cost and readily accessible. Sugarcane cane bagasse has an abundance of carboxyl features, can capture metal cations heavily in wastewater. There are many groups can be altered with a carboxyl group in sugar cane bagasse to increase the adsorption capacity and remove the specific pollutants, like hydroxyl, amine, sulfur, and cyclodextrin groups that form a stable complex with target metal in wastewater. These treatments displayed better adsorption capacity and effectiveness than indigenous cellulose. The impact of different process parameters like initial concentration of heavy metal, pH value, amount of biosorbent, in mono- and multi-component systems. As the results of adsorption experimental the adsorption capacity, isotherm models and kinetic models were reported.

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Chapter 16
Chelating Materials for the Removal of Heavy Metals from Water

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Abstract Water is considered as a vital substance in the environment. Heavy metals can contaminate the water sources through different natural processes but mainly through human activities. Heavy metal ions do not degrade in nature. This characteristic has achieved that researchers work hard in the development of different treatments to remove heavy metals from water. Accordingly, several treatments for remediation of contaminants have been performed, including ion exchange, reverse osmosis, filtration, electrodialysis, precipitation, electrochemical process, biological treatment, coagulation/flocculation, and adsorption. Within these treatments, adsorption has emerged as an efficient and low–cost biotechnology. Numerous materials have been applied to adsorb heavy metals to remediate contaminated water, including resins, nanomaterials, membranes, biomass, industrial and agricultural wastes, metal organic frameworks, composites, chelating materials, among others.

In this chapter we have a special focus on the use of different chelating materials such as membranes, nanomaterials, polymers, resins, surfactants, chitosan and its derivates, covalent and metal organic frameworks and hybrid materials, to remove heavy metals from water. The state of the art application of these chelating materials was carefully reviewed and discussed throughout the chapter. The adsorptive potential of chelating materials to remove heavy metals can be evidenced. The adsorption processes emphasize the relevance of numerous functional groups present on the chelating materials, which can form metallic complexes with the target elements. In the majority of the reviewed works, a removal efficiency higher that 70% was reached. Finally, other relevant information related to adsorption is presented in the chapter.

Keywords Heavy metals · Remediation · Removal · Aqueous solutions · Waste water · Chelating materials · Metal chelates · Equilibrium · Thermodynamic · Kinetics

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16.1 Introduction

Water is a fundamental substance for human beings survival and ecosystems healthy maintenance. This valuable resource has been threatened for years by several factors, including the disappearance of water bodies, water erosion and chemical contamination (Liao and Huang 2013). The problem of chemical pollution in natural waters is concerning researchers worldwide because such pollution is not only restricted to an environmental problem but also extends to the development of productive processes that make use of this resource and human health through drinking water or consuming contaminated fish and seafood (Escudero et al. 2018; Inyinbor Adejumoke et al. 2018). For this reason, water remediation turns into a necessary and overarching instance that must be implemented in order to protect the quality of water and the entire ecosystem.

16.1.1 Water: Our Source of Life, with Heavy Metals

Heavy metals can be present in water due to a natural origin or human activities related to mining, industry, urban effluents, fertilizers (Vukovic et al. 2011). Due to the economic growth of many countries, industrialization has been favored and hence the generation of large amounts of industrial wastes. It is the case of some Asian countries, for instance, Vietnam, which generates around 10 million tons of industrial wastes per year (Huynh 2010). Electronic wastes have been also increasing in the last decades; however, their recycling is often carried out informally with recyclers that has not knowledge about the possible toxic compounds or elements that can be contained in e-wastes (Perkins et al. 2014). Heavy metals represent a great risk for human health because of their toxicity and dangerous effects (Tchounwou et al. 2012). Table 16.1 shows a list of the main anthropogenic sources of some heavy metals and their consequences on human health.

Heavy metals toxicity is influenced by factors such as their concentration and speciation, which are also conditioned by physico-chemical characteristics of water. Moreover, as heavy metals cannot be degraded, their accumulation in the nature is ensured for a long period of time, which is concerning due to metals can reach biota, drinking water and food. For these reasons, researchers are hard working in the development of different treatments that can be useful for heavy metals remediation. In this sense, numerous materials have been applied to remove heavy metals from contaminated water, including resins, nanomaterials, membranes, biomass, industrial and agricultural wastes, metal organic frameworks, composites, chelating materials, among others (Abdullah et al. 2019; Feng et al. 2018; Joseph et al. 2019; Repo et al. 2013; Velkova et al. 2018; Yang et al. 2019). Chelating materials offer several advantages to be used for heavy metal remediation because they are highly selective with targeted metallic ions, are economical, easy to obtain and can be reused several times (Sharma et al. 2013).

Table 16.1 Anthropogenic sources and human health effects of heavy metals

Heavy metal	Anthropogenic sources	Health effects	Reference
Arsenic	Mining activities, burning of fossil fuels and industrial wastes, pesticides, wood preservatives.	Cardiovascular, neurological, and respiratory damage, carcinogenic effects.	Hong et al. (2014), Saha and Paul (2016)
Cadmium	Industrial activities (e.g. plastics and batteries fabrication), fertilizers.	Kidney and bones damage, reproductive, disorders, carcinogenic effects.	Godt et al. (2006)
Chromium	Metallurgical industry and pigments.	Pulmonary, kidney, liver, gastrointestinal, skin damage, reproductive alterations.	Achmad et al. (2017), Kotaś and Stasicka (2000)
Copper	Industrial wastes, fertilizers, additives used for controlling the growth of algae.	Liver, gastrointestinal and brain damage.	Mohod and Dhote (2013), Uauy et al. (2008)
Lead	Industrial processes (e.g. arm industry), gasoline, pigments, electronics, printing.	Irritability, loss of concentration, anemia, encephalopathy, neuromuscular disorders, renal and reproductive affections.	Wani et al. (2015)
Mercury	Mining and agricultural activities, combustion of coal and oil, incineration of urban wastes.	Negative effects on the cardiovascular, nervous, digestive, renal, pulmonary and immune systems.	Rice et al. (2014), Wang et al. (2004)
Nickel	Industrial activities (e.g. stainless steel production), jewelry, electronics.	Allergies, lung fibrosis, kidney affections, pulmonary tract cancer.	Duda-Chodak et al. (2008)
Silver	Jewelry, silverware, photographic industry.	Liver and kidney hurt eyes and skin pigmentation, emphysema, bronchitis.	Drake and Hazelwood (2005)
Tellurium	Industrial practices (e.g rubber production), insecticides, electronics.	Kidney toxicity, hydrocephalus, Human colon cells toxicity.	Vij and Hardej (2012)
Thallium	Coal combustion and industrial wastes (e.g. cement production).	Nervous system effects, alopecia, anorexia, headache, pains all over the body.	Peter and Viraraghavan (2005)
Vanadium	Industrial activities (e.g. stainless steel, rubber or glass production).	Respiratory tract effects, biochemical disorders, neurological damage.	Fortoul et al. (2012)

16.1.2 Basic Principles of Metal Complexes and Chelates

Metal complexes are compounds formed by the combination between a metal, that appears as central atom, and a ligand, which is a ion or molecule with pairs of free electrons (Cotton et al. 1999). The bonding between a ligand with a central atom is usually represented by the donation of these pairs of free electrons from the ligand to the metal (Cotton et al. 1999). Monodentates ligands possess one donor atom and a single point of bond with the metal, whereas polidentates ligands or chelating agents are constituted by two or more coordinating atoms that can form a chelate through their association with a central atom (Cotton et al. 1999). The presence of polydentate ligands contributes with the stability of the chelate compounds. Chelate is a word derived from the Greek "Chela", which means clamp, due to the ring formed between the chelating agent and the metal is similar to the arms of a crab with the metal in its claws (Mortvedt 1985).

Several ions or molecules can act as ligands and form metal complexes and chelates. For instance, ethylenediaminetetraacetic acid is a ligand widely used for the softening of hard water, since it forms a chelate with calcium ions responsible for contributing hardness to water (Gardiner 1976). Chelating agents can be found in nature, for instance D-gluconic acid, D-glucaric acid, citric acid, malic acid, 2,3-dihydroxy benzoic acid, or can be artificially synthesized, such as ethylenediaminetetraacetic acid, diethylene triamine pentaacetic acid, ethylenediamine (Fischer and Bipp 2002; Kaushik 2015). Figure 16.1 show chemical structures of some chelating agents.

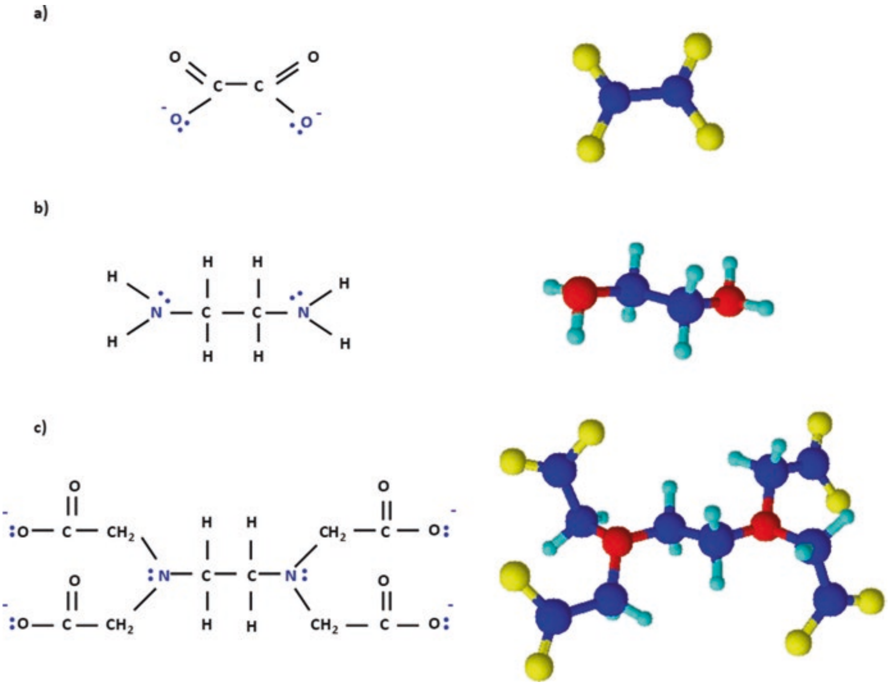

Fig. 16.1 Chemical structures of chelating agents often used to form metal chelates. (**a**) Oxalate ion; (**b**) ethylene diamine; (**c**) ethylenediaminetetraacetate ion. All examples present more than one donor atom, which are necessary to form stable metallic chelates. Free electron pairs of donor atoms are drawn as little blue circles (•). Atoms of tridimensional structures are colored as follow: Carbon (●); Nitrogen (●); Oxygen (●); Hydrogen (●)

First studies of application of chelating materials with removal purposes date from several decades ago, which are mainly focused on the elimination of toxic compounds from the body (Catsch and Lê 1957; Rosoff et al. 1961; Sowby and Taylor 1960) and the removal of pollutants from environmental matrices (Florence and Batley 1976; Kobayashi et al. 1975; Motojima et al. 1978). For instance, Sowby and Taylor studied the application of ethylenediaminetetraacetic acid and diethylene triamine pentaacetic acid to remove a radioelement (americium) deposited in rats (Sowby and Taylor 1960). Authors concluded that both chelating agents increased the removal of this element from the organism. However, diethylene triamine pentaacetic acid proved to be 12 times more effective than ethylenediaminetetraacetic acid.

Few years later, Motojima et al. investigated the effect of using a chelating material to remove radiocobalt from wastewaters (Motojima et al. 1978). A comparison between activated charcoal and activated charcoal impregnated with oxine as chelating agent was made. It was observed that the presence of a chelating agent highly improved the adsorption capacity of the material. Moreover, contrarily to activated charcoal, when oxine was used the material retained efficiently the cobalt the surface and the metal was not easily eluted trough a water flow.

The use of chelating materials with remediation purposes has been increasing up to date. Nowadays, a wide variety of chelating materials are used to remove heavy metal from contaminated environmental samples (El-Zahhar et al. 2019; Ferreira et al. 2019; He et al. 2019; Mohseni et al. 2019). However, it is a great challenge to synthesize new chelating material for remediation field, considering that different metal-ligand combinations generate compounds with different properties, such as solubility and polarity (Haas and Franz 2009). Thus, this manuscript will point to understand the formation and application of chelating materials to remove heavy metals from water. Different types of chelating agents, including membranes, nanomaterials, polymers, resins, surfactants, chitosan and derivates, covalent and metal organic frameworks, and hybrid materials, will be detailed and exposed as remediation tools for heavy metals removal. Finally, challenges, trends, and perspectives related to chelating materials for water decontamination will be presented and discussed.

16.2 Chelating Materials Used for Heavy Metal Removal

Numerous chelating materials of different nature have been employed for removing heavy metals ions from water effluents. In this section, it will be presented and discussed the chelating materials currently used for heavy metal remediation. Table 16.2 presents a summary of these chelating materials and the most important parameters that characterize the adsorption process.

Table 16.2 Different chelating material used for heavy metal removal from aqueous solution

Name of material	Pollutant	Optimal adsorption conditions				Adsorption capacity (mg/g)	Removal (%)	Reference
		pH	T (°C)	Time^{a} (min)	$C_o{}^{b}$ (mg/L)			
Chelating membranes								
Glycidyl methacrylate in polyacrylonitrile with amination with 2,4,6-triaminopyrimidine	Copper(II)	5	25	n.r.	0.1^{c}	110.83^{d}	90.0	Zhang et al. (2019b)
Polyvinylidene fluoride/ divinylbenzyl triethylenetetramine -cu	Copper(II)	6	25	n.r.	100	64	n.r.	Mokhtar et al. (2018)
Polyacrylonitrile/polydopamine -Fe nanoparticles	Chromium(VI)	<5.5	25	≈ 80	18	n.r.	89.0	Liu et al. (2019)
Polyacrylonitrile / poly(3,4-dihydroxy-L-phenylalanine)Fe nanoparticles							92.0	
Polyethyleneimine -coffee	Arsenic(III)	5.5	40	≈ 200	0.5	13.2^{e}	>90.0	Hao et al. (2018)
	Arsenic(V)				0.5	46.1^{e}		
Polyethersulfone /polydopamine	Lead(II)	5.4	25	720	300	20.23	n.r.	Fang et al. (2017)
	Cadmium(II)					17.01		
	Copper(II)					10.42		
Polyacrylonitrile/polyaniline -Nylon Core-Shell	Lead(II)	6.5	25	7	50	960.0	96.7	Almasian et al. (2018)
	Cadmium(II)					911.7	95.1	
Chelating nanomaterials								
Thiol – multi-walled carbon nanotubes	Mercury(II)	6.0	70	> 15	n.r.	57.87	n.r.	Singha Deb et al. (2019)
Dithiocarbamate – multi-walled carbon nanotubes						191.52		
Multi-walled carbon nanotubes - Triazole dendrimers	Mercury(II) Lead(II) Nickel(II)	7.0	n.r.	n.r.	n.r.	n.r.	70–90	(Iannazzo et al. 2017)
Graphene oxide with ethylenediaminetetraacetic acid	Lead(II)	6.8	n.r.	18	100	479	n.r.	Madadrang et al. (2012)

Polyacrylonitrile nanofibers – ethyleneglycol	Lead(II)	7.0	n.r.	30	100	8.8[f]	>99	Morillo Martín et al. (2018)
	Copper(II)	7.5		60		6.1[f]		
	Zinc(II)	7.2		120		7.2[f]		
Thiol functionalized aluminium oxidehydroxide	Mercury(II)	n.r.	23	240	200	110[e]	n.r.	Xia et al. (2017)
	Lead(II)					66[e]		
	Cadmium(II)					49[e]		
Nano NH_2- mesoporous silica	Lead(II)	5.0	70	80	1000	63.28	76–97	Javadian et al. (2017)
Mercaptoamine-functionalised silica-coated magnetic nanoparticles	Mercury(II)	5–6	45	120	50	292	n.r.	Bao et al. (2017)
	Lead(II)	6–7				355		
Chelating polymers								
Polyacrylonitrile hydrolyzed	Lead(II)	7	30	600	10	145[e]	90–99	Bhunia et al. (2018)
	Cadmium(II)					156[e]		
1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione - diethylenetriamine (1)	Cadmium(II)	6	25	n.r.	1[d]	(1) 23.09	90–99	Cegłowski et al. (2018)
	Cobalt(II)					(2) 69.4		
	Chromium(III)					(1) 15.87		
	Copper(II)					(2) 31.67		
1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione - pentaethylenehexamine (2)	Nickel(II)					(1) 4.12		
						(2) 9.8		
						(1) 27.198		
						(2) 62.68		
						(1) 21.16		
						(2) 26.43		

(continued)

Table 16.2 (continued)

Name of material	Pollutant	Optimal adsorption conditions				Adsorption capacity (mg/g)	Removal (%)	Reference
		pH	T (°C)	Time^{a} (min)	C_o^{b} (mg/L)			
Poly-ammonium dithiocarbamate	Copper(II)	6	25	20	100	245.53	≈ 100	Chen et al. (2018)
	Nickel(II)					234.47		
	Zinc(II)					226.76		
Sodium lignosulfonates	Copper(II)	7	n.r.	30	10	n.r.	93–98	Kochkodan et al. (2018)
Polyethyleneimine								
Poly(tannin-hexamethylendiamine)	Chromium(VI)	2.5	30	2880	160	283.29	≈ 100	Liu et al. (2018a)
Chelating resins								
Polyamidoxime resin	Copper(II)	5.4	25	120	18^{d}	2.62^{f}	n.r.	El-Bahy and El-Bahy (2016)
	Manganese(II)	5.6			15^{d}	2.21^{f}		
	Nickel(II)	6.0			18^{d}	1.42^{f}		
Amidinothiourea polystyrene bead	Mercury(II)	5	40	100	600^{e}	370.4	97	Deng et al. (2016)
Resin with acyl and thiourea groups	Silver(I)	6	30	720	100^{d}	6.078^{e}	n.r.	Huang et al. (2019)
Chloromethylated polystyrene-N-methyl thiourea chelating resin	Mercury(II)	4	35	>600	2	347	100	Zhuo et al. (2017)
Poly([(2-methacryloyloxy)ethyl] trimethylammonium chloride)	Chromium(VI)	4.0	25	20	20	45	95	Santander et al. (2017)
Magnetic iminodiacetate chelating resin	Copper(II)	5.5	25	25	5^{d}	2.5	≈75	El-Bahy (2018)
	Lead(II)	5.5		25		1.9		
	Cadmium(II)	6.0		20		1.3		
	Zinc(II)	6.0		20		1.5		
Bisthiourea/thiourea/glutaraldehyde resin	Silver(I)	5.9	60	200	2000^{d}	6.80^{e}	91	Atia et al. (2014)
	Gold(I)	1.8	27			5.78^{e}		

Chelating surfactants								
Sodium dodecyl sulfate	Lead(II)	<7.0	21	n.r.	1^{d}	n.r.	≈ 95.0	Hąc-Wydro et al. (2016)
Sodium N-lauroylsarcosine							≈ 95.0	
Sodium dodecylbenzenesulfonate							≈ 75.0	
Ziziphus spina-christi	Lead(II)	6.0	25	n.r.	0.48^{d}	n.r.	90.7	Saleem et al. (2019)
	Copper(II)						88.2	
Polymer-surfactant aggregates	Cadmium(II)	1.0	25	15	n.r.	n.r.	97.0	Shen et al. (2016)
Polyethyleneimine – Sodium dodecyl sulfate	Zinc(II)						86.0	
	Chromium(III)						73.0	
Chitosan and derivates								
Chitosan (C4)	Copper(II)	5.5	25	240	0.787^{d}	165.2	n.r.	Moreira et al. (2018)
	Chromium(VI)	2.0		360	0.962^{d}	182.0		
Ethylhexadecyldimethyl ammonium bromide impregnated	Cadmium(II)	3	25	45	100	341.3^{e}	≈ 100	Shekhawat et al. (2017)
	Mercury(II)				20	43.43^{e}		
Dromaius novaehollandiae- chitosan	Lead(II)	4	30	70	20	70.42^{e}	93.5	Anantha and Kota (2016)
Feather–chitosan								
Chitosan-Alginate nanocompound	Chromium(VI)	5	n.r.	300	100	108.8	65	Gokila et al. (2017)
Fe_3O_4-Chitosan	Vanadium(V)	5	20	10	10	186.6^{e}	99.9	Omidinasab et al. (2018)
	Lead(II)	6				192.3^{e}	92.3	
Chitosan-metal nanoparticles	Copper(II)	5.2	30	30	1000	405	99.5	Kong et al. (2018)
	Nickel(II)					315	72	
Waste paper-chitosan aerogel	Copper(II)	5.5	20	504	n.r.	156.3^{e}	≈ 90	Li et al. (2000)

(continued)

Table 16.2 (continued)

Name of material	Pollutant	Optimal adsorption conditions				Adsorption capacity (mg/g)	Removal (%)	Reference
		pH	T (°C)	Time[a] (min)	C_o[b] (mg/L)			
Covalent and metal organic frameworks								
[Cu_3(1,3,5-benzenetricarboxylate)$_2$(H_2O)$_3$]	Cerium(III)	6.0	25	n.r.	1000	353	99.0	Zhao et al. (2019)
Metal-organic frameworks with centers containing Zr and S	Mercury(II)	6.8	25	120	10	824	99.0	Li et al. (2018a)
Melamine- metal-organic frameworks	Lead(II)	6.0	40	120	10	205	97.6	Yin et al. (2018)
Bi(triazine-2,4,6-triyl-tribenzoic)]·N,N-dimethylformamide.6H_2O	Lead(II)	5.2	n.r.	45	50	50.87	90	Zhang et al. (2019a)
N-riched covalent organic frameworks	Cadmium(II)	7.0	25	30	80	396.82	98.0	(Dinari and Hatami 2019)
Covalent organic frameworks – Covalent organic frameworks - p-Phenylenediamine	Lead(II)	4.5	25	≈ 1200	300	185.7[e]	96.5	Li et al. (2019a)
						140[e]	95.6	
Hybrid materials for chelating metals								
Al(OH)3-poly(acrylamide-dimethyldiallylammonium chloride)- dithiocarbamate	Copper(II)	4	n.r.	30	50	225.3	90	Liu et al. (2018b)
	Lead(II)	6		10		246.7	98	
Magnetic chitosan-graphene oxide nanocomposite	Copper(II)	7	25	≈ 40	100	217.14[e]	n.r.	Hosseinzadeh and Ramin (2018)
Graphene oxide-chitosan-ferrite nanocomposite	Chromium(VI)	2	27	600	50	270.27[e]	96	Samuel et al. (2018a, b)
Modified silica gel with a bis(pyrazole)butane	Zinc(II)	6	25	30	140	86.51	Zn(II)	Radi et al. (2017)
	Lead(II)				120	35.26		
	Cadmium(II)				50	26.96	Zn(II)	
	Copper(II)				50	20.24		

3-(5-ethoxybenzenethiol-imino-methyl)–salicylic acid fixed onto the mesoporous silica	Arsenic(III)	4	35	≈ 750	100	162.00[e]	76.84 73.62 94.31	Liao et al. (2019)
	Cadmium(II) Lead(II)					205.83[e] 730.79[e]		
3-(5-ethoxybenzenethiol-imino-methyl)–salicylic acid / mesoporous silica	Lead(II)	5.5	n.r.	60	5	175.16	98	Awual (2019)
Metal-organic frameworks – Graphene oxide	Nickel(II)	n.r.	n.r.	≈ 25	300	1152	94	Faradonbeh et al. (2018)

n.r. Not reported. [a]Equilibrium time. [b] C_o: Initial Concentration. [c] mmol/L. [d] mmol/Lm^2. [e] Theoretical Q_{max}. [f] mmol/g

16.2.1 Chelating Membranes

The separation of heavy metals by membranes has gained increasing importance, since they have an excellent capacity to sequester metal ions from aqueous solutions. In recent years, treatments for metals removal using membranes have been refined with the combination of the advantages provided by adsorption and ultrafiltration, which has reduced energy costs (Tian et al. 2018). Compared with other technologies, chelating membranes offers a water treatment in a single step, where the membrane acts as a barrier that prevents the passage of heavy metals and allows the passage of other constituents (Zirehpour and Rahimpour 2016). To obtain a good removal performance it is necessary to optimize the size and distribution of the membrane pores, the surface charge, the solution flow, and the chelation of metals by related ligands, among other factors (Abdullah et al. 2019).

For all the benefits that separation by membranes offers, this type of material has dominated the field of water purification and has been considered a sustainable ecological strategy (Buruga et al. 2019). However, when membrane treatments have been applied for water remediation, a complexation of the metals in solution was needed prior to the retention by ultrafiltration in the membrane. In this sense, it is required an exhaustive affinity test between complexing compounds and metal ions and the optimization of the separation capacity of the membranes (Hosseini et al. 2016). The simplification of these individual processes has been achieved with the recent developments of metal chelating membranes, where metals are retained by complex surface interactions with functional groups available in the pores of the membrane, allowing the separation of metal ions in an effective and selective manner. The mechanism by which a chelating membrane is able to retain metal ions in aqueous solution is shown in Fig. 16.2.

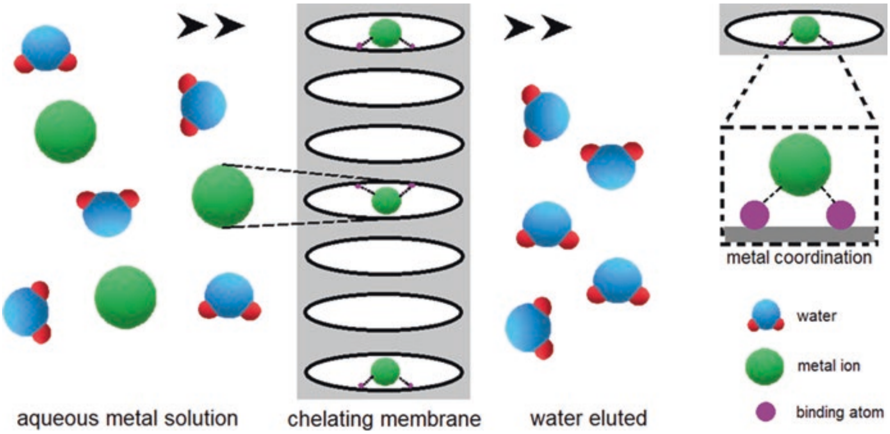

Fig. 16.2 Schematic representation of the chelate formation between metal ions and chelating membranes. The metal ions in solution interact with the chelating membrane by coordination reactions with ligands that are part of the structure of the membrane. In this way, the metal ions are retained while the rest of the constituents of the aqueous solution are eluted from the membrane. (Modified after Zhang et al. 2019b)

A current research work by Zhang et al. showed the potential of a metal chelating membranes to efficiently complex copper(II) ions (Zhang et al. 2019b). The synthesis of this membrane basically involved a grafting of glycidyl methacrylate in polyacrylonitrile with the subsequent amination with 2,4,6-triaminopyrimidine. The membrane was exposed to copper solutions at pH 5.0 in conical flasks and stirred at 160 rpm at 25 °C for 24 h. The effluent was collected every 5 minutes for copper measurement by absorption atomic spectrophotometry. The regeneration of the membrane was possible *in situ* with the use of a 0.1 x 10^{-3} mol L^{-1} nitric acid solution. This interesting study allowed increasing the pollutant treatment volume twice when using organic acids, which suggests that the membrane can be used for the treatment of simulated wastewater.

This metal ion was also studied by Mokhtar et al., who developed a selective polymeric membrane for copper(II) ions that was based on the application of ion imprinting technique (Mokhtar et al. 2018). The synthesis was based on the formation of divinylbenzyl triethylenetetramine from triethylene tetramine and divinylbenzene, which forms a polymerizable chelating monomer. Subsequently, a complex is formed with copper(II) and then polymerization occurs within the pores of polyvinylidene fluoride to produce a membrane loaded with copper(II), which is subsequently leached. The diffusion experiments showed a selective separation-retention of copper(II), contrarily to other assayed metal ions, such as nickel(II). The amount of heavy metal that was adsorbed by the ion-imprinted adsorbent was 3.76 times greater than that obtained with the non-imprinted material. Studies at optimal conditions of pH, temperature, and shaking time allowed achieving an adsorption capacity of the metal ion of 64 mg g^{-1} (Table 16.2).

In order to maximize the hydrophilicity and chelating power of the polyacrylonitrile membrane, Liu et al. made a self-polymerization of this membrane with polydopamine and poly(3,4-dihydroxy-L-phenylalanine) (Liu et al. 2019). Under this reaction, functional groups hydroxyl and carboxylate were added on polyacrylonitrile membrane. Finally, iron nanoparticles were immobilized in the materials for subsequent use to retain the chromium(VI) contained in the aqueous solution. Based on scanning electron microscope with energy dispersive spectrometer and X-ray photoelectron spectroscopy, it was demonstrated that the removal of chromium(VI) consisted of the adsorption of the chromium(VI), subsequent reduction to chromium(III), precipitation, and partial desorption of the reduced metal. According to the authors, the complexation of chromium(VI) through functionalized membranes are due to the interaction of $HCrO_4^-$ and CrO_4^{2-} and the hydroxyl and carboxyl functional groups that make up the chelating membrane.

Hao et al. developed a membrane methodology applied to a pilot scale for the retention of arsenic present in water samples (Hao et al. 2018). In this work, a cellulose membrane was synthesized with amino functional groups derived from the coffee powder previously used, which contributes with the principles of green chemistry. For the synthesis, it was required to collect the spent coffee from local coffee shops; it was washed several times to eliminate the soluble compounds. Then, a coffee bleaching stage was carried out, which consisted of immersing the coffee in 5% g ml^{-1} sodium hypochlorite in a conical flask overnight. The floating cellulose was separated by a Buchner funnel and mixed with constant stirring in a polyethyleneimine solution. Finally, the material was washed with deionized water and dried. The maximum adsorption capacities obtained were 13.2 and 46.1 mg g^{-1} for arsenic(III) and arsenic(V), respectively. According to the authors, an efficient removal of total arsenic is achieved, where the complexation of arsenic through the amino groups of the chelating membrane used is involved.

Although there are numerous works published in the literature in which the perspective of the remediation of heavy metals using chelating membranes is addressed, few of these works specifically use the principle of the complexation of metals for subsequent elimination. Among them, Fang et al. designed an asymmetric polyethersulfone ultrafiltration membrane where the internal pores deposited polydopamine nanoparticles (Fang et al. 2017). Lead(II), cadmium(II) and copper(II) were the ions under study. The membrane allowed to obtain a greater adsorption capacity for lead(II) ion (Table 16.2). The researcher demonstrated that the introduction of polydopamine nanoparticles allowed a better performance of the membrane and remarkable capacity of adsorption of heavy metals. The maximization of the adsorption capacity is due to the three-dimensional distribution of the polydopamine nanoparticles in the cross section of the polyethersulfone membrane that provides more active sites, increasing the contact time between the membrane and heavy metals. According to the authors, the possible mechanisms involved on the retention occur through physic interactions and metallic complexes formation.

Almasian et al. prepared a membrane of polyacrylonitrile and polyaniline with a nylon core, which was modified with diethylenetriamine to separate lead(II) and cadmium(II) from aqueous solutions (Almasian et al. 2018). According to the authors, the modification of the membrane increased the hydrophilicity, improved the antifouling property and allowed a greater permeability. Excellent adsorption capacities were obtained for the assayed heavy metals (Table 16.2). Maximization of adsorption capacity was achieved by incorporating additional amino groups on the surface of nanofibers by reaction between diethylenetriamine and polyacrylonitrile polymer. The authors report that the adsorption was due to the chelation produced by imine and amine groups that are part of the polyaniline structure.

16.2.2 Chelating Nanomaterials

Nanotechnology development has favored the creation of different nanomaterials and nanocomposites, which are used in the biomedical, textile, agricultural, electronic, industrial and environmental field (Munusamy et al. 2016). In this section, it will be discussed available nanomaterials and nanocomposites containing chelating agents used to remove heavy metals from water. Carbon nanotubes have been applied to remove heavy metals from aquatic matrices due to large surface area (Abdel Salam 2013; Abbas et al. 2016).

However, it has been reported that by functionalizing the surface of the carbon nanotubes with chelating materials, a greater selectivity towards metal ions can be achieved (Ouni et al. 2019). Singha Deb et al. used thiol and dithiocarbamate ligands functionalized on multi-walled carbon nanotubes to remove mercury from wastewater (Singha Deb et al. 2019). Chelating with dithiocarbamate showed higher adsorption capacity than thiol ligands probably because of the presence of more S in the molecular structure. In a work developed by Iannazzo et al. triazole dendrimer-functionalized multi-walled carbon nanotubes were synthesized and applied to remove lead(II), mercury(II), and nickel(II) from wastewaters (Iannazzo et al. 2017). Moreover, terminal amino groups of the triazole dendrimer were derivatized to the corresponding α-aminophosphonates. Experimental results arrows that this material showed the best chelating abilities towards the heavy metal ions. Density functional theory calculations suggested that the chelating mechanism involves the two oxygen atoms of the phosphate group.

Graphene is a carbon-based nanomaterial that shows outstanding properties, including mechanical strength, elasticity, electrical and thermal conductivity (Novoselov et al. 2012). Graphene oxide and the reduced form are often applied to remove heavy metals from contaminated matrices. Graphene oxide is obtained by the oxidation of graphene, while its reduce form is obtained after the reduction of graphene oxide (Gao et al. 2011). Chelating agents are usually used to modify these nanomaterials and improve the adsorption potential for removing heavy metal ions. Madadrang et al. studied the graphene oxide with ethylenediaminetetraacetic acid adsorption for the lead(II) removal from aqueous solutions (Madadrang et al. 2012). At pH 6.8, a good adsorption capacity was obtained (479 mg g^{-1}), which was highly superior to that obtained for graphene oxide without chelating agent. Kinetic adsorption showed to be fast, completing the maximum removal percentage within 20 min. Authors suggested two mechanisms as responsible to explain lead(II) removal using the new adsorbent: (i) ion-exchange between metallic ions and groups of the ethylenediaminetetraacetic acid - graphene oxide surface, and (ii) chelation between lead(II) and ethylenediaminetetraacetic acid.

Nanofibers are other class of nanomaterials often used to adsorb pollutants due to high porosity and specific surface area (Kenry and Lim 2017). Morillo Martín et al. synthesized three chelating polyacrylonitrile nanofibers for the selective removal of heavy metal from water (Morillo Martín et al. 2018). The adsorption potential of these nanofibers was evaluated with different metal ions, as follow: ethylenediamine with lead(II), ethyleneglycol with copper(II) and diethylenetriamine with zinc(II). Adsorption capacities of 8.8, 6.1, 7.2 and mmol g^{-1} were obtained for each material, respectively. The adsorption capacity of these chelating nanofibers was demonstrated in this work, considering that all the assayed metal ions could not be retained in the nanofibers without functionalization.

The use of chelating nanowhiskers for remediation purposes has been also demonstrated (Druzian et al. 2018; Xia et al. 2017). Nanowhiskers or crystalline nanofibers are nanomaterials that can be obtained from the decomposition of crystalline materials into nano-entities with specific forms (Watthanaphanit et al. 2008). Xia et al. applied thiol functionalized aluminium oxidehydroxide nanowhiskers to remove mercury(II), lead(II), and cadmium(II) from water under static and dynamic filtration conditions (Xia et al. 2017). Preliminary adsorption results revealed that thiol treated-nanowhiskers were useful to remove individually the metallic ions from water. However, future studies are needed to optimize additional experimental variables, such as pH and regeneration of the filter.

Chelating silica-based nanomaterials are also excellent adsorbents used for removing heavy metals due to the good specific surface area and non toxicity (Mahmoud et al. 2016). Javadian et al. evaluated the adsorptive potential of nano NH_2- mesoporous silica for removing lead(II) ions from aqueous solutions (Javadian et al. 2017). Under optimal experimental conditions (Table 16.2), good removal efficiency was reached (99%). When the adsorption was applied to real wastewater samples, removal efficiencies were between 76% and 97%. This decrease on the retention percentage could be attributed to the matrix effect caused by real samples, which are often more chemically complex than an ideal aqueous solution. Moreover, thermodynamic results showed a spontaneous and endothermic adsorption process.

The use of magnetic nanomaterials for remediation purposes have been increased in the last years due to these materials avoid consuming time steps as centrifugation or filtration, and separation phase is controlled by a magnet only. Recently, a mercaptoamine-functionalised silica-coated magnetic nanoparticles has been synthesized and applied to remove mercury and lead ions from wastewater (Bao et al. 2017). The synthesis of the new magnetic material is schematized in Fig. 16.3.

The Brunauer–Emmett–Teller specific surface area of magnetic nanoparticles was 33.2 $m^2\ g^{-1}$. After silica coating, this surface area was three times greater than the previous one. However, the mercaptoamine-functionalised silica-coated magnetic nanoparticles showed a value of 71.9 $m^2\ g^{-1}$, which means that some mercaptoamine molecules entered into the pores of the silica shell. The optimization of experimental variables such as pH and temperature were performed (Table 16.2).

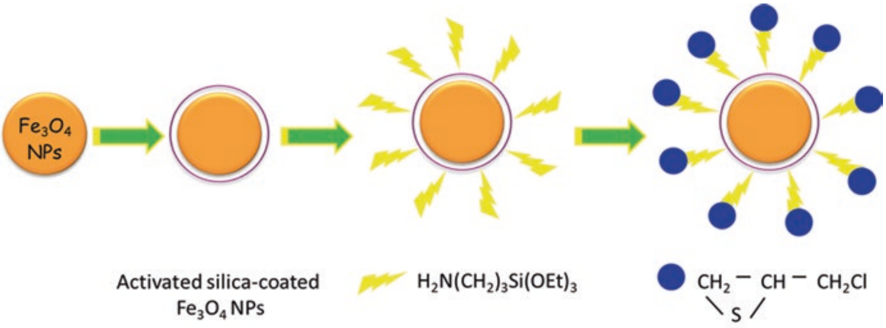

Fig. 16.3 Synthesis of mercaptoamine-functionalized silica-coated magnetic nano-adsorbent. Activated silica-coated Fe_3O_4 nanoparticles were initially prepared by a procedure previously reported (Bao et al. 2016). These nanoparticles were dispersed in toluene using sonication. Then, (3-aminopropyl) trimethoxysilane and zeolite grains were added. The obtained amino-functionalized silica-coated Fe_3O_4 nanoparticles were washed and put in contact with chloromethyl thiirane in an ice bath. After increasing the temperature and washing several times, the final chelating mercaptoamine-functionalized silica-coated magnetic nano-adsorbent was obtained. (Modified after Bao et al. 2017)

Thermodynamic studies showed that the adsorption was more spontaneous at higher temperatures, which could be probably due to an increase on the size of silica pores or mobility of metal ions.

16.2.3 Chelating Polymers

In the last years, polymeric materials have sprouted up as potential adsorbents for efficient removal of heavy metal contaminants from wastewater (Dutta and De 2017). Researchers have special interest of these materials due to low cost, high surface area and high mechanical strength, ease of handling, excellent functionalization and regeneration capability (Cegłowski et al. 2018; Zare et al. 2018). Bhunia et al. developed a very interesting work using a low-cost semi crystalline organic polymer as polyacrylonitrile to remove lead(II) and cadmium(II) (Bhunia et al. 2018). The authors proposed the preparation of the polymer and its hydrolyzed compound. The X-Ray Diffraction analysis and Fourier transform infrared spectroscopy results showed a strong chelation between hydrolyzed polyacrylonitrile and lead(II) and cadmium(II). Experimental adsorption capacities were 33 and 40 mg g^{-1} for lead(II) and cadmium(II), respectively. According to the researchers, chemisorption is the dominant uptake mechanism and the main responsible for chelation of lead(II) and cadmium(II) ions are carboxylate groups. The maximum desorption was achieved at pH 2, probably due to a competitive adsorption of H^+ with the adsorbed metals ions on the surface of the hydrolyzedcompound. The adsorbent was successfully applied for industrial effluents treatment.

Cegłowski et al. studied another interesting chelating polymer (Cegłowski et al. 2018). In this work, a simple reaction between diethylenetriamine and pentaethylenehexamine with 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione was proposed. The reaction was developed at room temperature with vigorous agitation for 1 hour, leading to the formation of two chelating polymers Inductively coupled plasma-optical emission spectroscopy was used for determination of cadmium(II), cobalt(II), chromium(III), copper(II), and nickel(II) ions concentrations. For both chelating polymers and all the assayed heavy metals, pH 6 was considered as optimal to reach the highest adsorption capacity. At this pH value, the free amine and amide groups of the polymers structures are highly available to form complexes with the metal ions. Finally, the authors demonstrated that when pentaethylenehexamine was used the chelating polymer was more effective than when diethylenetriamine was applied to purify wastewaters.

Chen et al. synthesized poly-ammonium dithiocarbamate and poly-sodium dithiocarbamate with different degrees of polymerization for removal efficiency of copper(II), nickel(II) and zinc(II) from wastewater (Chen et al. 2018). Adsorption capacity was performed by the addition of 0.1 g of poly-ammonium dithiocarbamate with 100 mg L^{-1} of each metal at pH 6 during 20 min. Finally, supernatant was filtered, and residual heavy metal ions were detected using an atomic absorption spectrophotometer. The results showed that the increase of poly-ammonium dithiocarbamate amount (0.01–0.1 g), reaction time (5–20 min) and temperature (10–60 °C) caused an increase of the adsorption capacity. Selective chelating agents, such as citric acid, tartaric acid, and ethylenediaminetetraacetic acid, on poly-ammonium dithiocarbamate were studied to remove of heavy metal ions. The authors demonstrated that poly-ammonium dithiocarbamate exhibited greater adsorption capacity when citric acid was used as chelating agent, and that poly-sodium dithiocarbamate was more successful when ethylenediaminetetraacetic acid was used. Finally, the researchers showed that a covalent chelate would be formed between the metal ions and the sulfur atom of the active group within the long-chained polymer structure.

Kochkodana et al. proposed the copper(II) removal by polymer enhanced ultrafiltration (Kochkodan et al. 2018). This new process is one of the most promising processes for wastewater treatments due to the outstanding advantages, such as high removal percentage, low consumption of energy, high selectivity and sensibility (Kochkodan et al. 2018; Qiu and Mao 2013). The adsorption takes place trough the complexation between the heavy metal and the chelating polymer. The macromolecular complex is retained by a membrane, whereas unbound metal ions pass through the membrane. In this work, different chelating polymers, particularly sodium lignosulfonates, polyethyleneimine and two dextrans, were evaluated. It was found that in the absence of a chelating agent, copper(II) removal percentage was not efficient (less than 10%), while with the chelating membranes, percentages around 97% were achieved. The authors proposed that this behavior was due to the high stability of the copper(II)-polymer complex that is formed. The polymers could be efficiently recycled, which reduce the costs of the whole process.

New chelating polymers were synthesized modifying the molar ratio between tannin and hexamethylendiamine for the removal of chromium(VI) from aqueous solutions (Liu et al. 2018a). The aqueous solution of these compounds was vigorously stirred for 48 h at 25 °C. Then, the synthesized poly(tannin-hexamethylendiamine) was centrifuged, washed and dried. According to the molar ratio, the polymers were identified from −2 to 5. It was observed that under the same experimental conditions, chromium(VI) removal percentage was highest for number 4 (mole ratio of tannin: hexamethylendiamine = 1:12.5) (≈100%). Regarding the possible adsorption mechanism, the researchers concluded that, under the working condition, hexavalent chromium is reduced to trivalent chromium and finally this species form a chelate with the functional groups of the adsorbent surface.

16.2.4 Chelating Resins

Chelating resins are defined as a class of crosslinked functional polymeric material with chelating groups, such as hydrazine, amidoxime, thiourea (Deng et al. 2016; El-Bahy and El-Bahy 2016; Huang et al. 2019). Chelating resins are usually applied to remove heavy metals from water. For instance, it has been synthesized a polyamidoxime chelating resin to adsorb copper(II), manganese(II), and nickel(II) in static and dynamic conditions (El-Bahy and El-Bahy 2016). The resin was synthesized by copolymerization of acrylonitrile with N,N-methylenebisacrylamide and a subsequent reaction of amidoximation. Experimental variables including pH, initial concentration of ions, and temperature were evaluated. It was found that pH values around 6.0 were optimal to reach the maximum adsorption capacity. As amidoxime has an amphoteric behavior, the basic NH_2 is protonated at acidic pH values, while at pH higher than 7, both protons and amino groups protonation is decreased, which favored the heavy metals adsorption.

Deng et al. used amidinothiourea as chelating agent to modify a macroporous chloromethylated polystyrene bead (Deng et al. 2016). The resultant chelating resin was evaluated to adsorb and remove mercury(II) from aqueous solutions. Removal percentages of 97.1%, 92.2% and 84.2% were reached at initial elemental concentrations of 200, 400, 600 mg L^{-1}, respectively. The retention of the pollutant on the chelating resin should be due to mercury(II) is coordinated by sulfur and the primary amine of amidinothiourea, or by the nitrogen of the imine and the primary amine.

Thiourea and acyl groups have been also used as chelating agent to modify a resin for the silver(I) removal from aqueous solutions (Huang et al. 2019). Kinetic studies developed in this work revealed that adsorption capacity was increased as time was prolonged, reaching the equilibrium after 12 h. Desorption of metal ions from the resin was carried out using 0.2 mol chloride acid and 0.5 mol thiourea as eluent, attaining a desorption efficiency higher than 95%. The resin could be reutilized up to five cycles of adsorption-desorption without significant adsorption capacity decrease.

Zhuo et al. synthesized a chloromethylated polystyrene-N-methyl thiourea chelating resin for the adsorption of mercury(II) (Zhuo et al. 2017). Pseudo-first and pseudo-second orders kinetic models were used to fit the kinetic data. Values of determination coefficients ($R^2 = 0.954$ vs. $R^2 = 0.983$) showed that pseudo-second order model is better to describe the adsorption process, indicating that the chemical adsorption is the step that control the rate of the process. Langmuir and Freundlich equilibrium models were also tested. Isotherms data were well adjusted by Langmuir model, which shows that mercury adsorption on the chelating material is a monolayer type.

Santander et al. synthesized a poly([(2-methacryloyloxy)ethyl]trimethylammonium chloride) chelating resin to adsorb and remove chromium(VI) from aqueous solutions (Santander et al. 2017). Batch experiments showed a removal of more than 95% in the first 15 min of the adsorption process. Kinetic assays were performed using different particle sizes of the chelating resin, and the best chromium removal percentage was achieved when the particle size was between 100 and 180μm (Fig. 16.4). Higher particle sizes (180–250μm) achieved the same removal percentage but after 45 min of the process. Authors suggested that minor particle size of the resin allow larger contact surface area of the chelating resin with the pollutant.

Magnetic chelating resins have been also used to remove heavy metals from water. For instance, El-Bahy et al. investigated the adsorptive potential of a novel

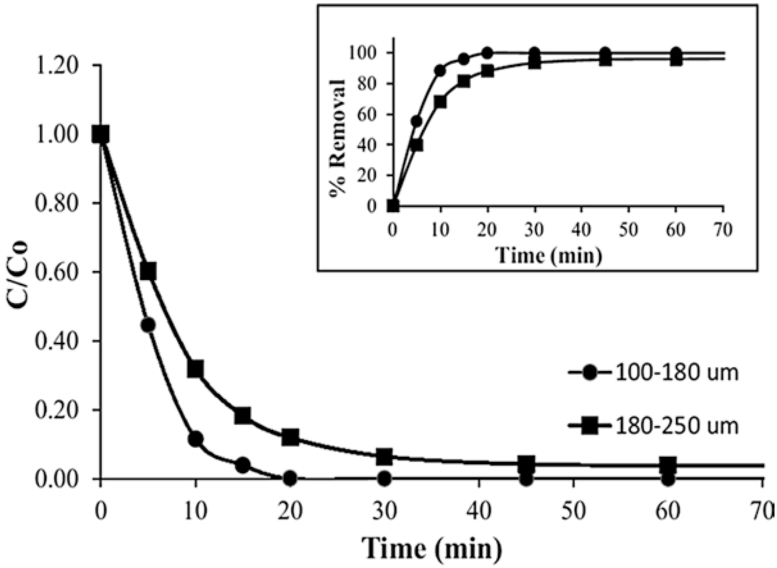

Fig. 16.4 Effect of Poly([(2-methacryloyloxy)ethyl]trimethylammonium chloride) chelating resin particle size on chromium(VI) removal percentage. A 95% chromium(VI) removal was reached using particle sizes from 100 to 180μm, meanwhile with particle sizes from 180 to 250μm this percentage is obtained after 45 min only. (Reprinted with permission of the copyright holders, Springer from Santander et al. 2017)

magnetic iminodiacetate chelating resin to remove copper(II), lead(II), zinc(II), and cadmium(II) from wastewater through batch studies (El-Bahy 2018). Additionally, column studies were performed for the removal of Cu(II). In this case, the effect of bed height, flow rate and initial copper(II) concentration on the removal percentage was investigated. Results showed that at higher bed heights, high removal percentages were obtained. On the other hand, when initial heavy metal ions and flow rate were increased, the removal values decreased. Data obtained from column experiments were in good agreement with Thomas and Yoon−Nelson models. The magnetic chelating resin demonstrated a good potential for the reutilization, in spite of a minimal decreased on the adsorption capacity was observed in subsequent cycles.

A magnetic chelating resin derived from bisthiourea-thiourea-glutaraldehyde have been evaluated as adsorbents for silver(I) and gold(I) (Atia et al. 2014). The magnetic chelating resins were synthesized mixing bisthiourea-thiourea-glutaraldehyde in the presence of Fe_3O_4 nanoparticles. A great advantage of this chelating resin is that it can be separated from the aqueous phase with a magnetic field, which is positive for technology developments. Possible mechanisms of the adsorption process were investigated. Authors indicates that at the optimal pH value (5.9), complexes are formed between silver(I) and nitrogen or sulfur atoms of the resin chemical structure. Additionally, to silver(I), these magnetic and chelating resins demonstrated to efficiently remove numerous metal ions from a wastewater.

16.2.5 Chelating Surfactants

Chelating surfactants have a hydrophilic head group that has the ability to bind to a metal, based on acid and/or basic major groups, and a hydrophobic tail which confers surface activity to the structure (Eivazihollagh et al. 2019). Chelating surfactants have physicochemical properties susceptible to pH because of the binding characteristics of donor atoms, which are involved in the mechanisms of chelation of metals (Eivazihollagh et al. 2017). The double functionality of the chelating surfactants opens up new areas of application. For example, chelating surfactants have been applied for the separation of metal ions in aqueous solution, and the metals have been recovered from the foam phase by electrolysis (Svanedal 2014).

The application in separation of metals from aqueous solutions is based on the technique known as "ionic flotation", where a surfactant is added to the solution, which is concentrated at the air - water interface with the chelated metal ions, then the flotation produces air injection and the stable foam phase is collected (Micheau et al. 2015). At lower critical micelle concentration of a surfactant, greater efficiency as foaming agent. Surfactants with long hydrocarbon chains are good foaming agents; however, this does not guarantee ionic flotation. The efficiency in the generation of foam depends on the ability of the surfactant for reducing the surface tension and the intermolecular cohesion forces between the surfactants. The ionic flotation technique shows potential in the treatment of large volumes of dilute aqueous solution containing heavy metals and offers advantages such as high selectivity and removal efficiency (Micheau et al. 2018). Figure 16.5 exhibits examples of

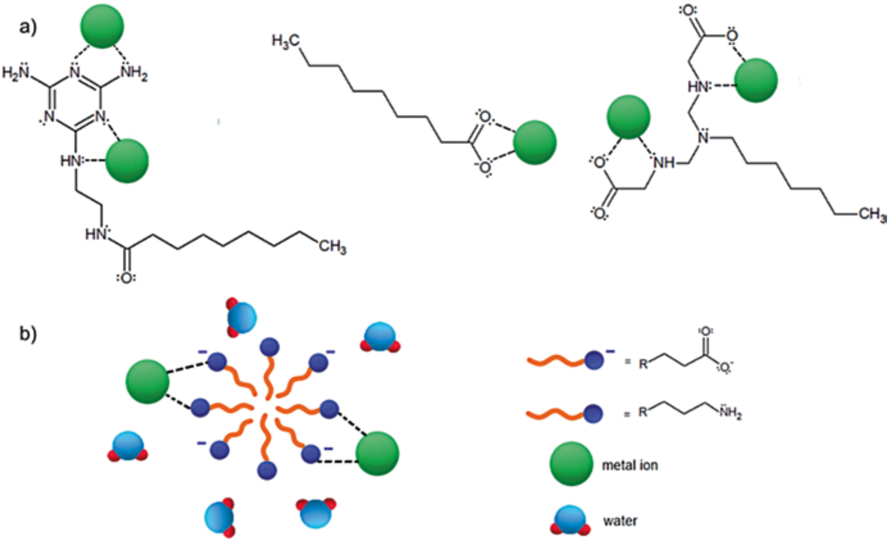

Fig. 16.5 (**a**) Examples of surfactant compounds with chelating capacity. The chelation of the metal ion occurs from the (I) N of amino groups and N of heterocycles, (II) O of carboxylic groups and (III) N of amino groups and O of carboxyl groups of the surfactants. (**b**) Schematic representation of the interaction between ligands of hydrophilic heads of surfactants in a micelle. The metal ions in solution undergo a coordination reaction with ligands that are part of the structure of the surfactant, which can be in free form or as part of a micelle

surfactant compounds with chelating capacity (a) and a scheme of the coordination reaction proposed between a metal ion and the ligands that are part of the hydrophilic head of surfactants that are forming a micelle (b).

Chelating surfactants have been used as chemical agents for the chelation and removal of metal ions present in contaminated water. Hąc-Wydro et al. conducted a comparative study on the selectivity of different anionic surfactants to chelate lead(II) ions (Hąc-Wydro et al. 2016). The effect of the heavy metal ion on the aggregation of anionic surfactants was verified. The surfactants used for the experiments were sodium dodecyl sulfate, sodium N-lauroylsarcosine and sodium dodecylbenzenesulfonate. In accordance with the experimental results, sodium dodecyl sulfate presented the highest chelating capacity to the heavy metal. The authors confirmed that insoluble complexes are formed for all surfactants at lower concentrations than critical micelle concentration, and the precipitates differ in their stability. Furthermore, the researchers indicate that in contaminated water, where the level of surfactant is usually lower than critical micelle concentration, certain metals such as lead(II) could be chelated, generating a stable precipitate, which was subsequently eliminated by sedimentation or filtration.

Bio-surfactants have been usually used to treat wastewater due to the low toxicity and biodegradability. Saleem et al. developed a research work where a bio-surfactant was regenerated and reused to remove heavy metal ions (Saleem et al. 2019). Bio-surfactants were extracted from substrates of the *Ziziphus Spina-Christi* plant, which reduces the cost of production and makes it a greener treatment. The extracts were used for the preparation of colloidal gases for the copper(II) and lead(II) removal from aqueous solution. In a single-stage flotation, poor elimination of the ions was achieved; however, in multi-stage flotation, the lead(II) and copper(II) removal efficiency increased to 90.7% and 88.2%, respectively. The foam collected from the flotation columns was reutilized in the preparation of colloidal gases again. The authors comment that the assayed biosurfactants presents head groups typical of the structure of the saponin molecule, including fucose, galactose, rhamnose, glucuronic acid and quillaic acid, which have the ability to retain metal ions in solution by complexation.

Shen et al. developed an interesting work where polymer-surfactant aggregates were applied to remove cadmium(II), zinc(II) and chromium(III) from aqueous solutions (Shen et al. 2016). Furthermore, the researchers propose a recovery and recycling process of the bound metal ions from flocculated polymer-surfactant aggregate. Something remarkable about this work is that, after 6 cycles, the recovery efficiencies remained above 91%, 86% and 73% for cadmium(II), zinc(II) and chromium(III), respectively. It is also important to emphasize that when recovering and continuously recycling the starting products, the methodology presents significant capacity for saving chemical products and improves the sustainability of the process. According to the authors, the monomers of free surfactant bind to the metal ions, while the monomers that make up the polymer chain also bind to the metal ions. In this way, the complexation is given by both monomers of surfactant and the aggregates.

16.2.6 Chitosan and Derivates

Biopolymers are non-toxic, hydrophilic and biodegradable resources that have recently been used as adsorbents to remove heavy metals (Elgadir et al. 2015; Escudero et al. 2019). Chitosan is one the most abundant biopolymers on earth and is commercially produced by the partial chitin deacetylation, which is principally obtained from the exoskeleton of crustaceans and insects (Kanmani et al. 2017). This biopolymer also occurs naturally in some microorganisms such as fungal cell walls, green algae, as well as in some yeasts and protozoa (Dotto et al. 2017; Kyzas and Bikiaris 2015). Chitosan has a good adsorption ability for heavy metal ions due to the presence of amine and hydroxyl groups (Escudero et al. 2019; Igberase et al. 2019). Chitosan is also very sensitive to pH changes, has low thermal stability and poor mechanical strength, which difficult its use as adsorbent (Wang et al. 2019). However, many researchers have overcome these limitations by implementing chemical or physical modifications to the main structure of chitosan (Zhang et al. 2016).

Moreira et al. described a chemical modification of chitosan in order to make a new biopolymer with improved chemical properties, i.e. insoluble in acidic solutions (Moreira et al. 2018). A chitosan derivative was evaluated for removing copper(II) and chromium(VI) from aqueous solution. The point of zero charge was 9.1. At pH 4.5, the adsorption of chromium and copper on C4 were very similar. Nevertheless, from pH 4.5 the copper(II) adsorption was favored. It is important to note that $HCrO_4^-$ is the predominant species in acidic conditions, being hence C4 a novel adsorptive material not only for cationic but also anionic species (Table 16.2). The adsorption of these ionic heavy metals on C4 followed the pseudo-second order model. The most suitable model to describe the copper adsorption was the Freundlich model, while the Langmuir model described better the adsorption of oxyanions of chomium(VI) on C4. The regeneration study was performed with nitric acid and the result showed a poor desorption, principally of chromium(VI).

A similar study was presented by Almeida et al., where the authors synthesized a chitosan derivative -C2- with zwitterionic characteristics, which was applied for the removal of anionic and cationic species (de Almeida et al. 2016). In this case, C2 was produced by chitosan with methyl iodide and ethylenediaminetetraacetic acid dianhydride. The metal ions were adsorbed through ion exchange and complexation with the carboxylic acid and amine groups of C2.

Shekhawat et al. used simple impregnation of chitosan with a ionic solid, Ethylhexadecyldimethyl ammonium bromide impregnated, for cadmium(II) and mercury(II) removal (Shekhawat et al. 2017). This adsorption occurs by previous formation of chloro-complexes with the metal ions. The mechanism showed that protonated amino groups of chitosan interacted through electrostatic and van der Waals interactions with tetrachlorometalate complexes of cadmium(II) and mercury(II). In accordance with experimental data, the adsorption of both metals on the adsorbent follow pseudo-second order kinetic model. The negative values of free energy, enthalpy and entropy change showed that the adsorption process is spontaneous, exothermic and causes to decrease in randomness in the surface where the adsorption process takes place. Through column adsorption studies, the authors demonstrated that it was possible to pass large sample volumes without saturating the column (1,1 L of 200 mg L^{-1} Cd(II) and 0.9 L of 50 mg L^{-1} mercury(II)). The adsorption efficiency decreased with the number of cycles, from almost 100% to approximately 65% in the tenth cycle.

Several authors are making great efforts to modify the surface of chitosan in a environmental friendly way (Sarode et al. 2018). In this way, Anantha et al. proposed the synthesis of a biopolymer composite with feather waste from a poultry (*Dromaius novaehollandiae*) and chitosan prepared from mushroom species (*Agaricus bisporus*), combined in the ratio of 5:1 in weight (Anantha and Kota 2016). In this work, the results obtained for the removal of lead(II) through a cheap and eco-friendly adsorbent were presented. Lead adsorption was evaluated trough to an initial optimization of experimental variables using a response surface methodology. A removal percentage of 93.5% was achieved at equilibrium time (70 min). Characterization studies suggested that the adsorption involves mechanisms of complexation between lead ions and N-H and O-H present in the adsorbent, chemisorption and ion exchange. The adsorption process obeyed to a pseudo-second order kinetic and followed the Langmuir isotherm model.

Gokila et al. synthesized nanocomposites of chitosan and alginate for removing chromium(VI) from wastewaters (Gokila et al. 2017). Initially, alginate nanoparticles were prepared by ionic gelation method. Then, chitosan nanoparticles were synthetized from chitosan and aqueous acetic acid solution. Afterword, both nanocompounds were mixed in the presence of glutaraldehyde crosslinker for 24 hours and chitosan-alginate nanocomposites were prepared. The optimum adsorption took place at pH 5. At lower pH, there is competition between H^+ and hexavalent chromium for the binding sites and chromium adsorption is decreased. At higher pH values, the formation of soluble hydroxyl complexes also causes a decrease on adsorption efficiency.

Magnetic nanoparticles have been also used in combination with chitosan to remove heavy metals. In this context, Omidinasab et al. used magnetite to synthetize a magnetic chitosan nanoparticles adsorbent to remove vanadium(V) and lead(II) ions from water (Omidinasab et al. 2018). In this work, shrimp shell wastes were used to obtained chitosan and these wastes were washed and passed through a size 50 mesh. To complete of chitin synthesis, sodium hydroxide solution was added and the sample was washed with hydrochloric acid solution to isolated inorganic matter. Then, the chitin was filtrated and washed with water until neutral pH. Finally, chitin was dried at 60 °C for 24 h. A scheme of the magnetic nanoparticules preparation is showed in Fig. 16.6. It is important to highlight that the equilibrium time for vanadium and lead was quickly reached (10 min). In this way, physical and chemical adsorption takes place on the removal of the metals.

An interesting work was also presented by Kong et al. (Kong et al. 2018). As a first step, a chitosan solution was mixed with a copper(II) and nickel(II) solution to quickly chelate the ions. Then, sodium phytate was added into the mixed solution to obtain chitosan-metal ion nanoparticles. Centrifugation was used to separate the

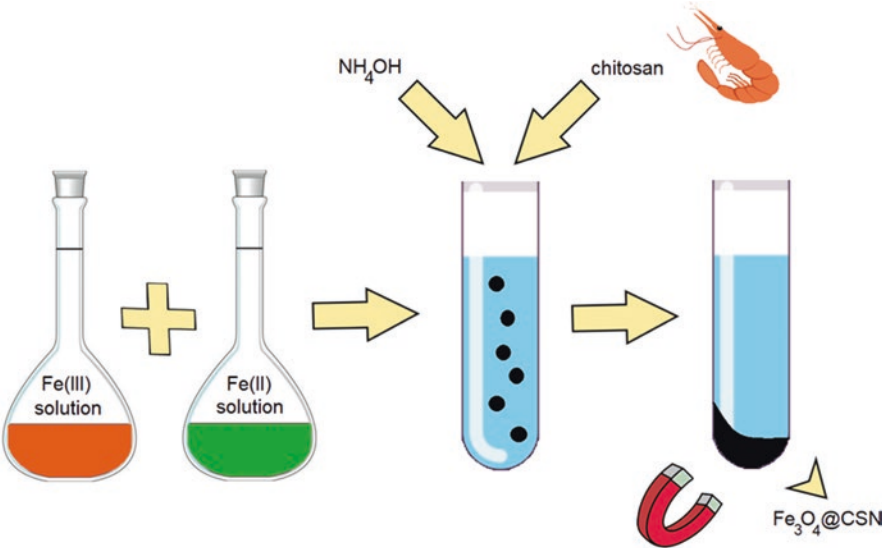

Fig. 16.6 Schematic representation of the synthesis of magnetite (Fe_3O_4) to synthetize a magnetic chitosan nanoparticles ($F_{e3}O_4$-CSN). Firstly, chitosan solution (1 g 100 mL^{-1}) was prepared by dissolving chitosan flakes in glacial acetic acid. Fe_3O_4 nanoparticles were prepared by the co-precipitation of ferrous and ferric salts with a molar ratio of 1:2 by 1.5 mol L^{-1} ammonium hydroxide solution at room temperature. The solution was vigorously stirred, at the same time, the chitosan solution was slowly dripped into the mixture. The prepared Fe_3O_4-CSN were collected using an external magnetic field and then, the excess of ammonium hydroxide was removed with deionized water. (Modified after Omidinasab et al. 2018)

nanoparticles. X-Ray Photoelectron Spectroscopy analysis showed that O and N atoms of chitosan have coordination bonds with the metal ions. The researchers reported that studying the individual solutions of each of the metal ions, the adsorption capacity of copper(II) was greater than that obtained for nickel(II) (405 mg g^{-1} vs. 315 mg g^{-1}). However, due to the competition of these ions for the active sites of chitosan, the adsorption capacity of both metals decreased when both ions were in a single solution.

The removal of copper(II) ions was also reported by Li et al. (Li et al. 2018b). In this work, the use of waste paper and chitosan was proposed. The synthesis of waste paper-chitosan aerogel was very simple. Briefly, chitosan and waste paper were put in contact with NaOH-urea frozen aqueous solution. Finally, the aerogel was obtained after 48 h of lyophilization. The authors demonstrated that a complex was formed by interaction between NH_2 group with copper ions. Kinetic results follow the pseudo-second order model ($R^2 = 0.98614$). The Langmuir model fitted suitably the experimental equilibrium data, showing a uniform chemical adsorption of single molecule layer.

16.2.7 Covalent and Metal Organic Frameworks

Metal-organic frameworks have been used within the coordination chemistry for the elimination of water pollutants, becoming the focus of a large number of investigations in the twenty-first century. Metal-organic frameworks are formed by metal ions or metal groups and organic ligands, connected in three-dimensional cells (Logan 2018). These compounds have been applied for the administration of drugs, gas storage, catalysis and detection of luminescence, bioimaging, among others (Kobielska et al. 2018).

The application of metal-organic frameworks as adsorbent materials has numerous advantages, including high surface area and porosity, which make metal ions more accessible to the adsorption and diffusion sites. Normally, the surface of the metal-organic frameworks ranges from 1000 to 10,000 $m^2 g^{-1}$ and the pores have a specific order based on their crystalline structure (Maurin et al. 2017). On the other hand, trough the selection of organic linkers it is possible to modulate the pore size and shape. Large-scale metal-organic frameworks can be manufactured from simple, low-cost synthetic materials, and can be functionalized through post-synthetic modification, which makes them more selective for certain toxic metal ions. These characteristics make metal-organic frameworks ideal candidates for the sequestration of toxic substances from aqueous solutions (Duan et al. 2016). Thus, it is possible to obtain metal-organic frameworks of complex structure, in a uniform and reproducible way. The properties of metal-organic frameworks are dominated mainly by their degree of structural ordering, hydrophilicity, surface area, functionality and pore size (Li et al. 2019b).

It has been achieved in the last years to improve the elimination performance of different elemental pollutants by metal-organic frameworks through different strategies. (a) Preparation of this compound with longer organic ligands, which facilitates the diffusion of metal ions (Howarth et al. 2015). (b) The design of defects in the metal-organic frameworks by adding to the precursor mixture. This allows to increase the pore size and introduce a greater number of reaction sites. (Wang et al. 2017). (c) Preparation of this compound with organic ligands that incorporate functionality by $-NH_2$, -OH and -SH groups. These metal-organic frameworks provide additional reaction sites and improve selectivity (He et al. 2017). (d) Metal-organic frameworksprepared with a specific functional group bound to the metal (Liang et al. 2016). (e) Hybridization with other functional materials that allows a higher metal removal performance due to the synergistic effect of the components of the hybrid material (Min et al. 2017). (f) Preparation of compounds composites, which prevent the formation of suspensions in water (Rapti et al. 2016). Figure 16.7 exhibits different strategies used in metal-organic frameworks to improve the performance to remove metals from aqueous samples.

A current work by Zhao et al. shows the use of this type of materials of $[Cu_3(btc)_2(H_2O)_3]$, where btc are the acronyms corresponding to 1,3,5-benzenetricarboxylate to remove cerium(III) from aqueous solution (Zhao et al. 2019). The adsorbent allowed obtaining an adsorption capacity of 353 $mg g^{-1}$

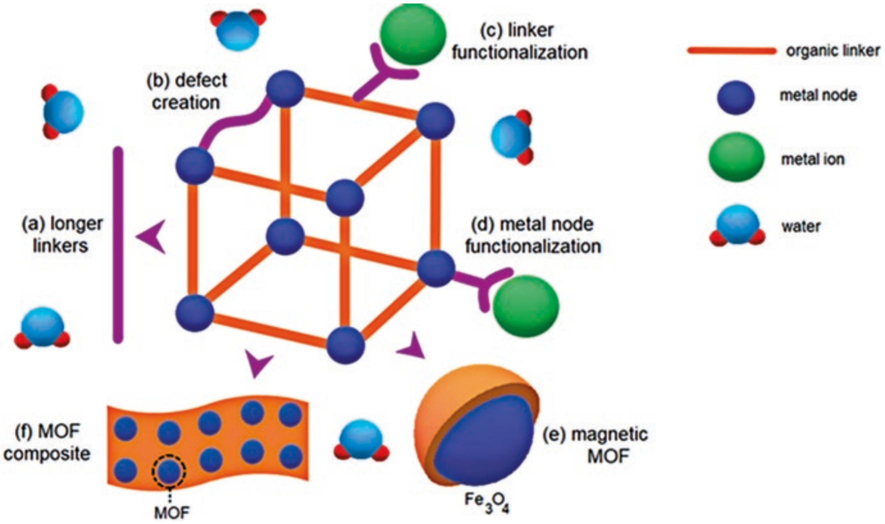

Fig. 16.7 Different strategies used in metal-organic frameworks (MOFs) to improve the elimination of analytes from aqueous solutions. (**a**) increase of the length of the linker, (**b**) creation of a defect in the organic linker, (**c**) functionalization of the organic linker, (**d**) functionalization of the metal node, (**e**) hybridization of the MOF by adding another material, for example, conferring magnetic properties, and (**f**) preparation of composite MOFs. (Modified after Li et al. 2019b)

at pH 6. The isotherm and kinetic results were consistent with Langmuir equilibrium model and pseudo-second order model, respectively. The removal efficiency reached 99% in 30 min using an initial cerium(III) concentration of 200 mg L^{-1} (Table 16.2). The presence of carboxylic groups in the adsorbent confers the complexing capacity of the material, thus allowing the retention of the metal ion of aqueous solutions.

Based on the need to obtain a solid absorbent that allow high removal efficiencies for Hg(II), Li et al. innovated in the transformation of the metal-organic frameworks type structure (Li et al. 2018a). This compound was functionalized with the addition of centers containing zirconium and sufur, conserving the original morphology. This material allowed to obtain a good regeneration capacity and selectivity towards mercury(II), since these ions ions have a complexing capacity with the thiol groups present in the metal-organic framework even in the presence of elemental concomitants. This material showed a regeneration a reutilization for more than 5 times without a significant decrease in the adsorption efficiency. This highly porous and selective material has potential for the decontamination of mercury(II) from wastewater.

Yin et al. synthesized a new modified metal-organic framework with melamine, which was applied to remove lead ions from an aqueous solution (Yin et al. 2018). This material showed a sphere-shaped morphology and a diameter of about 50 nm. Under optimal experimental conditions, the magnetic adsorbent allowed to obtain an adsorption capacity of 205 mg g^{-1}. It was suggested a chelation mechanism between lead(II) ions and amino groups (-NH_2) of the triazine bound to the material.

In counterpart, Zhang et al. reported the use of a metal-organic framework, which allows to effectively and selectively eliminate lead(II) from aqueous solutions (Zhang et al. 2019a). The adsorbent presents the following chemical structure [Bi(triazine-2,4,6-triyl-tribenzoic)]· N,N-dimethylformamide ·$6H_2O$. This material exhibits rapid adsorption kinetics and good adsorption capacity for lead (Table 16.2). Moreover, this material allowed high adsorption rates despite of the presence of different concomitant ions, which makes this methodology potentially applicable for the removal of lead from wastewater. The selective complexation of the metal was explained by the authors from the theory of Hard-Soft-Acid-Base, where in comparison with other metal ions, lead(II) is considered mild acid due to its high volume and high polarizability while other metal ions such as nickel(II), cobalt(II), chromium(III) and manganese(II) are generally considered as hard acid.

Other kind of emergent materials are the covalent organic frameworks, which are porous crystalline materials assembled by symmetrical and rigid organic building blocks through strong covalent bonds, forming an ordered π structure. This material can be of 2 or 3 dimensions, where light elements such as boron, carbon, oxygen and nitrogen are combined, forming covalent bonds of type B-O, C=N, C-N, C=C-N. The design of covalent organic frameworks have been achieved from building blocks, with the use of different organic substances (Chen et al. 2019). These materials offer highly tunable porosity, ordered channels, structural control, large specific surfaces, simple functionalization, low densities, and good chemical and thermal stability. These characteristics have allowed various applications such as gas storage, catalysis, sensors and chromatographic separations (Huang et al. 2016). Currently, the use of covalent organic frameworks as adsorbents has been linked to the removal of specific environmental contaminants (Lv et al. 2019). Figure 16.8

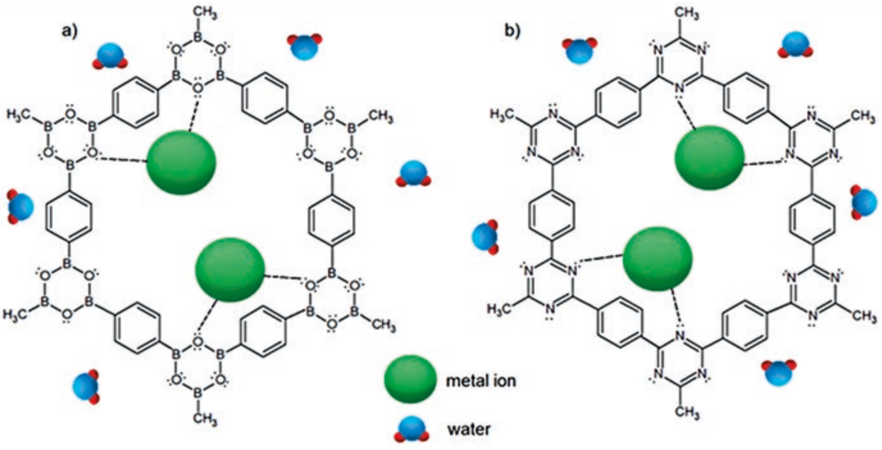

Fig. 16.8 Representation of covalent organic frameworks (COFs) structures. (**a**) Coordinated metal ion through electron pair free of O atoms, which is part of B-O bonds. (**b**) Coordinated metal ion by pair of free electrons of N atoms, which are part of N-C bonds

shows some examples of these structures in which the metal ion is coordinated by the pair of free electrons that have the oxygen and nitrogen atoms of the structures.

For the synthesis of covalent organic frameworks, various methods have been developed that include solvothermic, ionothermic, microwave and at room temperature synthesis. In general, covalent organic frameworks are mainly divided into three classes: (a) those that contain triazine with cyano groups, which are synthesized through nitrile cyclotrimerization; (b) those bound with boronate ester; and those linked by imine and hydrazone, which are constructed by dehydration of aldehydes with amines and hydrazides, respectively (Qian et al. 2018).

Dinari et al. took the advantage of these materials to remove cadmium(II) from aqueous solutions (Dinari and Hatami 2019). Basically, a covalent organic framework with high nitrogen levels was synthesized from the condensation of 2,4,6-tris(hydrazino)-1,3,5-triazine and 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine, achieving a highly ordered material of hexagonal structure. The authors demonstrated that the adsorption isotherms were consistent with Langmuir model and kinetic adsorption with pseudo-second order model. The synthesized material allowed to get a high adsorption capacity (396.82 mg g^{-1}). In addition, this material manages to gather profitable and environmentally friendly properties, easy manufacturing and absence of secondary products.

Li et al. synthesized two covalent organic framework through a polymerization reaction of acyl chloride and amino groups by mechanical ball milling at room temperature applied to remove lead(II) from aqueous solutions (Li et al. 2019a). Linear and aromatic diamine monomers were selected to construct these materials with different structures and functional groups, with ethylenediamine and p-Phenylenediamine to synthetized covalent organic framework with linear and aromatic diamine, respectively. The amide groups in the material skeleton behave as active adsorption sites for the capture of lead ions by multiple coordination. The covalent organic frameworks synthesized with linear diamines allowed a greater internal diffusion of Pb(II), which facilitated the adsorption of the pollutant on the material.

16.2.8 Hybrid Materials for Chelating Metals

In recent years, hybrid materials have been widely proposed to enhance the adsorption performance of different materials. According to several authors, the main strategy is to increase the active sites able to adsorb the target metal (Sajid et al. 2018; Zhao et al. 2018), besides to achieve greater stability, increase the specific surface area of the adsorbent and pore volume (Zhang et al. 2016). In this context, Liu et al. developed a new hybrid chelating polymer to remove copper(II) and lead(II) from wastewater (Liu et al. 2018b). In this work, it was proposed the synthesis of $Al(OH)_3$-poly(acrylamide-dimethyldiallylammonium chloride)- dithiocarbamate. Thermogravimetric analysis demonstrated that the adsorbent was thermostable. Furthermore, the adsorption experiments showed that it is an excellent adsorbent due to the easy access of the ionic metals to its structure and to the complete contact that is achieved between the lead(II) and copper(II) and the new sorbent, thanks to the "star-like" form. The adsorption of lead on the adsorbent was much faster than that reached for copper ions. The adsorption capacities were 246.7 mg g^{-1} and 225.3 mg g^{-1} for lead(II) and copper(II), respectively (Table 16.2). Additionally, the pseudo-second order kinetic model indicated that chemisorption took place in the sorption process. It was demonstrated that three steps influence the adsorption process: (1) transfer of heavy metal ions from the aqueous to the solid phase, (2) intraparticle diffusion of metal ions and (3) equilibrium.

Hosseinzadeh et al. also studied copper(II) removal was from aqueous solutions applying a new hybrid magnetic chitosan-graphene oxide nanocomposite (Hosseinzadeh and Ramin 2018). The scanning electron microscopy image of the material showed that firstly, the nanoparticles were successfully coated on the surface of polymer. Then, it can be also observed that a porous structure was formed on the polymers, which were adequate sites for metal adsorption process. The comparison of the Fourier transform infrared spectroscopy spectra of the adsorbent, before and after adsorption process, confirmed that carboxylate and hydroxyl groups played the main part in the ion adsorption via weak electrostatic interactions or Van der Waals forces.

A similar sorbent composed by graphene oxide-chitosan-ferrite nanocomposite was synthetized to remove hexavalent chromium from water (Samuel et al. 2018a). Metal ion was quantified by UV–visible spectrophotometer at λ_{max} = 540 nm. Transmission electron microscopy image showed the morphology of the adsorbent with a rough external surface, irregular colonies and no visibility of cavities, which is due to that Fe_3O_4 nanoparticles are embedded in the graphene oxide-chitosan. Through a scanning electron microscopy image, it could observe that graphene oxide and chitosan interacted with each other. Also, the presence of carbon, oxygen and iron nanoparticles was confirmed by X-Ray Diffraction analysis. The optimal conditions for removal of chromium were shown in Table 16.2. The results showed a minimum decrease in the removal percentage for each cycle. After ten cycles the % removal decreased from 96 to 80%, approximately.

An ecological hybrid material from the modified silica gel with a bis(pyrazole) butane derivative as a chelating ligand was obtained (Radi et al. 2017). The adsorption capacity towards zinc(II), lead(II), cadmium(II), and copper(II) in aqueous solution was evaluated. In accordance with the authors, the adsorption should be attributed to the chemical bond between ions metal and N-donor sites of the hybrid chelating adsorbent. The maximum adsorption capacity was much higher for zinc than for the rest of the assayed metal ions (Table 16.2). In fact, when the chelating material was studied in batch conditions with a mixture solution containing the four ions metals, it showed an extraordinary selectivity towards zinc compared to the other metal ions. However, the reasons of this selectively were not clearly detailed. The chelating hybrid material was successfully applied in real river samples for the removal of zinc(II). Finally, adsorbent regeneration was studied, and the experimental results showed that after five cycles, the adsorption capacity remained practically constant.

An interesting work was developed by Liao et al. (Liao et al. 2019). Hybrid bio-nanomaterials of nano hydroxy ferric phosphate and hydroxy ferric sulfate particles covering on a filamentous fungi were synthetized. Removal of arsenic(III), cadmium(II), and lead(II) using this sorbent was simultaneously studied in wastewater. The authors informed that the adsorption capacity of the hybrid adsorbent was greatly improved comparing to individual hydroxy nanoparticles. Data from equilibrium studies were in good agreement with the Freundlich model, which suggests that the adsorption of arsenic was produced by multilayer, with a non-uniform distribution over the heterogeneous surface. However, the Langmuir model was the best suited to represent the equilibrium data, revealing a monolayer adsorption process.

Awual et al. proposed a simple and very interesting the synthesis organic-inorganic absorbent to selectively remove lead(II) (Awual 2019). The ligand of 3-(5-ethoxybenzenethiol-imino-methyl)–salicylic acid was synthesized and then, by direct immobilization, was fixed onto the mesoporous silica. The formed complex exhibits a color in UV zone at 340 nm. The signal intensity depends on the concentration of the metal. This important characteristic was utilized by the researcher for determinate the optimum pH (5.5), the sensitivity to lead ion (0.19μg Pb L^{-1}) and the adsorbent selectivity. This last assay was carried out with numerous cations and anions, in which copper(II) presented a small interference in lead(II) analysis only. Lead ions concentration was performed by inductively coupled plasma-atomic emission spectrometry. The results showed that after seven cycles of desorption and regeneration with 0.20 mol L^{-1} HCl, percentage removal decreased only about 6%.

16.3 Conclusions, Trends, and Future Perspectives

This chapter has attempted to present several reports published by the scientific community in recent years, in which chelating adsorbents have been used to remove heavy metals from water samples. In this context, the performance of chelating materials such as membranes, nanomaterials, polymers, resins, surfactants, chitosan, covalent and molecular organic frameworks have been discussed. These particular adsorbents have at least one atom with pairs of free electrons that can form a chelate through their association with the ion metal heavy. As it was possible to observe throughout the chapter, several ions or molecules can act as ligands and hence form metal complexes and chelates. While higher is the number of atoms with free electrons (polydentate ligands), more union points between the ligand and the metal are possible, allowing form more stable chelating compounds with the metal ions and thus improve its removal.

In general, high removal percentages and adsorption capacities were achieved using chelating materials. It is worth mentioning that most of the studies were under statics conditions. Therefore, it is very important the development of more adsorption studies in continuous systems. On the other hand, with the aim of improving the adsorption performance of different adsorbents, hybrids materials seem to offer certain advantages in comparison with common chelating materials. These materials open the opportunity of synthesize novel adsorption materials trough the combination of chelating material and various compounds such as nanoparticles, nanomaterials and even with biomass (waste product, bacteria, fungi, among others). These hybrid materials could offer higher physical and chemical stability, an increased retention capacity, and add notable advantages for more efficient and straight forward use of these sorbents in future industrial processes.

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Chapter 17
Sources of Heavy Metals Pollution

Vhahangwele Masindi, Philani Mkhonza, and Memory Tekere

Abstract Heavy metals emanate from geogenic (natural) and anthropogenic (man-made) sources. These chemical species can poses severe ecological pollution and environmental degradation due to their high toxicity and non-bio-degradable nature. In this book chapter, the sources of heavy metals in the environment, pathways, ecological fate and footprints, eco-toxicological effects, regulatory frameworks, treatment technologies, valorization options and recovery in light of the future perspectives are explicitly discussed. The possible resources to be recovered such as metal hydroxides and their potential economic benefit are explicitly discussed. Furthermore, the avenues for heavy metals recovery in a circular economy concept are highlighted. Thenceforth, this book chapter has shown that the heavy metals could pose mutagenic, teratogenic and carcinogenic effects to living organisms on exposure. The link between heavy metals and various eco-toxicological studies and epidemiological reports are also discussed. Finally, the future research outlooks and potential avenues towards the minimization of ecological footprints of heavy metals pollution are duly underscored.

Keywords Heavy metals · Sources of heavy metals · Effects of heavy metals · Ecotoxicological effects · Pathways of heavy metals · Treatment technologies · Recovery of heavy metals

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17.1 Introduction

According to literature, any naturally occurring element having an atomic number and elemental density which is >20 and 5 g cm^{-3}, respective, is regarded a heavy metal. These metals include: Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Zn, and elements within the platinum group. These elements have a very fine line of toxicity and essentiality to living organisms. Even though, some elements are non-essential to living organisms at all but the ones of paramount concern include Cd, As, Hg, and Pb amongst others. On exposure, these elements can pose hazardous effects to living organisms due to their toxicity and are listed as priority pollutants by numerous organizations and regulatory entities (Babel and Kurniawan 2003; Fu and Wang 2011; Rai et al. 2019; Tangahu et al. 2011; Zwolak et al. 2019).

Furthermore, the aftermath of industrial and agricultural revolution led to intensive utilization of chemicals to enhance productivity in different sectors. This was also encouraged by a rapid increase in demand of goods and services, which can also be, linked to a rapid growth in population. Furthermore, a drastic growth in population has in-turn aggravated the demand of resources from industries. High production in industries is also linked to an increase generation of effluents rich in heavy metals amongst other pollutants. This poses massive impacts to different receiving environment and their precious resources. As such, environmental contamination by heavy metals has perpetually led to the degradation of the environment hence impairing its ability to foster life and render its intrinsic values (Akinwekomi et al. 2017; Masindi 2017a, b; Masindi et al. 2018a, 2019; Mavhungu et al. 2019).

Moreover, heavy metals are somehow referred to as trace elements due to their presence in low concentrations in the environment and living organisms (He et al. 2005). Albeit, they can pose notable environmental impacts to living on exposure, and at very minute levels. In certain instances, continuous deposition of heavy metals have led to eco-accumulation of heavy metals in the environment (air, land, soil) (Ahmed et al. 2019; Al-Khashman 2012; Christou et al. 2014; Feng et al. 2019; Kaur et al. 2018; Vareda et al. 2019). This can be explained by their non-degradable and persistent nature hence posing detrimental impacts to living organisms on exposure (Ayangbenro and Babalola 2017).

Due to their persistent nature, and when bio-consumed, heavy metals can bio-concentrate in living organisms, and bio-accumulate on repeated consumption. When bio-concentrated the fauna and flora, these organisms can die or be consumed, hence bio-magnify or bio-amplify the heavy metals, hence biodegrading the entire food web or food chain. This will eventually lead to the contamination of the whole system. For explanation purposes: Bio-concentration is the intake and retention of heavy metals in the body of the living organism. Bioaccumulation is the intake of heavy metals and their cumulative concentration in the organism. Bio-magnification refer to a process that occurs when heavy metals are transferred from one level to the other in the food chain to higher trophic levels.

Heavy metals are metallic elements with a high density and high atomic weight and they exist naturally within the earth's crust in the form of oxides, carbonates and sulphide (Abraham and Susan 2017; Ashraf et al. 2019; Basu et al. 2009; Chu et al. 2018; Hashim et al. 2011; Hou et al. 2019; Reijnders 2005; Vareda et al. 2019). According to literature, heavy metals has genotoxic, carcinogenic, mutagenic, and teratogenic properties in their matrices and they are more likely to deteriorate the health of living organisms on exposure (Amer et al. 2019; Liao et al. 2016; Liu et al. 2018; Quina et al. 2019; Zhang et al. 2019a; Zhang et al. 2019b). Furthermore, minute levels of heavy metals can pose toxic effects. They may also act as endocrine disruptors and induce developmental and reproduction depression as well as neurological disorders if not properly managed. (Verma and Dwivedi 2013).

Their hazardous and toxic nature makes them elements of environmental concern; hence, they need proper handling and management. These elements are essential for biological, chemical and physical functions of living organisms, but their uptake should be closely monitored since excess amounts can pose detrimental impacts to the cells and tissue of living fauna and flora (Verma and Kaur 2016). Even though heavy metals occur naturally within the environment via weathering processes. Human activities can also contribute towards the degradation of the environment by heavy metals via mining, agricultural, manufacturing, and metallurgical processes amongst others. These activities lead to the enrichment of the environment with heavy metals. Aquatic and terrestrial organisms will suffer from the intake of heavy metals on exposure. However, these organisms get exposure to heavy metals from numerous sources (Verma and Kaur 2016).

Processes that governs the transfer of heavy metals from the environment to living organisms are adsorption, absorption, contacts, ingestion, breathing, and osmotic difference. Their routes of transfer include inhalation, drinking or ingestion, and contact (Ahmed et al. 2019; Arnold et al. 2014; Bur et al. 2012; Christou et al. 2014; Dean et al. 2019; Sarah et al. 2019; Zhuang et al. 2018). In light of that, this chapter will focus on the sources of heavy metals, conditions that are conducive for their release into different receiving environments, spatial distribution, and environmental compartmentalization.

17.2 Heavy Metals Emitting Source

Contamination of the environment by heavy metals has been an ever more pronounced issue. This has been reported to pose both intended and unintended impacts to living organisms. Moreover, man-made and natural processes are the main activities that lead to environmental degradation. These activities can directly and indirectly introduce contaminants into different spheres of the environment. Henceforth, the subsequent sections, different sources of heavy metals are sufficely elaborated.

17.2.1 Point Source

Pollution of the environment by heavy metals can be caused by a source than can be easily identified or mapped used different technique. This can be determined by a traceable source. In that regard, the source for this type of solution is defined as a point-source pollution. In most instances, man-made sources are the major source of point source pollution and this may include mining activities, industrial processes and other forms of development (Ali et al. 2013; Maisto et al. 2011; Singh et al. 2015; Selim and Sparks 2001; Sparks 1995, 2005; Sparks and Sparks 2003). This type of pollution is easy to control since the source and composition is simple.

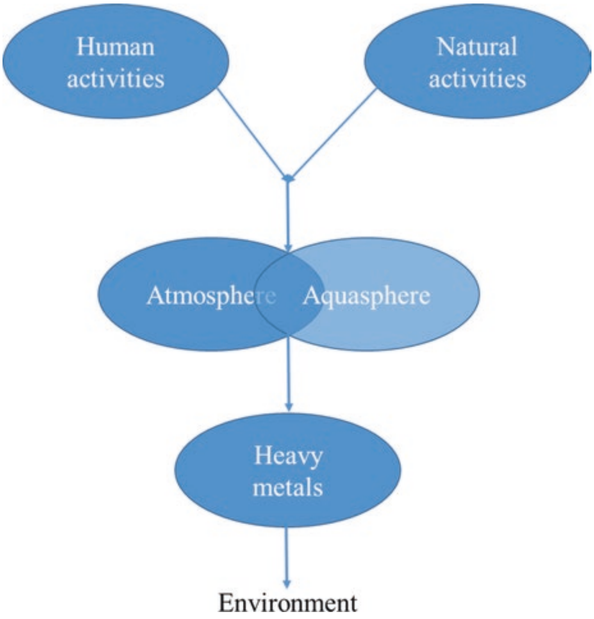
17.2.2 Non-point Source (Diffuse Source)

Non-point source of pollution is a source of pollution that emanate from an undefined sources or different sources of pollution. It represent a cumulative source of pollution. This can be from agricultural activities since they use different types of chemical, municipal effluents since they receive different sort of chemicals from different sources and urban run-offs since effluent can contain chemicals from exhausts and other urban processes. This type of pollution is very difficult to manage since the source is not clearly or well defined. As such, mitigation measure to put in place to control this type of pollution is not easy or practically viable. Mainly, natural processes such as weathering can also results in the formation of this type of pollution to the environment. This makes it hard to manage and contain (Azizullah et al. 2011; Reijnders 2005; Tabassum et al. 2014; Vareda et al. 2019; Wang et al. 2014; Zwolak et al. 2019).

17.3 Sources of Heavy Metals

Most prevalently, heavy metals can be found as hydroxides, oxides, sulphides, sulphates, phosphates, silicates, carbonates, and organic matrix amongst others. They emanate from natural and anthropogenic sources (Selim and Sparks 2001; Selim et al. 2001; Sparks 1995, 2005; Sparks and Sparks 2003; Langmuir 1997; Langmuir et al. 1997). However, anthropogenic sources has been classified as the main source and route in which heavy metals are distribute to different compartments of the environment. Transport media are mainly water, soil and air. Heavy metal laddened fractions will be released to the atmosphere, aqua-sphere and the terra-sphere via those transport media (Langmuir 1916, 1918, 1997; Langmuir et al. 1997). A process depicting different sources of heavy metals and their trans-sphere migration is shown in Fig. 17.1 below.

Fig. 17.1 A process depicting different sources of heavy metals and their trans-sphere migration



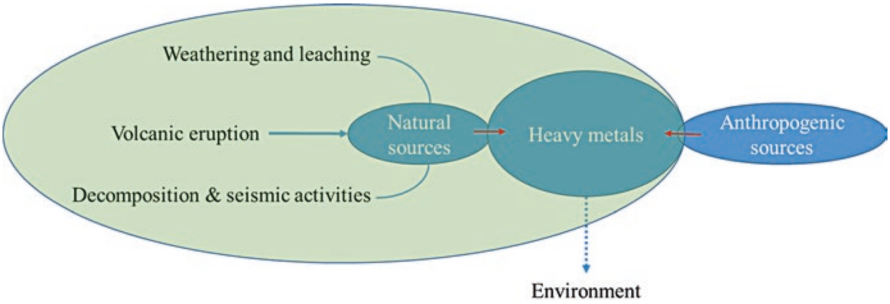


Fig. 17.2 A schematic demonstrating the process flow of heavy metals and their trans-sphere migration in a natural process

17.3.1 Natural Sources

Naturally, heavy metals can emanate from the following processes: leaching, weathering, volcanic eruptions, decomposition, and seismic activities amongst others (Langmuir 1997; Langmuir et al. 1997; Selim and Sparks 2001; Selim et al. 2001; Sparks 1989, 1995; 2005; Sparks and Sparks 2003). A schematic configuration demonstrating the process flow of heavy metals and their trans-sphere migration in a natural process is shown in Fig. 17.2.

17.3.1.1 Weathering

Weathering refers to a process, which breaks down rocks, soil, and minerals via their contact with the atmosphere, water, and living organisms. Weathering is an onsite process and it does not involve the movement of weathered materials. Specifically, weathering can be a physical, biological, and chemical process. Physical weathering entails the breakdown of heavy metals containing minerals via direct contact with micro-climatic conditions such as heat, water, ice and pressure. On the other hand, chemical weathering entails the reaction of chemicals in the rocks with micro-climatic conditions leading to the release of heavy metals from the host rock to the surrounding environment. Both physical and chemical weathering can occur concomitantly or subsequently in any given system. To be precise, a macule process which entails the physical abrasion of soil or rock particles by their movement of their surface leading to a reduction in their respective sizes hence increasing surface area, and making them more susceptible to chemical reactions and chemical attacks. Biological process entails the breaking down of rocks and soil molecules in the quest for nutrients for plants growth or for microorganisms to survive. The abstraction of nutrient leaves the rock vulnerable to other reactions. Breaking of rocks by plant roots to anchor a tree also lead to rocks disintegration and weathering. Minerals will therefore, be broken down into minute molecules and get converted to secondary minerals in certain circumstances (Selim and Sparks 2001; Selim et al. 2001; Sparks 1989, 1995, 2005; Sparks and Sparks 2003; Langmuir 1997; Langmuir et al. 1997). Minerals from the weathered rocks comprise problematic heavy metals that are of paramount concern in the environment. Colloidal chemistry has denoted that, heavy metals exist as abundant trace elements in the earth crust with the concentration of metals ranging from ppm to ppb (He et al. 2005). This also communicates to their toxicity since these elements are valuable to living organisms, however, to a certain extent or limit. Moreover, due to geochemical processes, heavy metals are released from the surrounding geologies, lithologies and strata to the environment. This also depends on a number of factors such as the physical activities taking place in the weathered area, micro-organisms to aid in the leaching processes, and the chemistry of the rock being attacked by aqueous medium. Natural weathering of bedrock has often resulted in the release of these metals into the environment and led to the enrichment of soil particles with heavy metals. Other natural processes that result in the release of heavy metals are volcanic eruptions, decaying of vegetation, comets, erosion due to insufficient soil cover and heavy rainfall (De Vivo et al. 2018).

17.3.1.1.1 Factors that Influence the Release of Metals from Rocks

pH

pH refers to the acidity and basicity of the solution (Langmuir 1997; Langmuir et al. 1997). It ranges from 1 to 14 (Fig. 17.3). Natural processes also influence the pH of the receiving environment. Reaction of atmospheric gases and geological materials also alter the pH of the receiving environment. For instance, in regions where sulphur and nitrogen gases are emitted, the rain from such areas will be acidic due to atmospheric reaction, thus leading to acidic precipitation. However, rain is naturally neutral or circum-neutral but atmospheric reactions affects its pH (Langmuir 1997; Langmuir et al. 1997; Selim and Sparks 2001; Selim et al. 2001; Sparks 1989, 1995; Sparks and Sparks 2003). In that regard, sulfur dioxide and nitrogen oxides are the main culprits in the atmosphere that lead to acid rain in addition to carbon dioxide that cause carbonic acid. These oxides react in the rainwater to produce stronger acids hence reducing the pH of the water to acidic state. Sulfur dioxide emanate from combustion of fossil fuels whereas nitrogen oxides comes from vehicles (Ahoulé et al. 2015; Candeias et al. 2018; Coelho et al. 2011; Flora 2015; Gulis et al. 2004; Nriagu 2011; Nriagu 1992; Zwolak et al. 2019). Highly soluble minerals such as evaporites will weather easily leading to the enrichment of waterbodies with heavy metals. Oxidation of sulphide bearing minerals will also contribute to the enrichment of water with heavy metals. Acidity from weathering of sulphide bearing rocks will leach metals from the surrounding geology hence increasing the dissolved heavy metals. However, weathering of carbonates such as limestone will lead to a neutral drainage that is rich in base metals. In that regard, that the reason you find neutral drainage or circum-neutral drainage in heavily mined areas with elevated levels of sulphide bearing minerals. However, heavy metals mainly precipitate with an increase in pH, as such, the carbonates will neutralize the formed acid mine drainage or acidic effluents to generate product minerals which are neutral (Langmuir 1997, Langmuir et al. 1997). A schematic presentation of pH and dominant species is shown in Fig. 17.3 below. The product pH determines the types of species to be available in a given aqueous medium. Mainly, pH is measured using pH probes. It is also used to determine the solubility of chemicals in aqueous medium.

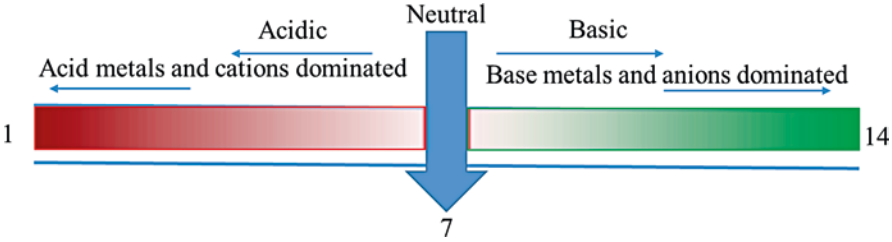


Fig. 17.3 A schematic presentation of pH

Temperature

Temperature denotes the difference between hotness and coldness. It is measured using a thermometer and it can influence the rate at which chemical reactions takes place. High temperature favor the dissolution of numerous compounds whereas low temperatures favors crystallization of numerous compounds in aqueous medium and soil fractions. In that regard, temperature influence the distribution of pollutants in the environment and their fates (Langmuir 1916, 1918, 1997; Langmuir et al. 1997).

Surface Area

Surface area denotes the surface of the material that is available for chemical reaction. This phenomenon is also linked to particle size since the lower particle size has high surface area and big particles has small surface area. According to literature, small particles has high surface area and they are susceptible to all forms of weathering whereas big particles has low surface area and they are resistant to numerous type of weathering. This parameter dictate how soil particles will release or adsorb heavy metals from soil fraction to the aqueous medium or any interaction thereof. The surface area of a substance can be determined using the Brunnet-Emmet-Teller (BET) (Selim and Sparks 2001; Seshadri et al. 2013; Sparks 1989, 1995).

Other Factors

Dissolution of heavy metals from soil matrices to the receiving water bodies and precipitation of metals from the aqua-sphere to the environment is some of the factor that influence the availability of heavy metals in the environment. These factors are governed by pH of the host environment. The equilibria of the solid phase is heavily dependent on those factors since they dictate the mobility, weathering, and precipitation of heavy metals in different spheres of the environment. These parameters depends on the saturation of the aqueous system. Super-saturation favors precipitation whereas under-saturation favors dissolution. The oxidation state of elements in the environment also influence the mobility of different contaminants. This is also dependent on the pH of the solution (Selim and Sparks 2001; Selim et al. 2001; Sparks 1989, 1995, 2005; Sparks and Sparks 2003).

17.3.1.2 Leaching

Leaching is the release of heavy metals from soil matrices using different leachants. A Leachant can be water, acid, base and other organic compounds. In most instances, rainfall and rocks fractures on the surface, the leachable fraction get into contact with aqueous media hence leading to the leaching of metals from the surrounding geology. This also depends on a number of factors such as the pH of the leaching solution, the buffering minerals, solubility and susceptibility of the rocks. In the chemical processing industry and metallurgical processes, leaching has a numerous applications, including separation of metal from ore using acid, and other leachants. Leaching is influenced by desorption, complexation processes as affected by pH, redox, dissolved organic matter and microbiological processes. The process itself is universal, as any material exposed to contact with water will leach components from its surface or its interior depending on the porosity of the material considered hence water is a universal solvent (Langmuir 1997; Langmuir et al. 1997; Alloway 1990; Bradl et al. 2005; Zhong et al. 2011).

17.3.1.3 Volcanic Eruption

Volcanic eruption is a natural process. It lead to the emission of particles to the earth surface. In most instances, the ash from volcanic eruptions also contain heavy metals that are toxic to the environment and living organisms. They usually get transported to the environment during rainfall since they will be washed off to the environment. Volcanic dust which is a component of volcanic ash, that get ejected during volcanic eruptions. They usually fly under the influence of wind, and then falls onto the ground during rainfall and when conditions are favourable. Volcano is formed from the dissolution of metals from the earth crust hence the resultant product is rich in heavy metals. According to the literature, volcano ash can contain Pb, Zn, Cu, Cd, Cr, Fe, and Al amongst other contaminants (Huff and Owen 2015; Liu et al. 2009, 2013). The trace metals contained in the volcanic dust falling onto ground migrate to the soil where they dissolve in water depending on redox, temperature and pH and they then get adsorbed by soil particles (Brey 1978; Delmelle and Bernard 2000; Forbes 1860).

17.3.1.4 Seismic Activities

Seismic activities such as earthquakes lead to the release of heavy metals into the environment. During earthquake the underground geology, get fractured hence exposing oxidisable and reactive materials to oxidizing conditions. During rainfall and underground leakages, water will react with fractured components of the soil hence leading to the release of heavy metals to the environment (Edwards and Pojeto Jr. 1997; Kawabe et al. 2012; Leclère et al. 2018; Shibata et al. 2012; Simonen et al. 2018).

17.3.1.5 Decaying of Organic Matter

Living organisms absorb metals and other chemicals as their nutrients. These nutrients or metals are essential for their growth. To a certain extent, plant can phytoremediate the soil hence accumulating all the metals on its matrices. When they die and decompose, those contaminants goers back to soil and they also lead to a release of metals to the environment. When they die and decompose, these nutrients are released back into the environment. The most common heavy metals found at contaminated sites are Pb, Cr, As, Zn, Cd, Cu, and Hg amongst others. These metals can bioaccumulation and bio-magnification in the food chain since they are available in the body matrices of decaying organic matter (Giuffréde López Carnelo et al. 1997; Hyks et al. 2009; Idaszkin et al. 2017; Ngulube et al. 2017; Singh et al. 2006; Yuan et al. 2013; Zhang et al. 2018).

17.3.2 Anthropogenic Sources

A map depicting different sources of heavy metals is shown in Fig. 17.4.

Increases in socio-economic activities due to population growth have been linked to the rapid increase of heavy metals present in the environment. Human activities such as mining, ore processing, agriculture and power production contribute immensely in metal contamination. Domestic activities such the use of laundry detergents also contribute to the concentration of heavy metals in wastewater which has adverse effects during reuse of the water for irrigation and during sludge disposal (Aonghusa and Gray 2002). The amount of heavy metals released by these activities varies with mining activities reportedly resulting in significant rates of contamination when compared to other activities and have long lasting consequences on the environment even when mining activities have ceased (Mohammed et al. 2011). Anthropogenic sources of heavy metals can be divided into two main categories namely; agricultural and industrial activities (Bradl 2005).

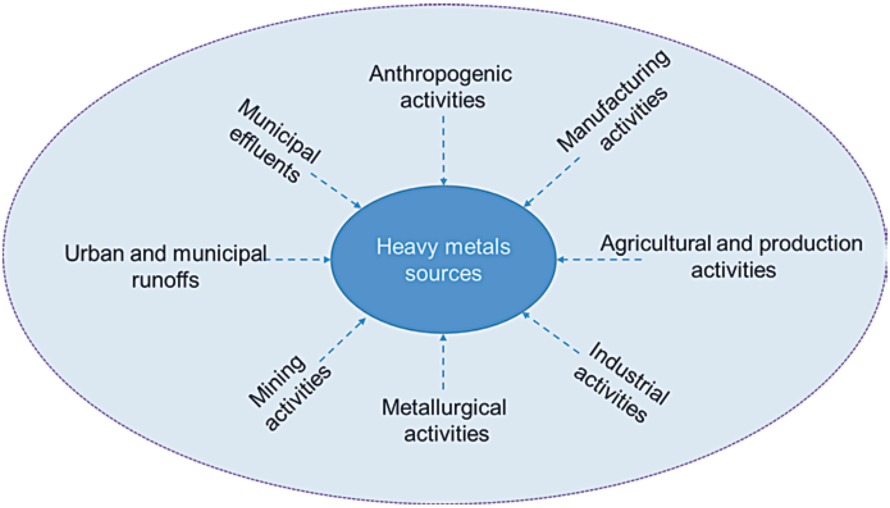


Fig. 17.4 Man induced sources of heavy metals in the environment

17.3.2.1 Agricultural Activities

The use of pesticides and soil amendments (organic and inorganic) is required in order to meet the increased demands in food production. Organic soil amendments include the by-products of processing mills such as sawdust and waste such as sewage sludge and bio-solids. The use of these pesticides and soil amendments introduces heavy metals into the environment and the extensive use of them result in contamination of surface waters and aquifers during different erosional processes (Azizullah et al. 2011; Diagboya and Dikio 2018; Marie 2019; Sophia and Lima 2018; Zhang et al. 2015).

17.3.2.1.1 Pesticides

Pesticides are chemicals or compounds that are designed to kill or stop the growth of pests (fungi, weed, and insects amongst others), with herbicides designed for weed, fungicide for fungi and insecticide for insects (Wallace 2015). Phenylmercuric acetate (fungicide) and lead arsenate (insecticide) are some of the many pesticides used in fruit plantations, and these pesticides contain heavy metals such as mercury, arsenic and lead which contaminate the environment on exposure (Bradl 2005). The usage of metal-based pesticides has since been discontinued due to their toxicity and adverse effects on human health (Bradl 2005). However, they drastically contribute to an increase in the concentration of heavy metals in the environment (Azizullah et al. 2011; Marie 2019; Sophia and Lima 2018; Zhang et al. 2015).

17.3.2.1.2 Soil Enhancers

Soil amendments are important in replenishing nutrients in the soil and keeping it suitable for agriculture hence the use of bio-solids, sewage effluents and fertilizers. Bio-solids are organic materials present in animal waste, sewage sludge and industrial waste such as pulp sludge from the production of paper (Adriano 2001). These solids are used for soil enhancement because of the nutrients they contain and their ability of improving the properties of soil such as pH, porosity, fertility, and water retention (Silveira et al. 2003).

Bio-solids do not only contain soil enrichment nutrients but they also contain heavy metals such as Pb, Ni, Cd, Cr, Cu and Zn, which are toxic in high concentrations. The concentration of heavy metals present in bio-solids is determined by the source of waste with domestic waste resulting in bio-solids with lower concentrations than industrial waste (Bradl 2005). Different sludge treatment methods are available and they have different rates of heavy metal removal, which affects the amount of metals present in the sludge (Yoshizaki and Tomida 2000).

The application of fertilizers is essential in improving the quality of soil and improving agricultural yields as fertilizers contain nutrients, which are important for plant growth and nutrition. The overuse of macronutrient fertilizers (nitrogen, phosphate and potassium also known as NPK) leads to the leaching of these nutrients and the contamination of water resources and causing eutrophication (Goncalves et al. 2014). This phenomenon is prevalent in developing countries where extensive agriculture is predominant. This occur when a receiving environment enriches the water bodies with nutrients. The introduced nutrients will foster the growth of aquatic plants. Another concern with the use of fertilizers is the presence of heavy metals within them such as Cd, As and Pb. The presence of these metals varies with each fertilizer with phosphate based fertilizers demonstrating the presence of high levels of trace metals especially cadmium which is the most toxic heavy metal (Goncalves et al. 2014). Different rocks are utilised for the production of phosphate-based fertilizer and the type of rock used has an influence on the amount of heavy metals present, as sedimentary rocks tend to have higher cadmium concentrations than magmatic rocks (Bradl 2005).

The usage of sewage effluent for cropland irrigation is a cost effective method for recycling nutrients in order to maintain the quality of the soil whilst also ensuring the reuse of water resources. It is essential that appropriate irrigation together with high-level water monitoring be imposed in order to prevent overloading the soil with macronutrients and heavy metals, which are constituents of sewage effluents (Feigin et al. 1991). The plant uptake or absorption of these metals is affected by the presence of natural organic matter within the soil as organic matter influences the solubility of these trace metals (Feigin et al. 1991).

17.3.2.2 Mining Activities

Mining of valuable minerals lead to the exposure of minerals and associated fractions to different weathering conditions. This lead to the enrichment of the environment with heavy metals. This is attributed to the fact that miners attempts to unearth a number of other mineral resources associated with the desired minerals hence exposing them to a number of earthly processes such as air and rain. These ingredients foster the weathering of mineral resources. For example, mining of gold, coal and other precious metals lead to the exposure of sulphide bearing minerals to oxidizing conditions as shown in Table 17.1 (Amos et al. 2015; Baker and Banfield 2003; Dold 2017; Fernando et al. 2018; Johnson and Hallberg 2005; Kefeni et al. 2017; Mayes et al. 2009; Park et al. 2019; Pozo-Antonio et al. 2014; Simate and Ndlovu 2014).

The chemical constitution of the resultant drainage depends on the composition of mother rocks being explored. The mine drainage can be acidic, neutral and basic but this depends on the mineral being weathered. More prevalently, AMD is

Table 17.1 Sulphide bearing minerals that lead to the formation of metal rich drainage

Mineral phase	Composition	Mineral phase	Composition
Pyrite	FeS_2	**Molybdenite**	MoS_2
Marcasite	FeS_2	**Millerite**	NiS
Pyrrhotite	Fe_xS_x	**Galena**	PbS
Chalcocite	Cu_2S	**Sphalerite**	ZnS
Covellite	CuS	**Arsenopyrite**	FeAsS
Chalcopyrite	$CuFeS_2$	**Cinnabar**	HgS

characterized by acidic pH that ranges from 1 to 4. The acidic nature of AMD lead to the leaching of metals from the surrounding rocks and supporting structures including lithologies hence enriching the receiving environment with iron, manganese, aluminium, sulphate, and potentially toxic and hazardous heavy metals such as lead, copper, mercury, cadmium and zinc. Acid mine drainage has been declared a problematic legacy of mining the sulphide rich ore deposits (Sheoran et al. 2011; Peretyazhko et al. 2009; Johnson and Hallberg 2005; Bálintová and Singovszká 2011). It contains chemical species that are potentially toxic to terrestrial and aquatic organisms on exposure (Sracek et al. 2004). As such, this effluent emanating from mining activities needs to be contained and treated to prevent contamination of receiving aquatic ecosystems.

17.3.2.2.1 Formation of Acid Mine Drainage (AMD)

Acid mine drainage (AMD) is formed from the oxidation of sulphide minerals leading to the formation of a metalliferous drainage which is very acidic. The acidic nature of the resultant drainage leaches heavy metals from the surrounding stratas hence enriching the receiving environment with notable amount if heavy metals. Microorganisms also facilitate the AMD formation reactions (Zhao et al. 2012; Hallberg 2010; Candeias et al. 2014; Amos et al. 2015). Below is the equation that denotes the oxidation of sulphide minerals, using pyrite as an example (Amos et al. 2015):

$$2FeS_{2(s)} + 7O_{2(g)} + 2H_2O\ bacteria \rightarrow\ 2Fe^{2+}_{(aq)} + 4H^{+}_{(aq)} + 4SO^{2-}_{4(aq)} \quad (17.1)$$

17.3.2.3 Chemistry of Acid Mine Drainage and its Generation

The formation of AMD from pyrite can be represented by three basic chemical reactions, pyrite oxidation, ferrous oxidation and iron hydrolysis (Eq. 17.2). Pyrite (FeS_2) is the dominant form of sulphur mineral in coal and gold lithology and stratigraphy. During pyrite oxidation sulphur is oxidized to sulphate and ferric iron is released (Eqs. 17.2, 17.3, 17.4 and 17.5). The acidity formed promotes leaching of other minerals (Al, Mn and trace metals) which are associated with the mined strata (Zhao et al. 2012; Sracek et al. 2004; Amos et al. 2015).

17.3.2.3.1 Chemistry of Pyrite Oxidation

During pyrite oxidation, ferrous iron and the sulphur are oxidized; however, water and oxygen are the ingredients that facilitate the oxidation process. Aerobic conditions favours the availability of Fe(III) into the aqua-sphere (Eqs. 17.2, 17.3, 17.4 and 17.5) (Zhao et al. 2012; Sracek et al. 2004; Amos et al. 2015; Sheoran et al. 2011; Sheoran and Sheoran 2006; Peretyazhko et al. 2009; Nordstrom et al. 2015; Johnson and Hallberg 2005).

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{\ 2-} + 4H^+ \quad (17.2)$$

Initial oxidation of FeS_2 leads to the formation of ferrous iron (Fe(II)), ($SO_4^{\ 2-}$) sulphate and (H^+) acidity. In addition, Fe (II) and $SO_4^{\ 2-}$ are colourless hence the water is clear.

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (17.3)$$

Thereafter, Fe(II) react with O_2 and H^+ to form ferric (Fe(III)) ions and (H_2O) water. The conversion of Fe(II) to (Fe(III) consumes a mole of acidity (H^+).

$$4\mathrm{F}e^{3+} + 12H_2O \rightarrow 4Fe\left(OH\right)_3 + 12H^+ \quad (17.4)$$

Furthermore, Fe(III) hydrolyse in water to form $Fe(OH)_3$ hence generating more moles of acidity. In a similar fashion, other metals such as Al, Zn, and Cu amongst others may also undergo hydrolysis depending on pH hence making it much more viable to recover valuable minerals as the pH increases.

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{\ 2-} + 16H^+ \quad (17.5)$$

Lastly, the oxidation of recurring pyrite or other metals by ferric iron can take place. The Fe(III) is generated in reaction steps 1 and 2. This is the cyclic and self-propagating part of the overall reaction and concomitantly takes place very rapidly and continues until either ferric iron or pyrite and other metals are depleted from the system. In this reaction, Fe(III) is the oxidizing agent, not oxygen and water. Fe(II) and Fe(III) in solution are the source of acidity due to their reactions that lead to acidity (H^+).

In that regard, contamination of surface and subsurface water by AMD has raised public concern globally. This is attributed to the nature of toxic and hazardous heavy metals that has the potential to degrade the receiving compartment of the environment and their ability to sustain life (Torres et al. 2014; Simate and Ndlovu 2014; Netto et al. 2013; Mapanda et al. 2007; Macedo-Sousa et al. 2007; Levings et al. 2005; Gray and Delaney 2010; Gray and Vis 2013; Zhao et al. 2012; Sracek et al. 2004; Sheoran et al. 2011; Quispe et al. 2013; Peretyazhko et al. 2009; Nordstrom et al. 2015; Kim 2015; Johnson and Hallberg 2005; Frempong and Yanful 2006; Cheng et al. 2009).

17.3.2.4 Chemical Composition of Acid Mine Drainage in South Africa

Typical composition of acid mine drainage in South Africa. This effluent is substantially rich in heavy metals; however, this is dependent on the type of AMD and their respective pH since they are defined according to pH.

Gold mining AMD (Tutu et al. 2008), Coal mining AMD and, neutral drainage water (Madzivire et al. 2010, 2011, 2013, 2014; Masindi et al. 2014; Gitari et al. 2008; Gitari et al. 2006).

Table 17.2 The relevant criteria for discharge of acidic and sulphate-rich water as compared to DWS water quality guidelines

Parameter	AMD: Gold mining	AMD: Coal mining
pH	2.3	2.5
EC	22,713	13,980
Na	248.4	70.5
K	21.6	34.2
Mg	2.3	398.9
Ca	710.8	598.7
Al	134.4	473.9
Fe	1243	8158.2
Mn	91.5	88.2
Cu	7.8	–
Zn	7.9	8.36
Pb	6.3	–
Co	41.3	1.89
Ni	16.6	2.97
SO_4^{2-}	4635	42,862

As shown in Table 17.2, Acid mine drainage emanating from coal and gold mining in South Africa is rich in dissolved Fe, Al, Mn, Ca, Na, Mg and traces of Cu, Co, Zn, Pb and Ni (Akinwekomi et al. 2017; Commission 2010; Dabrowski et al. 2014; Hobbs and Kennedy 2011). The quality of these water is above the required standards, limits and specifications. In that regard, it can be noted that this kind of effluent can pose massive environmental impacts to different receiving environment on discharge.

17.3.2.5 Industrial Activities

Industrial activities are considered as major contributors of heavy metals towards environmental contamination (He et al. 2005). Industrial sources of heavy metals include the mining of minerals from the earth's crust, metallurgical processes such as ore processing, energy production and the disposal of waste (Tchounwou et al. 2012). Metallurgical processes also lead to the contamination of the environment.

17.3.2.5.1 Mineral Exploration

Mining is one of the most significant activities towards economic growth and development of many countries. Increased mining activities, poor mining methods, lack of research and lack of resources have led to mining being one of the major sources of contamination of water bodies (Mensah et al. 2015). Mining results in waste mainly present as tailings and depending on the type of mining method used, ore rocks together with tailings are exposed to oxidizing conditions (water and oxygen) which results in the weathering of these rocks, leaching of heavy metals and the subsequent formation of metal rich acid mine drainage (AMD) (Saleh 2018). Petroleum contains heavy metals and crude oil spillages are some of the major contributors of heavy metal contamination within the environment especially near drilling rigs in oil producing countries (Akpoveta and Osakwe 2014).

17.3.2.5.2 Energy Production

A rapid growth in population, industrialization and urbanization have proportionally contributed to a rapid demand of energy to power numerous activities that are fundamental to human needs. Renewable source of energy have been advocated for since they are environmentally friendly, however, they do not produce sufficient energy. In that regard, the combustion of fossil fuels such as coal and petroleum remains the major sources of energy irregardless of their detrimental consequences on the environment, human and animal health (Sadorsky 2014). During energy production, fly ash is produced as a by-product since coal is mainly used for power production. Moreover, depending on the chemical composition of parent coal materials used, degree of coal preparation, cleaning and pulverization conditions, and the prevailing climate, the composition of coal fly ash tends to vary widely (Adriano et al. 1980; EPRI 1986; Openshaw 1992; Daniels et al. 2002; Fatoba 2008; Petrik et al. 2005). According to Gitari et al. (2006), Coal fly ash is a ferro-alumino silicate material dominated by Al, Si, Fe, Ca, K, S, Mg and Na oxides in concentration higher than those found in the parent coal along with carbon, nitrogen and various trace elements which includes As, B, Be, Cd, Co, Cr, Cu, Ga, La, Mn, Hg, Ni, Pb, Sc, Ag, Tn, Sr, V, Y, Zn and Zr (Table 17.2) (Smith et al. 1980; Young 1993; Iyer 2002; Daniels et al. 2002; Petrik et al. 2005; Gitari et al. 2006; Mahlaba et al. 2011; Kearsley and Wainwright 2003; Koukouzas et al. 2011).

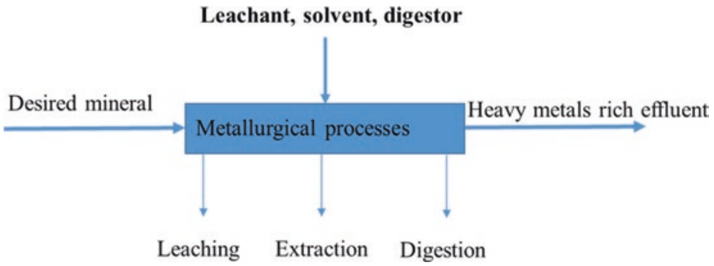
In that regard, fly ash is concentrated in heavy metals is the main coal residue from the combustion of coal for power generation (Mupambwa et al. 2015). The type of coal (lignite, bituminous, anthracite) used for power generation and the combustion conditions (reaction temperate) have an effect on the concentration of heavy metals present in the fly ash (Bradl 2005). Fly ash is recycled and utilized in the construction industry however, the rate of its production is higher than its consumption rate resulting in most of ash ending up in dumps sites and ash ponds, which results in the leaching of, trace metals into groundwater.

The aforementioned trace elements are partitioned on fly ash because they are more volatile and fly ash remains in the burner for a shorter period of time during combustion so they are released altogether with fly ash. On cooling those elements form spherical amorphous particles or coat the ash particles during condensation (Kutchko and Kim 2006; Natusch et al. 1975, Iyer 2002). Some elements occur in higher concentrations than the ones found in soil for example, Al, Ca and Fe occurs in concentrations which are similar to the ones that are found in soils. Na is available in concentrations generally exceeding the ones found in soils. The S content of fly ash is greater relative to soil and it plays a significant role in maintaining the pH of fly ash leachates which normally ranges from 4.5 to 12 (Mattigod et al. 1980; Murarka et al. 1991).

Trace elements (As, B, Pb, Ni, Se, Sr, V and Zn) occur in higher concentrations in fly ash relative to coal and soil (parent materials). The mineralogical composition of fly ash is determined by the parent coal material because each coal has varying mineralogical composition. The combustion temperature affects the degree of volatilization of some minerals (Gitari et al. 2006). Moreover, there is a relationship between particle size and element composition of coal fly ash (Iyer 2002). Petrik et al. (2005); Davison et al. (1974) reported that there is an increase in elemental composition with a decrease in particle size for the following elements: As, Cd, Cu, Ga, Mo, Pb, S, Sb, Ti and Zn, these elements tend to be present as sulphide minerals or associated with organic fractions, and they are more volatile during combustion and tend to become enriched in particle size surfaces than silicate and oxides. But the non-volatile matter (Al, Fe, Si, Mn, Mg, Ba, Ca, Ti, Co, Ce, Eu, Hf, La, Rb, Sc, Sr, Ta, and Th) elements shows little partitioning by particle size. There are elements such as Na, K, Be, Cr, Ni, Sc, U, and V which show intermediate partition behavior (Adriano et al. 1980). Their concentration gradient is caused by the volatilization of element on combustion followed by their consecutive condensation on fly ash spherules. The most volatile element condenses the last on small particles. When elements are partitioned on small particles in higher concentration, the easier it takes to be leached when they are in contact with the aqueous media (Adriano et al. 1980; Eary et al. 1990; Petrik et al. 2005; Fatoba 2008).

17.3.2.5.3 Metallurgical Processes

Post mining activities, desired minerals are taken to metallurgical house for purification. This process involves the extraction of valuable minerals for further processing. During the process, unwanted materials known as residues are also produced and they include heavy metals. Reclamation or re-mining of minerals from tailings can also lead to production of a stream of heavy metals that are problematic to the environment (Chmielewski et al. 1997; Reijnders 2005).



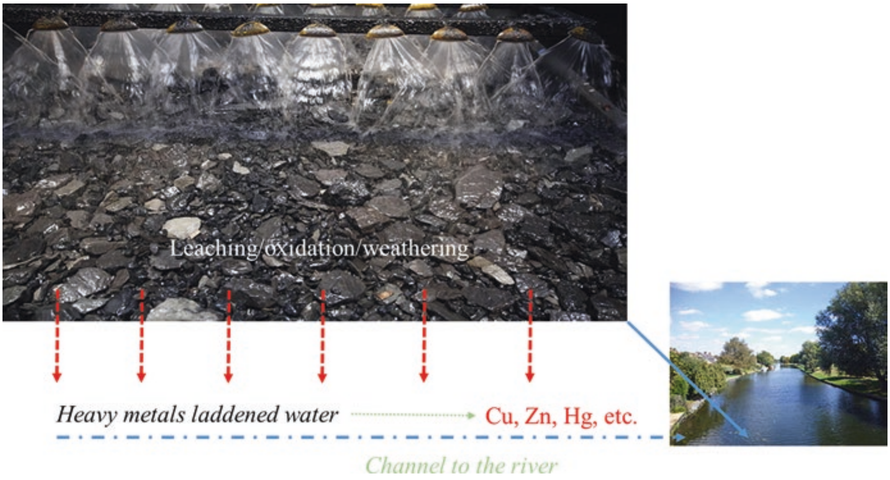


Fig. 17.5 Migration of heavy metals pollution plume from a coal washing facility

Different solvent extraction, leaching and digestion processes are used to harness the desired mineral from the mineral of interest. This processes lead to the generation of residues that are rich in heavy metals. For instance, gold tailings are rich in minerals that can lead to the generation of AMD. During reprocessing or re-mining, the liquid phase used for reprocessing will acquire heavy metals. Heavy metals such as Zn, Cu, Ni, and Hg amongst others can be present in the tailings. This will then be the main routes at which this metals are leached into the environment. Leaching of tailings can also enrich the environment with heavy metals (Chmielewski et al. 1997; Masindi et al. 2018b; Masindi et al. 2018c; Reijnders 2005) (Fig. 17.5).

17.3.2.5.4 Run-Offs

Urban, peri-urban and rural activities leads to the release of heavy metals to the environment. This is mainly caused by exhaust from moving vehicles, leakages from moving vehicles, domestic septic tanks and other manufacturing processes. Advancements in infrastructures such as housing, roads and railways has significantly contributed in the transportation of heavy metals to different receiving environments. This lead to elevated levels of contaminants in the receiving streams nearby. Heavy metals from the moving vehicles, petrol spillages, light industries emission and many more contribute to the emission of heavy metals in urban areas (Zhang et al. 2015). Fertilisers and chemicals used to enhance the greener areas in urban lead to the enrichment of urban environment with heavy metals. During rainfall, heavy metals will be washed away to nearby environment (Zhang et al. 2015). Illegal dumping and misuse of dumping site in urban areas lead to the discharge of heavy metals into the environment. Essential, these metals from different urban facets get washed off by run-offs to nearby environments hence enriching the environment with heavy metals. This makes it unsuitable for myriads of defined uses (Davis et al. 2001; Liu et al. 2018; Vardhan et al. 2019).

17.3.2.6 Approaches towards Source Mapping

Regular monitoring:	This can be achieved by monitoring the concentration of identified heavy metals and link them to specific sources. Catchment management forums via frequently monitoring the catchment systems and identifying the loading sources via upstream engagement and scheduled sampling.
Instrument used:	Different analytical techniques can be used to analyze pollutants in the receiving environment. Instruments such as ICP-MS, FAAS, GFAAS, AAS, IC, photo-spectrometer can be employed to determine the level of contaminants in different sources of pollutants.

17.3.3 Toxicological Impacts of Heavy Metals

Through anthropogenic and natural sources, heavy metals accumulate in the environment, with plants absorbing these metals from contaminated soil and water. The contamination of heavy metals occurs throughout the ecosystem as these metals pass from one contaminated to another with humans accumulating them in their tissues through the ingestion of contaminated plants and animals, inhalation and skin contact. Due to the harmful effects of these metals, different regulator bodies worldwide have set limits for their presence in potable water, soil and air. Exposure to concentrations above the recommended limits has health effects, which can be chronic, acute, mutagenic and carcinogenic depending on the heavy metal exposed to and the level of exposure (Verma and Dwivedi 2013). Table 17.3 presents the recommended limits of various heavy metals in drinking water as set by the World Health Organization (WHO), Environmental Protection Agency (EPA: United States) and Department of Water and Sanitation (DWS: South Africa). The table also present the health effects on humans that are caused by continuous exposure to the various contaminants (Table 17.3).

17.3.4 Pollution Abatement Techniques

Different techniques have been used to stabilize the release of heavy metals into the environment. This prevent environmental contamination by heavy metals. These processes uses different mechanisms such as complexation, adsorption, precipitation, and absorption hence preventing contamination of the environment with heavy metals.

Table 17.3 Recommended Limits for Heavy Metals in Potable Water and their toxic effects

Heavy metal	Chronic health limit (μg/L)			Health effects
	WHO (UN 2007)	**EPA** (EPA 2009)	**DWS** (DWS 2015)	(Ayangbenro and Babalola 2017, EPA 2009, Tchounwou et al. 2012, Verma and Dwivedi 2013)
As	10	10	10	Cancer (skin, bladder, liver, kidney), cardiovascular disease, nervous system problems
Cd	3	5	3	Renal dysfunction, cadmium pneumonitis, bone disease, kidney disease
Cr	50	100	50	Dermatitis, male reproductive system damage, lung cancer
Cu	2000	1300	2000	Anemia, liver and kidney damage.
Pb	10	15	10	Loss of memory, high blood pressure, short attention span
Hg	1	2	6	Blindness, dementia, gastrointestinal problems, kidney damage, decreased fertility
Ni	70	–	70	Increased risk of cancer (lung, nasal), kidney failure, and cardiovascular diseases
Se	10	50	30	Liver damage, hair or nail loss, numbness on fingers or toes
Zn	3000	5000	5000	Anemia, kidney and liver failure, prostate cancer

17.3.4.1 Stabilization

Different techniques have been used to stabilize the release of heavy metals into the environment. This prevent environmental contamination by heavy metals. Different chemicals are used to stabilize heavy metals in soil. This process is mainly mechanism driven. For example, Shin and Kim (2016) evaluated a chemical stabilization of heavy metals using three amendments (i.e., red mud, apatite, and a red mud/apatite composite) made up of industrial by-product and natural mineral. More so, these compounds bind to the contaminants via adsorption or create conditions that are unsuitable for metals to leach into the environment (Cetin et al. 2012; García et al. 2004; Rijkenberg and Depree 2010; Santos et al. 2012; Shin and Kim 2016).

17.3.4.2 Phytoremediation

This process entails the use of plant species with specific affinity to heavy metals. Fundamentally, plants uses heavy metals in the soil as their nutrients and they absorb them for their growth. In soil, plant metabolism significantly play a pivotal role to the chemical stabilization of heavy metal ions within the vadose zone of the soil, their role will limit leaching, mobility, bioavailability, and hazardous impacts of heavy metals. This process is basically known as phyto-stabilization and it is orchestrated by the absorption and accumulation of heavy metals on the roots. Furthermore, heavy metals can precipitate in the rhizosphere zone due to binding onto organic compounds and changes of heavy metal oxidative state. Simplistically, cations such as heavy metals bind to pectins in plant cell walls and to the anionic charged plasma membranes (Anawar et al. 2015; Ashraf et al. 2019; Fangueiro et al. 2018; Sheoran et al. 2013; Valentín-Vargas et al. 2014; Yang et al. 2016).

17.3.4.3 Reaction Control

In certain instances, the release of heavy metals into the environment is controlled by the prevention of substances that can facilitate the reaction to take place. For instance, a clay lining to prevent ingression of water can control the oxidation of metalliferous rich tailing and oxygen. In doing that, contamination of the environment by heavy metals would have been prevented since water and oxygen promote the leaching of heavy metals into different receiving environments (Johnson and Hallberg 2005; Park et al. 2019; Simate and Ndlovu 2014). This process eliminate one of the ingredients in a chemical reaction hence making the reaction not to take place since the precursor are not enough (Johnson and Hallberg 2005).

17.3.5 Pollution Treatment Techniques

Post pollution abatement, numerous processes such as leaching, weathering and oxidation takes place. This lead to the contamination of the environment with heavy metals. As such, water quality specialists, process engineers and environmental managers adopt different treatment technologies to remove the contaminants. These technologies uses different mechanisms and they range from precipitation (Aklil et al. 2004; Alcolea et al. 2012; Fu and Wang 2011), adsorption (Fu and Wang 2011; Motsi et al. 2009), ion exchange (Erdem et al. 2004; Fu and Wang 2011), filtration (Ferella et al. 2007; Fu and Wang 2011), electrolysis (Luo et al. 2014; Tao et al. 2014), phytoremediation (Aggarwal and Goyal 2007; Ali et al. 2013; Asad et al. 2019; Kaur et al. 2018; Tangahu et al. 2011) and crystallization (Masindi et al. 2016; Masindi et al. 2017b; Xie et al. 2018; Zheng et al. 2011). Heavy metals removal can take place using combined mechanisms.

17.3.5.1 Precipitation

This is a pH dependent process. Metals are precipitated at different pH gradients. To achieve that, an alkaline generating agent will be reacted with heavy metals rich water. After some time, the pH of the water will increase and contaminants will commence to precipitate at varying pH gradients. Researcher has explored the recovery of metals at different pH gradients. Different chemicals are used to increase the pH of water and they include, lime, limestone, soda ash, caustic soda, periclase, brucite, and different waste materials. However, these materials are rich in either

Mg, Ca, and Na elements amongst other contaminants (Alcolea et al. 2012; Balintova and Petrilakova 2011; Barakat 2011; Fu and Wang 2011; Matlock et al. 2002; Patil et al. 2016; Rao et al. 1992; Masindi et al. 2017a).

17.3.5.2 Adsorption

This is a surface phenomenon, whereby, contaminants are adsorbed onto the surface of the material. However, this depends on numerous factors such as charge difference, the point of zero charge, and exchangeable fractions. Heavy metals are adsorbed onto the surface of different materials, which are negatively changed. Adsorption of heavy metals onto an adsorbent can be quantified using the grams of heavy metals onto the grams of the adsorbent. It is the adsorbent vs adsorbate relationship. Different mechanisms are used to point out mechanisms of heavy metals adsorption and they include Langmuir and Freundlich adsorption isotherms. This phenomenon also depend on several factors such as concentration, time, co-existing ions, temperature, pH and ionic strength amongst others. Researchers have used a number of materials such as zeolite, clays (bentonite, vermiculite, and kaolinite), base minerals, powdered activated carbon (PAC), granular activated carbon (GAC), and waste materials amongst others (Bhatnagar et al. 2011; Bhattacharyya and Gupta 2008; Cheng et al. 2019; Demirbas 2008; Figueiredo and Quintelas 2014; Fu and Wang 2011; Kobielska et al. 2018; Masindi et al. 2015; Miretzky and Cirelli 2011). To attain a synergy, other materials can be combined as composite to fabricate materials that numerous functionalities and mechanisms (Hua et al. 2012; Mu and Wang 2016; Tran et al. 2017).

17.3.5.3 Ion Exchange

This is a surface phenomenon as well, whereby; contaminants are adsorbed onto the surface of the material via the cation and anion exchange capacity. In most instances, ion exchange resins are used or a media with high ion exchange capacity is used as well. Clay minerals has high ion exchange capacity and they attenuate heavy metals using this mechanism. Elements are replaced by using density and charge variance. This process is known as the cation exchange capacity (CEC). This can be determined using different methods (Abdel-Aziz et al. 2013; Ngulube et al. 2017; Pitcher et al. 2004; Potgieter et al. 2006; Srivastava et al. 2005; Volzone 2004; Westholm et al. 2014).

17.3.5.4 Filtration

Heavy metals can be removed from aqueous medium using filtration membranes. Membrane depends on a driving force to remove heavy metals from aqueous solution. It can depend on the concentration gradient or pressure difference. For heavy metals removal, different types of membrane are used and they include microfiltration (MF), ultrafiltration (UF), nano-filtration (NF), reverse osmosis (RO), membrane distillation and electro-dialysis (ED) (Fu and Wang 2011; Abdullah et al. 2019a, b; Barakat 2011; Patil et al. 2016).

17.3.5.5 Phytoremediation

Phytoremediation is a process of removing heavy metals from aqueous solution using biological components of the environment (plants). The phenomena has been widely explored for heavy metals removal from contaminated land and soil environments. This method has been reported to be very effective. This can be justified by the fact that plants absorb heavy metals from soil and soil/water interface as their nutrients. This aid in the attenuation of heavy metals from soil environment (Aggarwal and Goyal 2007; Ali et al. 2013; Bolan et al. 2011; Chirakkara and Reddy 2014). Plants components can be used for phyto-stabilization, phyto-extraction and phyto-remediation. Challenges with this technique is the time required for the land to be decontaminated. It also require vast space of land (Ali et al. 2013; Kaur et al. 2018; Tangahu et al. 2011).

17.3.6 Advances in Heavy Metals Management

Sludge generated from the treatment of heavy metals and disposal challenges experienced from the treatment of heavy metal rich sludge and by-products. Industries are opting for product minerals beneficiation and valorization.

17.3.6.1 Valorization and Beneficiation

Valorization refers to attaching value to a heavy metal rich waste and attach some potential for beneficiation. In most instances, heavy metals can be recovered from the environment and waste materials for beneficiation purposes. Waste material such as limestone and magnesite and dolomite mining can be beneficiated for metal rich water treatment. Heavy metals can be fractionally recovered at different pH and get beneficiated. Authors have recovered Fe- minerals from a heavy metal laddened solution for other applications such as adsorbents synthesis, pigments synthesis and other industrial applications. Acid mine drainage is rich in heavy metals, as such, researchers recovers then and employ them for numerous industrial applications. Akinwekomi et al. (2017) explored the recovery of Fe(III) and Fe(II) from acid mine drainage and explore their application for magnetite synthesis. Masindi et al. (2018c) explored the use of calcined cryptocrystalline magnesite for the reclamation of heavy metals from AMD in a sequential manner. These metals and product minerals has a number of industrial applications.

17.4 Conclusion and Future Perspectives

From this chapter, it was highlighted that the major sources of pollution in the environment is anthropogenic and natural sources. It was also highlighted that a number of conditions favors the release of heavy metals from different components of the environment; however, the release of heavy metals is governed by pH, temperature, dissolution, redox, and precipitation potential. Mining and metallurgical processes has been identified as the main culprit which contribute significantly towards heavy metals pollution. As such, it can be noted that anthropogenic activities are the biggest contributor of heavy metal contamination in the environment. Natural contamination of the environment can be driven by leaching and weathering of different minerals rich components in the environment hence leading to the enrichment of the environment with heavy metals. These metals are available on the earth's crust and they include Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Zn, and elements within the platinum group. These metals have the ability to accumulate in the environment since they are non-degradable. Humans like all living organisms require certain amounts of metals like copper for their wellbeing and their deficiency will results in a number of medical conditions. The intake of high amounts of metals has adverse health effects, which include cardiovascular diseases and cancer with excessive levels resulting in acute effects since these elements are genotoxic, carcinogenic, mutagenic, and teratogenic to living organisms on exposure. In order to prevent the accumulation of heavy metals within the environment and reduce their inhalation and ingestion by humans, and regulations have been set up to limit the amount that human activities can release into the environment. As such, different pollution sources have a number of technologies, which are used to control the release of heavy metals into the environment. These technologies include the control of the ingression of substances that can facilitate chemical reaction that lead to the release of heavy metals. If pollution abatement techniques are not effective, different institution, use different technologies to curtail the impacts of heavy metals in the environment. These technologies rely on different mechanisms to remove heavy metals from the environment and they include precipitation, adsorption, ion exchange, filtration, and phytoremediation. These technologies assist in preventing the contamination of the environment by heavy metals hence making these industries compliant to different regulatory requirements. As a future perspective, industries are focusing on valorization and beneficiation of metals rich streams and effluents. They reclaim heavy metals in different streams and valorize them. This a good approach since waste generation will be minimized via an environmental friendly approach. This will also respond to the circular economy phenomenon.

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