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Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water

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Preface

Water is a major earth component controlling the well-being of ecosystems. However, water quality is actually threatened by pollution with metals, pesticides, drugs and pathogens issued from rising urbanisation and industrialisation. There are more that 700 organic, inorganic and microbial pollutants responsible for water pollution. Pollutants of concern include inorganic elements such as antimony, arsenic, mercury, cadmium and platinum and organic compounds such as polybromonated diphenyl ethers, drug residues, pesticides, plasticizers and some phenols. As a consequence, there is a need for advanced, sustainable methods to clean waters. There are two main strategies to clean water: degradation of the pollutant by chemical and biological methods and pollutant removal by adsorption. Adsorption is gaining interest because all inorganic and some organic pollutant cannot be degraded under common conditions. Adsorption is usually cost effective and easy to handle. Research has recently focused on the development of greener adsorbents, which are both cheap and renewable, to replace classical, fossil fuel-derived adsorbents. Green adsorbents would indeed better meet the objective of the future circular economy where there will be no ‘waste’. This books presents advanced methods and adsorbents for the removal of metals and dyes. Adsorbents include carbon nanostructures, biomass, cellulose, polymers, clay, composites and chelating materials.

Chapter 1 by Oladipo et al. details the synthesis of activated carbon for heavy metals removal with a major focus on application in the aqueous phase. Types of activated carbons and various factors influencing their performance are discussed. Adsorption mechanisms and isotherms are also presented. Chapter 2 by Sabir et al. discusses polymeric absorbents for heavy metal removal. Chapter 3 by Vences-Alvarez et al. reviews technologies to remove arsenate and fluoride for water, including processes used in full-scale water treatment. Recent advances in the synthesis of highly efficient adsorbents are highlighted. Chapter 4 by Hızal and Yılmazoğlu explains why the montmorillonite clay is well-adapted to remove metal ions. The latest environmental applications of montmorillonite composites are discussed. Properties and applications of cellulosic materials are presented in Chap. 5 by Nag and Biswas, where adsorption mechanisms and metal toxicity are elaborated. Chapter 6 by Yurekli covers the recovery of heavy metals using membrane

Photo. Lake Etang de la Bonde in the Lubéron Mountains, Southern France. (Copyright: Eric Lichtfouse 2019)

adsorbers. Here, the effect of the type of metal oxide nanoparticles, their sizes, amount and deposition methods on the morphological properties and performances of the membrane are discussed. Chapter 7 by Berrettoni et al. highlights the sequestration capabilities of metal hexacyanoferrates for different heavy metals. This chapter gives also the basics of the electrochemistry and key applications such as the recovery of the rare-earth cesium from wastewaters. Chapter 8 by Sabir et al. presents the use of agriculture waste absorbents for heavy metal removal. Chapter 9 by Vishnu et al. focuses on the synthesis, characteristics and use of nanoparticles as adsorbent to remove metals. Methods for metal removal from wastewater are further discussed in Chapter 10 by Maharana et al., with focus on low cost adsorbents such as industrial solid waste-red mud, fly ash and rice husk. Dyes from effluents of textile, paper, plastic and cosmetic industries are reviewed in Chapter 11 by Wołowicz and Wawrzkiewicz, with adsorbents such as activated carbons, low cost adsorbents, natural materials, biosorbents, nanomaterials, composites and ion exchange resins. Chapter 12 by Pelin Demircivi details the removal of boron from wastewater using various adsorbents adapted to, for example, the type of functional groups on the surface and the charge of surface. Waste fruit cortexes can be used to remove metals, as shown in Chapter 13 by Shangeetha Ganesan. Chapter 14 by Biswas and Nag lists the various sources of metal contaminations and their hazardous effects. Types, modification and regeneration of biosorbents are also discussed. Dye classification, toxicity and treatments by physical and biological methods are reviewed in Chapter 15 by Sardar et al. and Chapter 16 by Moattari.

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Chapter 1
Synthesis of Activated Carbons for Heavy Metals Removal

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Abstract This review provides information on the utilization of activated carbon as adsorbent for heavy metals removal with a focus on the aqueous phase. Activated carbon is known to provide large surface area for adsorption. Agricultural residues (biowastes) which are renewable, highly efficient, and of low cost, have been used as precursors for synthesis of activated carbon applied in heavy metals uptake. In this review, details of types of activated carbon, methods of their preparation, and surface modification and treatment of activated carbon via oxidation, sulfuration, and nitrogenation are presented. Various factors affecting the performance of activated carbon as well as its physicochemical properties are also discussed. The possible adsorption mechanisms of heavy metal ions typical of different adsorbents are also summarized in this review. The overview also expounds adsorption isotherms, adsorption thermodynamics, and adsorption kinetics as they influence the adsorption process.

Keywords Activated carbon · Heavy metals · Surface modification · Adsorption mechanism · Adsorbent · Adsorbate · Isotherms · Kinetics · Thermodynamics · Agricultural wastes

1.1 Introduction

Numerous natural phenomenon and anthropogenic activities have been reported as the source of heavy metals into the environment. The ions of heavy metals such as Cr, Co, Cd, Pb, and Hg are injurious to human health and other living forms (Sud et al. 2008). Several bodies have proposed and set maximum limits for these toxic heavy metals, specifically in aqueous media. However, rapid industrialization and urbanization have been promoting the continuous increase in the level of these contaminants in different water systems.

Due to the limitations of the conventional approach (such as ultrafiltration and reverse osmosis) in the removal of heavy metals, the search for an alternative technique has led to the adoption of activated carbon utilization for the removal of heavy metals. Besides the attributes activated carbon possesses, such as its large surface area and high surface reactivity, the associated high cost in its production has been the downside of its full commercialization. This has however prompted researchers to explore agricultural residues (biowastes) for its synthesis. The use of these biowastes as adsorbents has several advantages which include high efficiency, low cost, and regeneration ability as well as possibility for metal recovery (Dai et al. 2018; Mashhadi et al. 2016).

Potential removal of heavy metal ions by synthesized carbonaceous biowastes hinge on several factors which subsequently influence its adsorbing characteristics. Considerations based on the methods of preparation, forms of modification, treatment, and adsorption process conditions (pH, temperature, and initial concentration) are vital in understanding the mechanism of the adsorption process.

This present overview therefore provides an in-depth review on the synthesis, mechanism, and modification types of activated carbon. In addition, the essential characteristics of activated carbon, both physical and chemical properties, are well covered. Isotherms, kinetics, and thermodynamics of several works were appraised to draw a conclusion based on some selected adsorption variables.

1.2 Types of Activated Carbon

Depending on the industrial applications, methods of preparation, forms or shapes, as well as their sizes, activated carbon exists mainly in three categories, namely, (1) extruded or pelletized activated carbon, (2) granular activated carbon, and (3) powdered activated carbon (Çeçen 2000). Figure 1.1 shows the three categories of activated carbon.

1.2.1 Powdered Activated Carbon

Powdered activated carbon has a distinctive average size of 15–25 μm. Fine particles of pulverized carbon are the major constituents of powdered activated carbon, 95–100% of which will not be retained in a designated mesh sieve of 80 (0.177 mm) and below according to ASTM D5158-98. Powdered activated carbon is composed of high carbon content organic materials such as wood, lignite, and coal.

Fig. 1.1 Major classes of activated carbon – (**a**) extruded or pelletized activated carbon, (**b**) granular activated carbon, (**c**) powdered activated carbon (Wikipedia)

It is predominantly used as colloid dispersion medium in polluted phase and also in the removal of contaminants from aqueous, gaseous, and even solid environment. Due to its small particle size and tendency to form dust, powdered activated carbon is used directly as an add-on to other process units rather than being used singly. However, powdered activated carbon is not an ideal choice for applications that use considerable amount of activated carbon as it is not regenerated because of the challenges linked with recycling the carbon.

Powdered activated carbon finds typical applications in aqueous environments. Heavy metals ions such as Hg can be adsorbed using powdered activated carbon prepared from *Casuarina equisetifolia* leaves with varying particle size from 45 to 75 μm (Ranganathan 2003). Powdered activated carbon has been extensively used to remove various gaseous pollutants discharged into the atmosphere through flue gases. Example of such pollutants includes zero valent metals (e.g., Hg and Pb), polycyclic aromatic hydrocarbons, and organic compounds (e.g., polychlorobenzenes, furans, dioxins). Bais et al. (2008) successfully applied powdered activated carbon for separation of organic pollutants such as fluoranthene and hexachlorobenzene from gas stream.

1.2.2 Granular Activated Carbon

Granular activated carbon exists in granular or extruded form of coal. It may also be developed through the granulation of pulverized powders using high-temperature binders such as coal tar pitch. In both fixed and moving systems, smaller granular activated carbon is particularly suited to liquid phase applications, while larger granular activated carbon is better for vapors and gases.

Granular activated carbon has an average particle size of 1–5 mm which is relatively large and has a proportionately smaller external surface area than powdered activated carbon. In addition, not less than 90% of its weight is held back on a standard mesh sieve size of 180 μm (80 mesh). Its reusability, ease of handling, regenerative properties, and offer of lower pressure drop make granular activated carbon advantageous over powdered activated carbon.

Typical environmental applications of granular activated carbon are in the removal of heavy metals. Toxic pollutants such as Pb is released into the environment as part of the end product of lead acid batteries, refineries operations, fuel combustion, and fertilizers made from phosphate, mining activities, and emissions from vehicles. It has been reported that Pb has significant impact on human health and the environment (Dwivedi et al. 2008). Literature study shows that granular activated carbon packed bed and batch system have been used to remove Pb effectively (Chelme-Ayala et al. 2009). Granular activated carbon can also be employed in the removal of pesticides (Chelme-Ayala et al. 2009), insecticides (Daneshvar et al. 2007), and volatile organic compounds (Bansode et al. 2003) from contaminated groundwater and soils.

1.2.3 Extruded Activated Carbon

Extruded activated carbon is a blend of powdered activated carbon (anthracite or coal) and binder, which are extruded at high pressure into a cylindrical-shaped pellets with diameters varying from 0.8 to 130 mm. Activated catalysts, like potassium hydroxide, are mixed prior to extrusion to achieve a specific pore structure (Gupta 2017). Extruded activated carbon creates minimal dust, gives a low-pressure drop-in system, and has high mechanical strength which is an essential factor in the gas–phase applications.

1.3 Methods of Preparation of Activated Carbon

Activated carbon is an amorphous form of carbon which has been subjected to specific treatments in order to acquire a sophisticated internal pore structure, large specific surface area, good surface reactivity, and appropriate physical forms (Dias et al. 2007; Yahya et al. 2015). As a result of these features, activated carbon is widely used as adsorbent for pollution control in a host of environmental applications including the removal of heavy metals, volatile organic compounds, nitrates, and color from wastewater and industrial effluents (Akpen et al. 2011; González-García 2018; Onyeji and Aboje 2011). Widespread applications of activated carbon, availability of feedstock, increasing awareness, and stringent regulations regarding environmental pollution are among the driving forces for research in this area (Roman et al. 2013). The forms, precursors, features, and applications of AC are shown in Table 1.1.

1.3.1 Feedstock for Activated Carbon Production

Coconut shell, coal, and wood are the most commonly used feedstocks for activated carbon production. However, attention has recently shifted to agricultural residues (biowastes) as cheaper and readily available alternatives due to their high carbon contents, low ash and inorganic contents, relative rigidity, and the need for their proper disposal as wastes. While some studies focus on agricultural waste materials of substantial rigidity such as shells and stones of fruits that include oil palm, olives, dates, cherries, and coconuts, others consider residues and processing wastes such as olive cakes, sawdust, rice husks, cotton stalk, coffee husks, spent grains, sugarcane, and sugar beet bagasse. Table 1.2 shows the typical feedstock for the production of activated carbon. High carbon, high volatile solids, and low ash contents are necessary for high yield of activated carbon with good pore volume and surface area (Lua et al. 2006).

Table 1.1 Forms, precursor, properties, and applications of activated carbon

Form of activated carbon	Precursor	Feature	Application
Granular activated carbon	Coconut shell, palm oil shell	PS[**] greater than 100 µm	Column filler for gas or liquid treatments, metal recovery, and remediation
Powdered activated carbon	Wood sawdust, milled almond, and coconut shells	PS[**] lesser than 100 µm; PD[$] approximately 20 µm) Adsorption is very effective due to the smaller PS, but settling and removal are slower and often require replacement after several cycles of usage	Metal recovery, wastewater treatments, and catalysis
Activated carbon fibers	Carbon fibers, e.g., from coal tar or petroleum pitch (diameter 5–10 µm), polyacrylonitrile, and phenolic resins	Very high SA[*] (approximately 2000 m^2/g); AR[ss] greater than 10; well- defined pore structure leading to high adsorption capacity and high packing density. More expensive than powdered activated carbon and granular activated carbon due to fiber processing cost	CH_4 and H_2 storage, air filter in gas masks, wastewater treatments, SO_2, NO_x, and VOCs removal
Activated carbon cloths	Rayon, fabrics, and textile waste	Extremely high SA[*] and PV[#]; faster adsorption kinetics, large adsorption capacity, and lightweight	Medicals (cell therapy, stem cell growth);,heavy metals recovery, VOCs[##] and vapor recovery, gas separations, electrical and electrochemical applications

∗Surface area = SA;[**]Particle size = PS; [$]Particle diameter = PD; [$$]Aspect ratio = AR; [#]Pore volume = PV; [##]VOCs = volatile organic compounds
Sources: Dias et al. (2007); Roman et al. (2013); Cukierman (2013); Kostoglou et al. (2017).

1.3.2 *Preparation of Activated Carbon*

Three major steps are required in the preparation of AC, namely: (1) pretreatment, (2) activation, and (3) carbonization as shown in Fig. 1.2. While activation involves the use of reagents, carbonization (or pyrolysis) requires the application of heat treatment to raise the carbon content of the precursors (González and Pliego-Cuervo 2013). Particle size is very important in material handling such as in mixing precursors with catalyst and impregnation reagents as well as in determining the textural properties of the produced activated carbon (Auta and Hameed 2011; Gurten et al. 2012). Hence, unit operations including milling, grinding, and sieving are often used to pretreat raw materials in order to achieve required particle sizes (Alslaibi et al. 2013). The works of Şentorun-Shalaby et al. (2006) and Müller (2010) among

Table 1.2 Typical feedstock for activated carbon production

Precursor	Carbon (wt. %)	Ash (wt. %)	References
Petroleum coke	77.50	0.60	Lee et al. (2014)
Palm shell	50.01	1.10	Yahya et al. (2015)
Lignite	62.50	5.50	Lee et al. (2014)
Coconut shell	48.63	0.10	Yahya et al. (2015)
Cassava peel	59.31	0.30	Sudaryanto et al. (2006)
Banana peel	10	10	Romero-Anaya et al. (2011)
Guava seeds	65.2	0.3	Largitte et al. (2016)
Bamboo	45.53	6.51	Hirunpraditkoon et al. (2011)
Wheat straw	46.50	3.23	Zanzi et al. (2001)
Sugarcane bagasse	47.30	0.9	Zanzi et al. (2001) and Boonpoke et al. (2011)
Soft coal	72.50	7.00	Lee et al. (2014)
Hard coal	90.00	8.50	Lee et al. (2014)
Walnut shell	45.10	1.30	González et al. (2009)
Corncob	46.80	0.90	Yahya et al. (2015)
Rice husk	36.52	16.70	Boonpoke et al. (2011)
Olive stone	44.8	1.40	Yakout and El-Deen (2016)
Almond shell	50.50	0.60	González et al. (2009)
Orange peel	20.40	3.10	Köseoğlu and Akmil-Basar (2015)
Jatropha curcas	37.00	6.00	Tongpoothorn et al. (2011)
Kenaf	15.7	3.4	Hosseini et al. (2015)

others showed that adsorption rates generally increase with decrease in the particle size of activated carbon and an increase in its mesopore volume.

Pretreatment is followed with the activation process which can be accomplished by either physical or chemical treatments (Alslaibi et al. 2013). The former involves a two-step process of carbonization at high temperatures of between 600 and 900 °C (Ioannidou and Zabaniotou 2007) followed by steam or CO_2 activation, while the precursor is first impregnated by an activating agent such as NaOH or $ZnCl_2$ and then followed by carbonization at a relatively lower temperatures of between 300 and 700 °C (Giraldo and Moreno-Piraján 2012) in the chemical activation treatment (Yahya et al. 2015). Activation helps to develop initial porosity by dehydration and degradation of the biomass structure (González-García 2018). Features of the two activation methods are illustrated in Table 1.3.

Recently, research efforts have shifted to carrying out the carbonization process in microwave rather than in conventional furnace as this has been reported to consume less energy and requires lower carbonization temperature and duration (Alslaibi et al. 2013). Above all, it results in the development of activated carbon with higher surface area and mesopore volume (Hesas et al. 2013).

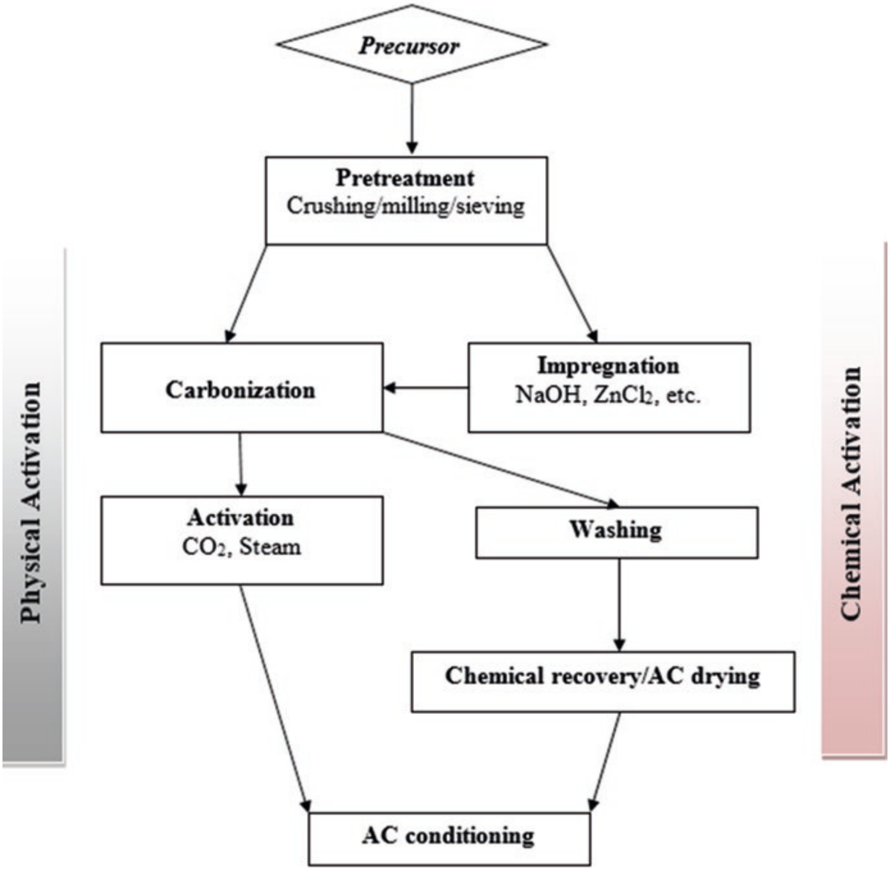

Fig. 1.2 Flow sheet of activated carbon production via physical and chemical activation

1.4 Types of Surface Modification and Treatment of Activated Carbon

Several factors are considered to affect the metal adsorption capacity of activated carbon, such factors include surface chemistry, surface porosity, and pore size distribution (Gupta et al. 2015a, b). The understanding of these factors prior to the modification of activated carbon is essential as this will assist in modifying their physiochemical properties to enhance their affinity for contaminants of great concern in an environmental media, such as in wastewater (Rivera-Utrilla et al. 2011). Chemical modification of the surface of activated carbon significantly changes their adsorption capacities since adsorption process has to do with retaining of contaminants at the surface of the adsorbents. Surface chemistry of activated carbon is dependent on the quantity and inherent characteristic of functional groups present

Table 1.3 Comparisons between the physical and chemical activation methods

Feature	Physical activation	Chemical activation
Reagents	CO_2 (Nabais et al. 2010; Nasri et al. 2014)	H_3PO_4, $ZnCl_2$ (Cruz et al. 2012)
	Steam (Bouchelta et al. 2012; Ghouma et al. 2015; Tsyntsarski et al. 2015)	NaOH, KOH (Gu and Wang 2013)
		$FePO_4$, $CaHPO_4$ (Ramírez-Montoya et al. 2015)
		H_2SO_4 (Nethaji and Sivasamy 2011)
Operating conditions	Temperature: 800–900 °C and activation time: 1–5 h (Ioannidou and Zabaniotou 2007; Ngernyen et al. 2006; Rizhikovs et al. 2012)	Temperature: 160–200 °C and activation time: 2–6 h (Adegoke and Adekola 2010; Malarvizhi and Ho 2010)
Application examples	Olive stone, walnut shell – steam (González et al. 2009)	Shear butter wood – K_2CO_3, H_3PO_4, HNO_3 (Adegoke and Adekola 2010)
	Pistachio nut shell, coconut shell – CO_2 (Guo et al. 2009; Lua et al. 2006)	Rice husk – $ZnCl_2$ (Yahaya et al. 2010)
Merits and demerits	While physical activation is relatively simple, chemical activation involves extra process stages such as washing and impregnant recovery (Lee et al. 2014). Chemical activation is more expensive due to the cost of chemicals, and it leads to exposure to toxic chemicals (Alslaibi et al. 2013). It however requires lower activation temperature and time (Danish and Ahmad 2018). Chemical activation also results in higher surface area and pore volume (Yahya et al. 2015)	

(Yang et al. 2019). These functional groups are attached to heteroatoms at the carbon surface, and the functional groups are therefore categorized based on the heteroatom attached at the carbon surface as oxygen-containing, nitrogen-containing, and sulfur-containing functional groups (Yang et al. 2019). Reagents usually employed for chemical modification include basic solutions, organic acids, organic compounds, and oxidizing agents, where the functional groups are covalently and chemically bonded to the surface of the activated carbon (Gupta et al. 2015b). Rivera-Utrilla et al. (2011) broadly categorized surface modification and treatment techniques of activated carbon into four, viz., (1) oxidation, (2) sulfuration, (3) ammonification, and (4) coordinated ligand anchorage.

1.4.1 Surface Modification by Oxidation

The functional groups with oxygen attachment such as –OH, –COOH, –C–O, and –C=O are commonly created at the surface of carbon adsorbent by oxidation (Lu et al. 2015; Wepasnick et al. 2011). Carbon materials are oxidized under reflux condition in the presence of some reagents such as the inorganic acids (HNO_3, H_2SO_4) and oxidizing agents (H_2O_2, $KMnO_4$, NaOCl) (Sarkar et al. 2018; Xue et al. 2012).

Oxidation of activated carbon can either be dry oxidation or wet oxidation. In dry oxidation, oxidizing gases like O_3, CO_2, and steam are employed, while the wet oxidation involves oxidizing solutions like H_2O_2, aqueous O_3, and HNO_3 (Rivera-Utrilla et al. 2011). The amount of oxygen on the carbon surface can be controlled by adding the appropriate dose of oxidizing agent and at the desired experimental conditions like reaction time and temperature (Yang et al. 2019). Many reports on the oxidation of activated carbon with H_2O_2 concluded that minimal textural modifications are impacted at the carbon surface, although both increase and decrease in surface area were reported (Rivera-Utrilla et al. 2011).

1.4.2 Surface Modification by Sulfuration

Functional groups with sulfur attachment such as C–S, S=O, and C=S are introduced to carbon sorbent surfaces through sulfuration treatment. This can be achieved through reaction of carbon with sulfur or sulfur-containing compounds such as H_2S, SO_2, K_2S, and N_2S (Yang et al. 2019). Depending on the treatment conditions, this technique also alters the porous structure of the carbon sorbent either with increasing or declining specific surface area or volume of the pores. Carbon-sulfur complexes show similarities in terms of non-stoichiometry character and physicochemical performance. These complexes can neither be completely extracted with solvent nor heat treatment decomposition under vacuum, but they can rather be eliminated as hydrogen sulfide by heat treatment in hydrogen at temperature range of 973–1046 K (Rivera-Utrilla et al. 2011). Activated carbon modified with sulfur-containing groups has proven to be effective in adsorbing many metal species such as Cd(II), Cu(II), Cr(VI), $HgCl_2$, Hg(II), Pb(II), and Zn(II) in solutions (Rivera-Utrilla et al. 2011).

1.4.3 Surface Modification by Nitrogenation

The introduction of nitrogen-containing functional groups such as –NH, $-NH_2$, –C–N, and $-C \equiv N$ onto the surface of carbon sorbent matters is done by nitrogenation, and this is usually achieved through reactions with ammonia (NH_3), urea (CH_4N_2O), and amines (RNH_2) (Li et al. 2017). The incorporation of nitrogen-based functional groups on carbon sorbent surface increases its basic properties and hence enhances its metal adsorption capacity (Yang et al. 2019). The presence of these functional groups on carbon surface has been reported to have insignificant effect on porosity of the carbon material (Kasnejad et al. 2012). Activated carbon modified with nitrogenated agents has shown to have higher adsorption capacity for Pb(II) and Cu(II) compared to commercial activated carbon (Budaeva and Zoltoev 2010). Ammonia has been widely chosen as the nitrogenated agent for activated carbon surface modification, and it has been effectively tested in various applications ranging from toxic heavy metals, anions, and organic compound contaminants (Rivera-Utrilla et al. 2011).

1.4.4 Surface Modification by Coordinated Ligand Functionalization

Literature has shown that different coordinated ligands have significantly modified activated carbon characteristics such as textural and chemical properties with the aim of improving the adsorption capacity of activated carbon (Rivera-Utrilla et al. 2011). Chemical composition of modified activated carbon by coordinated ligand functionalization is dependent on the ligand employed, and this has been portrayed to increase surface basicity, negative charge, nitrogen, chlorine, and the sulfur content (Justi et al. 2005; Li et al. 2009). Published articles have demonstrated that activated carbon with ligands at the surface has increase metal adsorption rate, non-leachability of the ligands into the contaminated solutions and the ease of regeneration of activated carbon ligand modified adsorbents (Rivera-Utrilla et al. 2011).

1.5 Factors Affecting the Performance of Activated Carbon

Performance of activated carbon mainly depends on both the physicochemical properties of its precursors and the production routes (González-García 2018). Activated carbon parameters that have been found to have significant influence on its performance as adsorbent are summarized in Table 1.4.

1.5.1 Effects of Physical and Operational Parameters

It has been broadly reported that the higher the surface area and pore volume of activated carbon, the better its performance as an adsorbent (Alslaibi et al. 2013; Danish and Ahmad 2018; Müller 2010; Roman et al. 2013). With respect to this, Şentorun-Shalaby et al. (2006) and Alslaibi et al. (2013) reported that the finer the particle size, the higher the specific surface area and pore volume which in turn leads to higher adsorption capacity. While investigating the removal and recovery of lanthanum (La) using different adsorbents, Iftekhar et al. (2018) concluded that adsorbent materials with functional groups such as amine, carboxyl, and hydroxyl have higher adsorption capacity and, thus, efficiently removed La over an extensive range of pH. Also, the effects of phosphoric acid (H_3PO_4) concentrations as activating reagent on the pore structure and surface chemistry of olive stone-based activated carbon were investigated by Yakout and El-Deen (2016). It was reported that increasing the reagent concentrations increases the surface area and pore volume of the activated carbon produced; however, the reverse is the case for the yield of activated carbon. The effects of various factors on the properties as well as the performance of activated carbon are shown in Table 1.5.

Table 1.4 Parameters influencing the performance of activated carbon

Parameter	Unit	Description	References
[a]BET surface area	m^2/g	Textural property as the total surface area per unit weight of the AC	Müller (2010), Roman et al. (2013) and Sudaryanto et al. (2006)
Pore volume	m^3/g	Average size of a single void in the AC consists of micro and mesopores	Alslaibi et al. (2013), Dias et al. (2007) and Danish and Ahmad (2018)
Particle size	µm or mm	The finer the particle size, the larger the surface area of the carbon and possible increase in microporosity	Alslaibi et al. (2013)
Fractal dimension		Degree of roughness or irregularity of the surface of the AC	Dıaz-Dıez et al. (2004), Hesas et al. (2013) and Yakout and El-Deen (2016)
Adsorption capacity	cm^3/g	Performance parameters of AC, determined via any or all of the followings: adsorption of methylene blue (MB index), acid blue 29 dye (AB29), phenol adsorption, and N_2 adsorption at 77 K	Dias et al. (2007), Hesas et al. (2013) and Yahya et al. (2015)
Yield	% or gg^{-1}	Percent of carbon in the precursor that is left in the AC	Foo and Hameed (2012) and Alslaibi et al. (2013)
Surface functional group		Hydroxyl, carbonyl, amine, and alkenes	Iftekhar et al. (2018) and Danish and Ahmad (2018)

[a]BET - Brunauer–Emmett–Teller, AC – activated carbon

1.6 Physicochemical Characteristics of Activated Carbon

As earlier pointed out, the nature of activated carbon can be easily influenced by its mode of production and properties of the raw materials used as precursors for its synthesis. The choice of material, the process used in activation, and factors considered during synthesis will define the physical constituents and general performance of the produced activated carbon (Leimkuehler 2010). Mohammad-Khah and Ansari (2009) have shown that among the significant properties of activated carbon, the constituent of the ash, the phenomenon of the surface chemistry, and the activating carbon pH are the significant chemical properties of activated carbon.

1.6.1 Physical Characteristics of Activated Carbon

(i) **Surface area (m^2/g):** The nature of the surface of activated carbon can be observed by an electron microscope by revealing its structures. The microscope reveals carbon particles that are extremely complex and porous. Instances where carbon particles displayed structure that is graphite like and coarse show that the distance between the particles is barely separated in few nanometers (Pradhan 2011). The surface area available for adsorption of carbon is usually

Table 1.5 Effects of various factors on the properties and performance of activated carbon

Factor	Precursor	Condition	S_{BET} (m^2/g)	V_T (cm^3/g)	Yield (%)	References
Concentration of activating reagent	Wood	50% H_3PO_4	761	0.297	–	Budinova et al. (2006)
		70% H_3PO_4	1910	0.582		
	Olive stone	50% H_3PO_4	257	0.123	36.8	Yakout and El-Deen (2016)
		80% H_3PO_4	1218	0.6	31	
Activation reagent type	Apricot stone	H_3PO_4	1387	0.954	–	Youssef et al. (2005)
		$ZnCl_2$	728	0.358		
		Steam	683	0.16		
	Macadamia nutshell	KOH	1169	0.529	–	Mohamed et al. (2010)
		$ZnCl_2$	1718	0.723		
		CO_2	802	0.3		
	Cotton stalks	KOH	729.3	0.38	–	Mohamed et al. (2010)
		K_2CO_3	621.5	0.38		
Precursor type	Almond shell	Steam, 850 °C	601	0.37	–	González et al. (2009)
	Walnut shell		792	0.52		
	Olive stone		813	0.55		
	Cocoa pod husk	$ZnCl_2$	780	0.58	–	Cruz et al. (2012); Boonpoke et al. (2011)
	Rice husk		927	0.56		
Particle size	Apricot stones	0.85–1.7 mm	1157	0.39	4.7	Şentorun-Shalaby et al. (2006)
		1.7–3.35 mm	1035	0.36	9.5	
		1–3.35 mm	1092	0.37	9.4	
		3.35–4 mm	790	0.30	10.5	
	Highly activated GAC	63–100 μm	1413	0.599	–	Müller (2010)
		100–250 μm				
		250–500 μm				
		500–600 μm				
Activation temperature and time	Apricot stone	Steam, 850 °C, 2 h	900	0.38	–	Mohamed et al. (2010)
		Steam, 800 °C, 4 h	1092	0.37		
Carbonization temperature	Phenol resin	600 °C	2107	1.09	64.7	Du et al. (2010)
		700 °C	1129	0.55	57.5	
		800 °C	1049	0.49	56.8	
Impregnation ratio of reagent to precursor	Coconut husk	0.25			75%	Foo and Hameed (2012)
		1.25			87%	
		2.00			76%	

S_{BET}, BET surface area; V_T, total pore volume calculated by Brunauer–Emmett–Teller technique, and this can be sourced from nitrogen adsorption data of 0.05–0.2 relative pressure range. The application of Brunauer–Emmett–Teller equation to isotherms of adsorption–desorption of nitrogen at a temperature of 77 K will also help in revealing the surface area of activated carbon (Naderi 2015). The process of activating carbon influences its distinct features to the level that the Brunauer–Emmett–Teller surface area of the activated carbon range from 250 to 2410 m^2/g, and the pore volume changes from 0.022 to 91.4 cm^3/g (Ioannidou and Zabaniotou 2007). Generally, if no activation process is made on the carbon, the Brunauer–Emmett–Teller surface areas are usually below 500 m^2/g (Murzin 2012). The internal surface area of an activated carbon falls between 500 and 1500 m^2/g, and this large internal surface area makes the adsorbent potent (Wigmans 1989).

(ii) **Density (g/ml):** Pycnometer is used to determine the actual density of activated carbon. The density of activated carbon depends on the starting material, adopted method of production, process mode of activation, and the final output of the resulting carbon. For instance, the density of activated carbon from a wooden source is lower when compared to that from coal (Chiang et al. 1998).

(iii) **Porosity (Φ):** Porosity with sizes of nanometers or less cannot be exactly imaged even in sophisticated instruments such as scanning electron microscope. However, an alternative technique has been developed using physical adsorption of gases, immersion calorimetry, and of small-angle X-rays scattering to characterize porosity (Marsh and Reinoso 2006). Microporosity has the proportions of molecules and turn to be an indicator showing the relevant information about the adsorption active site. Hence, there is a binding force between porosity and adsorption. The industrial functionality of activated carbon relies on its retention capacity, i.e., the time it takes the carbon to retain the adsorbed species at specific operating conditions without getting desorbed (Marsh and Reinoso 2006). Thus, molecules of smaller sizes are more porous. Contrariwise, molecules of larger size experience a closed porosity. Consequently, *closed porosity* is at a point when porosity is not accessible to a specified adsorbate. Closed porosity is not a steady parameter but advances toward zero (cm^3/g) but most time never attain zero for activated carbon due to size decrease in the adsorbate molecule (Marsh and Reinoso 2006).

(iv) **Pore volumes and size distribution, V_T (cm^3/g):** The surface of activated carbon has a pore size that defines its adsorption capacity, a chemical structure that stimulates its interaction with adsorbates of polar and nonpolar form, and active sites which confirm its chemical interactive effects with other molecules (Ioannidou and Zabaniotou 2007). The pore size distribution of activated carbon can be classified into three which are micropores, mesopores, and macropores. The micropores size of activated carbon is a significant property that measures its adsorption capacity (Pradhan 2011). Dubinin–Radushkevich equation is used in ascertaining the micropore volume of activated carbon, while the mesopore volume and pore size distribution can be estimated using Barrett–Joyner–Halend adsorption approach and the density functional theory, respectively (Ahmed and Theydan 2012).

(v) **Iodine number (mg/g):** Iodine number is recognized as a crucial factor used in characterizing the efficiency of activated carbon as it measures the activity level in carbon. High iodine number indicates a high degree of carbon activation (Pradhan 2011). Activated carbon adsorbs iodine at a spontaneous rate, and this makes iodine number a signal of the total surface area of the activated carbon. It is usually measured using ASTM D28 standard method.

(vi) **Moisture content:** This emanates from the polar functional groups on the surface of the activated carbon which gives information regarding the active site for water adsorption. Commercially, activated carbon has been reported to be transported when provision is made available for contact with the atmospheric condition. Therefore, atmospheric moisture needs to be considered when transporting activated carbon (Zhou et al. 2001). The weight difference of the carbon before and after adsorption signifies the water content present in the sample. The constant dry weight method is used in determining the moisture content and its effects on activated carbon.

1.6.2 Chemical Characteristics of Activated Carbon

(i) **Chemical structure and surface morphology:** Adsorption isotherm structure gives necessary information on the process of adsorption and magnitude of the surface area reachable to the adsorbate. London dispersion or van der Waals is usually the binding force associated with activated carbon (Crini and Lichtfouse 2018). Activated carbon does not have strong affinity to certain chemical compounds such as alcohols, hard acid and bases, metals, and most inorganic compounds. The pore structure and the internal surface area can be analyzed with mercury porosimetry or physical adsorption measurements (Figueiredo and Moulijn 2012). The bonding element in water (H, O) together with all other atoms has a significant influence on adsorption. Boehm (1966) method shows how the oxygen bound surface functional groups could be measured in adsorption. This titration method put forward by Boehm is usually used in identifying the acidic groups with different strengths on activated carbons. As a surface phenomenon, the adsorption frequency and the degree of activated carbon to a given adsorbate rely on its surface chemistry and pore texture (Guo and Rockstraw 2007). Hence, the surface chemistry and structural appearances of carbon will define the diffusion of adsorption surface sites and their accessibility during synthesis (Zhang et al. 2005). The surface morphology of the carbonated and activated product can be analyzed using scanning electron microscope, but for the characterization of its functional group, Fourier transform infrared spectroscopy will be better for the analysis (Maulina and Iriansyah 2018).

(ii) **Ash content (%)**: Ash content is the inorganic remains after oxidation. The composition of the ash and their distribution cause the activated carbon to have strong catalytic effects and affinity for water (Chiang et al. 1998). The characteristics of any type of activated carbon are affected by the content of the ash it possesses. When ash is present in excess, it could lead to the blockage of the pores on the activated carbon so that there is not enough space for the surface area of the carbon (Schröder et al. 2007). Ash content rises with continuous change in concentration of activating agent as this result in decrease of the organic compounds of activated carbon. Nevertheless, there is a relatively fixed amount for the content of an inorganic compound in activated carbon (Maulina and Iriansyah 2018). Activated carbon ranges of 1 to 12% ash content have been reported based on raw material variation used as a precursor in synthesis. The weight difference between the initial and final mass of the carbon is used in calculating the ash content of activated carbon in mass per gram. Standard test method (ASTM D2866–83) can be used in estimating the totality of the ash content in activated carbon.

(iii) **pH of activated carbon**: pH is a significant factor that must be considered for effective adsorption process. It affects the binding forces around the surface morphology and charges of the activated carbon (Boehm 1994). Non-carbon atoms such as nitrogen, oxygen, and sulfur found on activated carbon surface affect the surface acidity and the whole adsorption process (Zhang et al. 2005). For the adsorption process to be effective, pH must be controlled before and after process activation. For example, the necessity for pH in metal adsorption could be traceable to the ionic charge of the functional groups on the adsorbent and the chemistry of the metal solution (Attia et al. 2010). The standard test method (ASTMD3838–80) is usually used for the determination of pH in activated carbon.

(iv) **Volatile matter**: Gases and vapor driven off during thermal decomposition of coal are usually referred to as volatile matter. The increase in activator concentration causes a decrease in a number of volatile matters in the activated carbon. This can be clearly explained in that activators bring about change in the structure and quality of activated carbon. Also, the carbon activator discharges substances that are volatile and causes micropore structure in activated carbon (Maulina and Iriansyah 2018). Non-carbon compound attached to the activated carbon surface area is drastically reduced when the activator is impregnated, while their entrance becomes feasible through the pores of the coal. Therefore, the pore surface is cleansed and enlarged due to the presence of the activator. The standard test method (ASTMD8832–98) is usually used for the determination of volatile matter in activated carbon.

1.7 Adsorption Mechanism of Activated Carbon

Adsorption is receiving great attention as a method for removal of heavy metals from polluted media, especially those contaminated with wastewater. Adsorption depends on the extent of mass transfer between the two phases involved (liquid and solid phase) (Azimi et al. 2017). The adsorption of heavy metal contaminants ion onto an adsorbent (i.e., activated carbon) consists of three main steps namely:

(1) movement of contaminants ion from the solution to the adsorbent surface, (2) adsorption onto the site of the particle, and (3) movement within the adsorbent particles. The synthesis of carbonaceous materials into activated carbon for remediating contaminants has been extensively described in literature. Agricultural residues (biowastes) can be utilized as cost-effective adsorption material for heavy metals ion uptake from polluted areas, thus reducing the environmental pollution with the approach of "treating waste by waste" (Dai et al. 2018).

Owing to the attraction between the synthesized activated carbon and heavy metal ions, the ions are bound via a complicated route which are influenced by several mechanisms such as chemisorption, physisorption, membrane diffusion, ion exchange, particle diffusion, electrostatic attraction, chelation, surface, and internal complexation (Sud et al. 2008). Biowastes used in synthesis of activated carbon portrayed a loose, porous arrangement and consist of carboxyl functional groups, hydroxyl functional groups, and other reactive groups as its main attributes, which promote their usage as adsorbents. In order to explain the synergy existing among the functional groups of activated carbon and ions of heavy metals, different modern techniques have been established to verify the presence of these functional groups, such methods include the Fourier transform infrared (FT-IR) and the Raman spectroscopy, nuclear magnetic resonance spectroscopy (NMR), electron spin resonance (ESR) spectroscopy, and X-ray absorption near-edge (XANES) among several others (Iqbal et al. 2009; Memon et al. 2008). Table 1.6 compares adsorption capacity of adsorbents and mechanisms for some heavy metal ions removal.

Table 1.6 Mechanism of adsorption and maximum adsorption capacity on different biowastes

Heavy metal ions (adsorbate)	Biowaste (adsorbent)	pH	Temperature (K)	q_m (mg/g)	Mechanism	References
Ni(II)	Hemp shive	6.0	293	160.00	Intraparticle diffusion	Kyzas et al. (2015)
	Cocoa shell	6.0	303	97.59	Intraparticle diffusion	Kalaivani et al. (2015)
	Mango peel	5.0	298	39.75	Ion exchange	Iqbal et al. (2009)
Cr(VI)	Teff straw	2.0	298	3.51	Chemisorption	Tadesse et al. (2015)
	Rice husk	1.5	303	11.40	Film diffusion and intraparticle diffusion	Singha and Das (2011)
Zn(II)	Walnut shell	5.0	313	7.48	Ion exchange	Najam and Andrabi (2016)
	Palm oil mill effluent	5.5	353	68.49	Chemisorption and intraparticle diffusion	Adebisi et al. (2017)

(continued)

Table 1.6 (continued)

Heavy metal ions (adsorbate)	Biowaste (adsorbent)	pH	Temperature (K)	q_m (mg/g)	Mechanism	References
Hg(II)	Raw date pits	5.0	293	52.63	Ion exchange	Rezgui et al. (2017)
	Unmodified rice husk	6.5	303	75.19	Ion exchange	Song et al. (2015)
Cu(II)	Potato peel	5.0	298	84.74	Particle diffusion	Guechi and Hamdaoui (2016)
	Raw pomegranate peel	5.8	323	21.37	Ion exchange	Ben-Ali et al. (2017)
	Casuarina fruit powder	5.0	303	4.55	Chemisorption and physical adsorption	Mokkapati et al. (2016)
	Peanut hull	4.0	298	14.13	Chemical and physical adsorption	Ali et al. (2016)
Pb(II)	Rice straw	5.5	298	42.55	Electrostatic attraction and physical adsorption	Amer et al. (2017)
	Coconut shell	5.5	298	26.14	Chemisorption	Sharaf El-Deen and Sharaf El-Deen (2016)
	Plukenetia volubilis L. shell biomass	3.0	323	17.07	Electrostatic attraction	Kumar et al. (2016)
Cd(II)	Sesame leaf and stem	6.0	298	84.74	Chemisorption	Cheraghi et al. (2015)
	Cork biomass	6.0	313	14.77	Chemisorption	Krika et al. (2016)
	Raw walnut shell	6.0	313	7.29	Share or exchange electronics and chemisorption	Najam and Andrabi (2016)
	Salix matsudana carbon	5.0	298	40.98	Chemisorption and intraparticle diffusion	Tang et al. (2017)
	Grapefruit peel	5.0	293	42.09	Ion exchange	Torab-Mostaedi et al. (2013)

q_m adsorption capacity

From Table 1.6, it can be concluded that the choice mechanism of adsorption is dependent on three major factors, namely, (1) the speciation of the contaminant ion, (2) origin of the biowaste, and (3) the synthesis process of the biowastes into activated carbon (Veglio and Beolchini 1997; Lesmana et al. 2009). Also, the operating parameters (pH and temperature) could as well be said to have influenced the mechanism of adsorption.

1.8 Adsorption Isotherms, Kinetics, and Thermodynamic Studies of Activated Carbon

1.8.1 Adsorption Isotherms

The study of isotherm data is fundamentally vital to ascertain the strength of the adsorbent. The relationship of the adsorbate (heavy metal ion) with an adsorbent (activated carbon) could be well explained by adsorption isotherms, which thus helps in maximizing the use of adsorbent. It is a usual tradition to relate the quantity of heavy metal ions uptake by an adsorbent and its concentration in solution by different isotherm models (Hadi et al. 2015).

In 1906, Freundlich introduced an empirical equation which was used to illustrate a heterogeneous system of non-identical adsorption sites. In the model, it was assumed that each adsorbate molecule could be adsorbed only on one adsorption site. However, besides the good representation it gives in some scenarios as depicted by the high correlation values, a well-accepted meaning of the fraction $1/n$ claimed to be relating adsorption intensity was unclear in various examined systems (Gokhale et al. 2008; Zhao et al. 2010). The inability of Freundlich's model to respond as Henry's law at low dilution systems has also been faulted. In addition, even with an evident increase in concentration, no definite adsorption uptake was observed; thereby no peak was noticed as opposed to a real system. Thus, the validity of this empirical isotherm only holds for narrow range of concentration (Foo and Hameed 2010).

Another model was developed on the assumption that adsorption occurs at the homogeneous sites with uniform level of energy (Langmuir 1916). This proposed model by Langmuir was initially expressed to explain gas–solid phase adsorption onto activated carbon but has since been employed to describe the response of various biosorbents. The isotherm hinge on the following theories, viz., (1) adsorption is restricted to monolayer coverage, (2) all surface sites are identical with the capacity to only take one adsorbed molecule, and (3) the potential of a molecule being adsorbed on a specific site is independent of its neighboring sites residency. Noticeable in the Langmuir isotherm is the saturation capacity ($q_{\max}$) which is expected to go along with saturation of a finite quantity of identical sites, and fundamentally, it should be independent of temperature. But, this is contrary to the real situation as narrow to moderate increase (Aydın et al. 2008; Dundar et al. 2008; Malkoc and Nuhoglu 2005) and decrease (Djeribi and Hamdaoui 2008; Padmavathy 2008) in $q_{\max}$ with temperature is mostly noticed. Furthermore, the value of K_LCe is much lower than 1 at utmost dilution which means it can be neglected; therefore, the Langmuir correlation can follow Henry's law. Thus, the isotherm equation makes the prediction of a uniform monolayer adsorption ability at elevated concentration (Hadi et al. 2015).

A need for another model was brought up by Sips in 1948 which took the combined expression of Langmuir and Freundlich isotherms. The isotherm assumed that one molecule may occupy more than one site (Sips 1948b). Despite the finite value

Table 1.7 Nonlinear equations of some selected adsorption isotherms

Isotherm	Nonlinear form	References
Freundlich	$q_e = K_F C_e^{1/n}$	Freundlich (1906)
Langmuir	$q_e = q_{\max} \dfrac{K_L C_e}{1 + K_L C_e}$	Langmuir (1916)
Temkin	$q_e = \dfrac{RT}{b} \ln\left(aC_e\right)$	Tempkin and Pyzhev (1940)
Dubinin–Radushkevich (D-R)	$q_e = q_{max}\, exp\ (-k_{ad}\varepsilon^2)$	Dubinin (1947)
Brunauer– Emmett–Teller	$q_e = q_{\max} \dfrac{C_B C_e}{\left(C_s - C_e\right)\left[1 + \left(C_B - 1\right)\left(C_e / C_s\right)\right]}$	Brunauer et al. (1938)
Sips	$q_e = \dfrac{K_s C_e^{\gamma} S}{1 + a_S C_e^{\gamma} S}$	Sips (1948a)
Toth	$q_e = \dfrac{K_T C_e}{\left(a_T + C_e\right)^{1/t}}$	Toth (1971)
Redlich–Peterson (R-P)	$q_e = \dfrac{K_{RP} C_e}{1 + a_{RP} C_e^{g}}$	Redlich and Peterson (1959)

of the uptake quantity portrayed at very high concentration by this model, a notable drawback is its inability to obey Henry's law at low concentration (Hadi et al. 2015). Over the years, several other isotherm models have been developed and proposed to describe the adsorption process. Generally, these models can be grouped into the two- and three-parameter models (Foo and Hameed 2010). Examples of the two-parameter isotherms are Langmuir, Freundlich, Dubinin–Radushkevich, Temkin, Flory–Huggins, and the Hill isotherm models, whereas the Redlich–Peterson, Sips, Toth, Koble–Corrigan, Khan, and the Radke–Prausnitz isotherm models are examples of the three-parameter isotherm models. The Brunauer–Emmett–Teller isotherm model is a multilayer physisorption theoretical expression commonly employed in the gas–solid equilibrium system (Foo and Hameed 2010). The functional forms of the widely used isotherms are listed in Table 1.7. For ease and simplicity, the Langmuir and Freundlich are the most often applied isotherm equations.

1.8.2 Adsorption Kinetics

Adsorption kinetics is very vital in the choice, design, and operations of reactor systems (He and Chen 2014). Prediction of the adsorption rate for a specific system helps to give useful information on the reaction pathways and mechanisms.

As a way of investigating adsorption mechanism with its possible rate-controlling steps, kinetic models developed have been used to evaluate the observations made from various works. Adsorption kinetics are expressed as the rate of solute that controls the residence time of the adsorbate in the solid–liquid boundary (Zhao et al. 2010). Kinetic studies have been mainly performed in batch reactions by investigating different variables, e.g., initial adsorbate concentration, particle size, adsorbent amount, pH values, and temperature with various adsorbent and adsorbate forms (Zhao et al. 2010). Mostly, the uptake of heavy metal ions via adsorption increases with time until equilibrium is attained between the quantity of adsorbates adsorbed on the adsorbents and the quantity of adsorbates remaining in solution. Adsorption reactions happened very fast at the early period and steadily slow down when approaching equilibrium. However, the time to attain equilibrium varies with the absorbate, adsorbent, initial concentration, and the nature of the solution. Based on solution concentrations, different models have been applied to understand the reaction order of adsorption systems. Examples of such models are the first-order and second-order reversible models, first-order and second-order irreversible models, pseudo-first, and pseudo-second order rate models, Weber and Morris adsorption kinetic model, Adam-Bohart-Thomas correlation, Bhattacharya and Venkobachar equation, Elovich's model, and Ritchie's relation (Foo and Hameed 2010; Saha et al. 2010). Among these models, pseudo-first-order model and pseudo-second-order models are commonly applied to explain adsorption kinetics in evaluating the extent of uptake. The expressions for some selected kinetic models stated are highlighted in Table 1.8 (Foo and Hameed 2010).

Fitting the model kinetic curves and comparing both the experimental and calculated q_e (amount of heavy metal ions in the synthesized activated carbon at equilibrium) values can be used to identify the best kinetic model. Also, the value of coefficient of determination (R^2) obtained can point to the best possible model. A high value of R^2 would suggest the best model to explain the adsorption kinetics.

Table 1.8 Functional equations of selected kinetics models

Kinetics model	Functional form
Lagergren model (pseudo-first-order)	$\frac{dq}{dt} = k_1 (q_e - q)$
Pseudo-second-order model	$\frac{dq}{dt} = k_2 (q_e - q)^2$
Bhattacharya and Venkobachar model	$\frac{dq}{dt} = k_1 C - k_2 C_s$
Elovich model	$\frac{dq}{dt} = \alpha \exp(-\beta q)$
Adam-Bohart-Thomas model	$\frac{dq}{dt} = k_{sorp} C (q_e - q) - k_{des} q$

1.8.3 Adsorption Thermodynamics

Extensive studies on the thermodynamics of metal ion adsorption have been broadly reported in literature. From some of these reports, two major adsorption processes as regards the thermodynamics of the system have been identified, namely, endothermic and exothermic adsorption systems.

An increase in adsorption as temperature increases connotes that the adsorption undergoes an endothermic process, whereas a decrease in adsorption as the temperature increases shows the exothermic nature of the adsorption system. Thermodynamic parameters such as the Gibb's free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) have been evaluated in many studies to check the feasibility and nature of the adsorption process. The parameters were computed using the Eqs. (1.1), (1.2), and (1.3).

$$\Delta G^{\circ} = -RT \ln K \tag{1.1}$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{1.2}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{1.3}$$

where R represents the universal gas constant (8.314 J/mol. K), T denotes the operating temperature in Kelvin, and K represents the equilibrium constant.

The isotherms, kinetics, and thermodynamic parameters of selected heavy metal ions are presented in Table 1.9.

Table 1.9 Isotherm, kinetic, and thermodynamic studies of some heavy metal ions

			Thermodynamic parameter			References
Heavy metal ions (adsorbate)	Isotherm model	Kinetic model	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	
Ni(II)	L	PSO	−20.78	−74.32	332.29	Alomá et al. (2012)
Cd(II)	L	PSO	−0.72	110.47	0.3795	Krika et al. (2016)
	L	PSO	−12.35	6.85	0.068	Zheng et al. (2010)
Cu(II)	L	PSO	2.4506	4.4366	6.171	Ali et al. (2016)
Zn(II)	L	PSO	8.0480	0.0006	−7.8301	Adebisi et al. (2017)
Pb(II)	L/F	PSO	5.9987	0.0408	6.2726	Adebisi et al. (2017)
	L	PSO	−3.876	−21.147	−0.057	Munagapati et al. (2010)
Cr(VI)	L	PFO/PSO	−29.39	0.04	0.10	Al-Othman et al. (2012)
	L	PSO	−5.3387	51.5834	0.1874	Singha and Das (2011)

L Langmuir; *L/F* Langmuir and Freundlich, *PSO* pseudo second order, *PFO* pseudo first order

In order to obtain a good adsorption result, ΔG° must be negative. This shows that the adsorption process is possible and spontaneous. A widely accepted rule follows that a decrease in the negative value of ΔG° with an increase in temperature is an indication that the adsorption process responds well at high temperatures. This may be due to increase movement of heavy metal ions in the solution with increase in temperature, and the attraction of the heavy metal ions on the synthesized activated carbon is high at high temperatures. Contrariwise, an increase in the negative value of ΔG° with an increase in temperature indicates that lower temperatures predict an easy adsorption.

The exothermic and endothermic nature of the adsorption process can be verified by the value of ΔH° obtained for any specific study. A negative value ΔH° indicates that the adsorption process is exothermic, while a positive value ΔH° indicates that the adsorption process is endothermic.

During the adsorption process, the heavy metal ions displaced more than one water molecule thereby resulting in the endothermic nature of the process, hence making ΔH° positive, whereas in an exothermic process, the energy released during the adhesion of bonds between the heavy metal ions and the activated carbon is greater than the energy absorbed in the breaking of bonds. Thus, this leads to the release of surplus energy in the form of heat making the ΔH° to be negative (Saha et al. 2010).

A positive value of ΔS° indicates the strong attraction of the synthesized activated carbon for the heavy metal ions. In addition, the positive value also points to increased randomness at the solid-solution boundary with some morphological alteration in the heavy metal ions and the activated carbon.

As shown in Table 1.9, most of the adsorption systems show that the Langmuir model portrays an adequate fit for the adsorption system as the model signals that the monolayer coverage is responsible for the adsorption of the metal ion onto the surface of the activated carbon rather than the multilayer adsorption (Hadi et al. 2014).

1.9 Conclusions and Future Investigation

Adsorption technology has been widely embraced for the removal of heavy metal ions from contaminated media, especially in water systems. Based on existing research works, this review extensively detailed the different areas of investigation associated with the adsorption process. The utilization of low-cost adsorbents synthesized from agricultural wastes into activated carbon is recommended since they are readily available and also renewable. The review also emphasized that the modification of these adsorbents helps increase their efficiency in heavy metals removal. Optimization of the adsorption system is vital, and this was discussed based on the isotherms and thermodynamics of previous studies carried out in batch systems. For future investigation, we suggest that subsequent research should be carried out in continuous adsorption systems as this will help to simulate a real-life scenario. This will thus prompt a new quest to understand the kinetics of the process as it applies to designing a system for large-scale applications.

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Chapter 2
Polymer Absorbents for Heavy Metal Removal

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Abstract Mixing of heavy metal and metalloid in water bodies is an established issue, and it is highly under scientific consideration by several research. The polymeric materials created so far have shown excellent outcomes and have the ability to be effectively implemented for the recovery of heavy metal from polluted waters and have the ability to be used in family use filter schemes in societies using mining and industrial wastewater-impacted borehole water. For metal processing sectors, desorbed metals can be useful. For metal processing sectors, desorbed metals can be useful.

Natural polymers also have outstanding characteristics such as low original price, nontoxic by-product manufacturing, comparatively easy design, and timely productivity. The properties of an optimal and suitable absorbent for removal dye include comprehensive surface area, high capacity and absorption capacity, pores with adequate size and quantity, comfortable accessibility, effective, economical, high mechanical stability, compatibility, simple regeneration, environmentally friendly, high selectivity to remove multiple dyes, and the needless use of high-tech processing. Researchers have therefore recently focused on extending compounds based on natural polymers.

Keywords Heavy metals · Water pollution · Adsorbents · Environmentally friendly · Green synthesis · Polymer-based sorbents · Remediation · Agricultural waste recycling · Natural sorbents

2.1 Introduction

Henry David Thoreau said in his book named Familiar Letter The writing of Henry David Thoreau that a beautiful house is useless if you don't have a clean planet to put your house on it (Thoreau 1895). The Earth, which is so crucial, faces great deal of hazard from its own people. Day after day, environmental quality is degrading since industrialization owing to human society's ignorance causes pollution. Major contaminants includes benzene derivatives, coloring agents, hydrocarbons, carboxylic acids, and inorganic carcinogenic materials such as metabolic waste.

Our planet is experiencing ever-increasing degradation of the three main environmental compartments, resulting in living humans facing aggregately poisonous components and compounds current in the environment, resulting in 40% annual human mortality (Pimental et al. 2007). Life quality has been upgraded in the last decade after the industrial revolution; now we are concerned about the mechanization epoch (by mechanical and computerized production units/machines) that severely harm environmental spaces along with the deterioration of commercial and economic exuberance in terms of health and loss of biodiversity (Dean and McMullen 2007).

2.2 Water Quality Degradation by Rapid Industrialization

It is a well-established fact that to sustain life on earth, water is essential. Water is a resource that can be used to transport products such as infectious agents, toxicants, and temperature gradient. It is well determined that the amount of complete water resources on the whole planet remains continuous, but their norms differ spatially and temporarily. The problem of water quality was attributable (Ebenstein 2012).

Due to the shift in financial resource management strategy, the problem of aqueous standard decline in growing countries is increasing. This declaration is justified by the following phenomenon of such states explosive fight to obtain a strong financial stance and expand the achievement goals of the state (Kithiia and Khroda 2011).

When there is a need for brisk economic growth, state stakeholders need to take measures to raise awareness among residents and industry owners of the application of standards that guarantee the safety of all living humans. New computerized age is well established now at the comprehensive atmospheric costs, thus enhancing the degradation of our environment (Hettige et al. 2000).

2.3 Environmental Degradation by Heavy Metal Accumulation

Heavy metal is not biodegradable and is environmentally persistent. In many industrial system work processes, heavy metals accumulate up to a toxic concentration in various environmental compartments and cause ecological damage. The effects of this degraded water quality include aquatic ecosystem disruption, which in turn causes biodiversity loss (Jaber et al. 2005).

Due to enhanced quantities of heavy metal and other pollutants released into industrial effluent, environmental stakeholders were concerned about their dangerous impacts when they were dissolved in freshwater resources (Say et al. 2006). By blending heavy metal containing waste water in the natural environment with the other compartment of the setting, freshwater resources are one of the most important sensitive medium toward quality degradation (Nurchi and Villaescusa 2012).

The example of heavy metals includes mercury (Hg), lead (Pb), sulfur (Zn), arsenic (As), cadmium (Cd), nickel (Ni), and chromium (Cr) which are nuclear components with at least five times the particular water gravity. They are also known as trace components because of their existence in environmental matrices at small levels (< 1000 ppm). Indeed, some of them were acknowledged as essential nutrients for organism (Say et al. 2006).

Although heavy metals are naturally occurring elements present inside the Earth's crust, the majority of environmental pollution and human exposure to heavy metals are caused by multiple anthropogenic operations such as military, industrial, agricultural, and waste disposal procedures. Heavy metals are also released through natural procedures such as rock weathering and volcanic eruptions to the ecosystem. Most heavy metals are extremely toxic to living organisms, particularly when they exceed the ecosystem's permissible boundaries. These pollutants can be absorbed by marine life and are resistant to biological decomposition. They have a tendency to be accumulated in living tissues once elevated levels of heavy metals join the food chain (Anirudhan and Ramachandaran 2008).

2.4 Heavy Metal Remediation: Conventional Approaches

Eliminating heavy metals from the wastewater before discharging it into the atmosphere is a scary problem of environmentalists. Environmental remediation therefore begins mainly with heavy metal clean-up. Different techniques have been introduced since the recognition of issues including neutralization, precipitation, ultrafiltering, electrodeposition, cementation, etc. (Erdemoglu et al. 2004).

There are, however, many inconveniences in the implementation of these techniques, such as bad sorbate selectivity, strong residual manufacturing, and induction of different metallic ions in the treated discharge effluent along with organic compounds generated during therapy that inhibit the process and also nonviable due to the cost factor (Say et al. 2006) .

2.5 Adsorption as Most Viable and Economically Feasible Remedy for Heavy Metals

The physical attachment on the surface of the sorbing substratum of gas, fluid, and solid elements/compounds is called the adsorption phenomenon. Using contemporary materials such as polymer, ceramics, and nanomaterials for synthesizing best adsorbents is common. The excellent sorbent must possess large pore volume, increased exterior layer, enhanced external layer features specific active sites, incremental holes volume present upon upper surface. Another property is the presence of mainly small holes, along with poor attraction forces between specie that get to be adsorb and substrate (The bond must be nonchemical bonding materials that make sorbate to desorb easily and they are low-cost raw materials) (Yang 2003).

Absorption method needs contact of liquid (should be treated) with strong stage capable of grasping this fluid and acting as a substrate. The absorbent must therefore have permeability and porosity along with an elevated region of surface. Figure 2.1 shows best relation among all component of adsorption system. The absorption mechanism includes capillary action, while the method of adsorption requires sorbate (fluid) contact with the surface of the sorbent (solid). In the absorption phase, the appealing forces needed for sorbate–sorbent surface interaction are regarded to be as weak as chemical bonding. In brief, the sorptive (adsorption or absorption) method depends on the distribution of particle size, microporosity, tubular or capillary structure (present in sepiolite), and active sites on surface (Ismail et al. 2010).

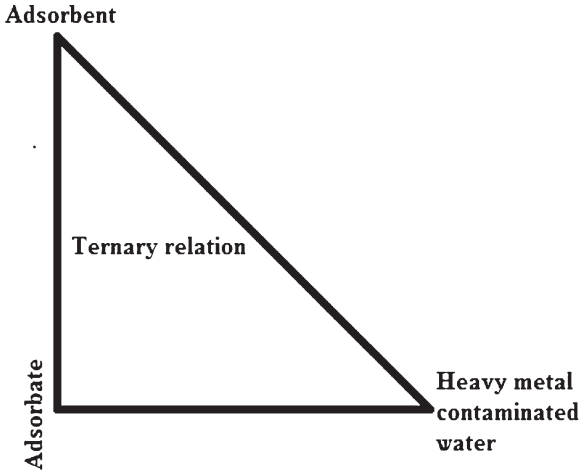

Fig. 2.1 Relation among all components of adsorption system

2.6 Choice of Adsorbent

However, selecting novel kinds of adsorbents is the biggest issue in this sector. Several adsorbents are used to culminate ions of heavy metal, e.g., activated carbon (Brigatti et al. 2000), zeolites (Chuang et al. 2007), clays (Carrado et al. 2001), and agricultural residues (Hettige et al. 2000). The significant drawbacks of such sorbents include small adsorption capacity, their comparatively poor bonding with heavy metal ions, and problems in some of them separating and regenerating from wastewater. Metal ions can be significantly removed by ion-exchange resins, but they have weak ion discernment and elevated swelling in combination with bad mechanical stamina (Koo 2006).

2.6.1 Conventional Sorbents

Adsorption is regarded to be the most environmentally friendly method for particular removal of such pollutants. The ion-exchange resins, chelating agents (ligands), and hybrid composite materials with carrier matrix (such as inorganic materials) and organic enhancers (such as polymers) are different sorbents in use (Say et al. 2006).

The activated carbon has been regarded as one of the most commonly used adsorbents in the last century. The toxic pollutants in industrial waste aqueous medium that has benzenols, pigments, and inorganic toxicants must be adsorbed strongly by charged charcoal produced from distinct fields of operations. But it is a reality that the heat charged use of charcoal in pollutant removal has faced costly reproduction in the long run as a result of adsorbent toxicity potential. In addition, it adsorbs separate chemicals unsystematically, minimizing their likelihood of being used again, making it more hard to regenerate the adsorbent. Meanwhile, for aqueous cleaning, many inexpensive adsorbing substrates are synthesized. Such adsorption substrates are accessible because of advantages that include either inexpensive substances produced through useless products that look financially captivating for industrial consumption. Although their extraction effectiveness and tensile strength need to be improved by improvements either by mixing with various other functional products or by grafting various chelating groups to increase the adsorption ability to be used in large fields (Pan et al. 2009).

Nonorganic metallic oxygen compounds developed during these phases; the chemistry belongs to their internal morphology along with their features of paralyzing hydrocarbon compounds on the bottom layer of adsorbent. To increase their surface activity Si-OH functionality has been improved onto surface active sites that get attached to dendrimers of functional groups of adsorbing species so they can take part in adsorption process of much petroleum waste material which is a characteristics inorganic precursor in nature. A functional group that already exists on the surface of oxygenated metal compounds to participate in the reaction of a functional group carrying a molecule that extends the size of the carbon chain becomes another factor in their potential application as adsorbents. But they have an important restriction on the strength of such organically altered exterior layers in mitigating pollutants from nonpolar solvents and aqueous solutions (Dogan et al. 2008).

Pollution from the environment has become a worldwide issue and is attracting a lot of attention. To meet their requirements, people are dependent on the natural environment. This interaction between people and environment can negatively impact the environment and the natural resources. This, as a result of demand for economical, industrial, and agricultural development, still outweighs the demand for a healthy natural environment. Moreover, the global development raises new challenges in environmental protection and conservation. The most common natural asset of our planet is water bodies (either fresh or saline) which are the gifts of God for human society which are facing serious threat of deterioration by heavy metals by anthropogenic sources. Another significant ecological issue associated with hydrosphere damage worldwide is the pollution of water bodies by heavy metal ions due to their hazardous environmental and human health impacts (Pan et al. 2009).

2.7 Polymers as Adsorbent for Heavy Metals

The weaknesses in other separation technologies to remove metallic ions dissolved in water resulted scientists to investigate alternate methods, for example, polymeric hydrogel network adsorption over a lengthy period of time. The use of hydrogels was launched a decade ago to confiscate toxic cations from dilute solutions. Thereafter, multiple fresh sizes were studied and reported by polymeric networks, beads, and hydrogels in the field of metal extraction. The hydrogels have distinct functional groups; they are similar with other techniques such as the extraction of solvents and the exchange of ions with the simplicity of operating condition with the method of strong phase ion exchange. The benefits of using hydrogels compared to other procedures are because of elevated sorption ability, deterioration of final products, and least difficult processing associated with volatile solvents (Ozcan et al. 2009). Polymeric adsorbents can be used in heavy metal adsorption owing to their simple regeneration and powerful mechanical characteristics compared to other adsorbents such as activated carbon, cellulose, etc. For example, macroporous synthetic polymeric adsorbents were used as perfect adsorbents for adsorption pollutants such as phenols from wastewater. Although polymers are preferred sorbents for toxic cation, high price of these products may impede their use as cheap adsorbents for the large-scale production of heavy metal-free water (Lagadic et al. 2001).

A number of local products can be used to eliminate heavy metals. Because of the following factors, it is discovered that the adsorbents are cheaper in price, such as natural products. The removal of heavy metals is more encouraging for agricultural waste, modified biopolymers, or industrial by-products.

- Economic
- Metal selective
- Regenerative
- Absence of poisonous sludge generation
- Metal regeneration
- High efficiency

In recent times, study has concentrated upon the usage of agronomic by-product polymers as sorbents by the biosorption method to remove heavy metals from industrial effluent. In addition, biopolymers pose a variety of distinct covalent functional groups, such as amines and hydroxyls, which enhance metal ion uptake effectiveness. When selecting the biomass for metal removal, consideration must be given to the origin of the biomass. The following can be obtained from biosorbent sources:

1. Decaying organic matter such as squid, bark, crab shell, lignin, krill, and shrimp
2. Colonies of algae
3. Microorganisms
4. Agro-related products (Li et al. 2002: Macht et al. 2010: Mitragotri and Lahann 2009)

2.7.1 Natural Polymers as Heavy Metal Adsorbent

Natural supporting materials are generally accessible in big amounts and low price and can be chemically altered to improve metal binding capacity. Natural polymers are distinctive materials owing to low-cost, readily accessible, reproducible sources, hydrophilic and stable biopolymers, secure, and free from side effects and flexible polymers. They also have great adsorption requirements to remove pollutants from colored wastewater, including coloring. Due to its quick and comfortable and inscrutable to poisonous contaminants, adsorption is a preferred technique compared to other techniques. Natural polymers also have outstanding characteristics

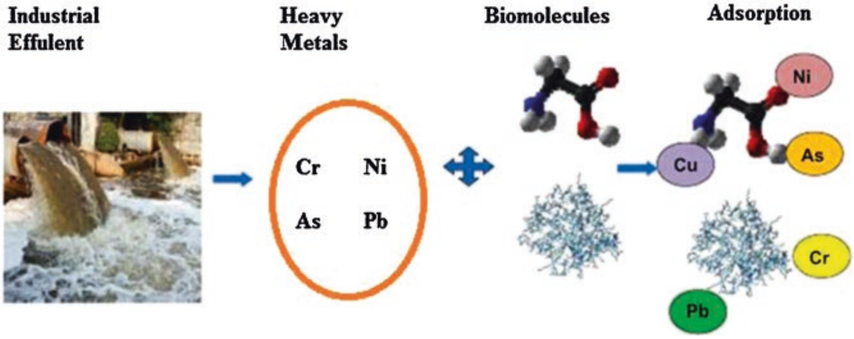

Fig. 2.2 Mechanism of heavy metal removal by biomolecules

such as low original price, nontoxic by-product manufacturing, comparatively easy design, and timely productivity. The properties of an optimal and suitable absorbent for removal dye include comprehensive surface area, high capacity and absorption capacity, pores with adequate size and quantity, comfortable accessibility, effective, economical, high mechanical stability, compatibility, simple regeneration, environmentally friendly, high selectivity to remove multiple dyes, and the needless use of high-tech processing. Researchers have therefore recently focused on extending compounds based on natural polymers (Nanda et al. 2011) (Fig. 2.2).

One of the most severe environmental concerns is wastewater containing heavy metal ions. Exposure to high concentrations of heavy metals can harmfully impact water bodies, putting human health and environmental compartments at risk. Adsorption using biopolymer appears to be a promising alternative technique among the different therapy techniques. Chitosan is a natural chitin-based polymer that has outstanding characteristics such as biocompatibility, biodegradability, and non-toxicity. In addition, chitosan is regarded as an efficient sorbent owing to the existence in its molecules of amino and hydroxyl groups that can serve as locations of attachment to metal ions. Chitosan derivatives have recently gained considerable attention as metal ion sorbents. These derivatives are ready either through physical or chemical changes or both to enhance the adsorption characteristics of chitosan. Chitosan, a chitin-produced amino polysaccharide, is naturally discovered in some fungi. Because of its biological compatibility, biological degradation, and antimicrobial properties, it is the most versatile biopolymer for a wide-spectrum of apps. This material is also considered to be an optimal adsorbent. The presence on the polymeric backbone of hydroxyl and amine groups can be used as chelating and response sites (Nurchi et al. 2012).

Peanut shells, corn stalk, and rice straw are natural cellulose sources as it is the primary structure phytocytology. Ordinary cellulose fibers are identifiable as chunk of the plant's cell walls, and microfibrils are organized into highly structured cellulose fibers through H-bonding in an intricate layer. Cellulose chains are prepared and organized into microfibrils and are the homo-polymer carbohydrate consisting of β-D-glucopyranose units coupled with β-1,4-glycosidic links. (Fig. 2.3).

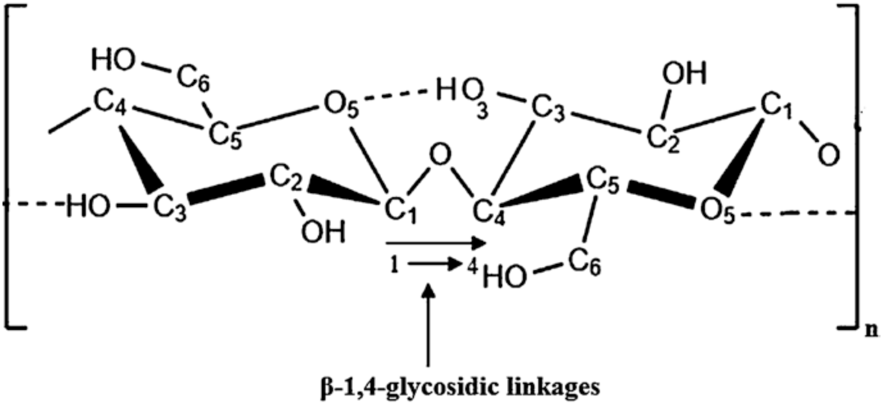

Fig. 2.3 Glycosidic linkage

Cellulose's main feature is an enormous amount of hydroxyl groups consisting of three groups of hydroxyl: C-2 and C-3 secondary OH andC-6 primary OH (Fig. 2.2). These groups of hydroxyl have affinities with heavy metal ions. However, raw agricultural residues are usually low load capacity, comparatively tiny metal ion binding constants, and low selectivity due to –OH groups engaged in pure cellulose intermolecular hydrogen bonds (C–H—-O) (Phan et al. 2009). Meanwhile, cellulose's crystalline structure impacts cellulose's adsorption characteristics as their flexibility decreases with a growing proportion of crystalline to cellulose's amorphous areas. Recent studies have suggested that chemical modifications can be carried out to destroy the hydrogen bonds, decrease the crystalline structure, and make binding sites more efficient in the form of crystalline cellulose and then create –OH groups more reactive to attach other functional groups and attain better adsorptive properties (e.g., ion-exchange properties). Najafabidi et al. prepared chitosan/graphene oxide (GO) nanofibrous, and their adsorption behaviors of Cu^{2+}, Pb^{2+} were investigated, and the results are shown in Fig. 2.4.

2.7.2 *Biopolymers from Agricultural Recycling*

Several agronomic by-products, e.g., straw, coconut husks, rice, wool, used coffee, waste tea (Boonamnuayvitaya et al. 2004), rice hulls (Ahmaruzzaman and Gupta 2011), cork waste (Psareva et al. 2005), seeds of *Ocimum basilicum* (Levankumar et al. 2009), coconut shells (Amuda et al. 2007), soybean keels and cotton (Sud et al. 2008), sawdust of walnut untreated coffee dust (Dahri et al. 2014), papaya wood(Hameed 2009), peanut hulls (Brown et al. 2000), and citrus peel (Ajmal et al. 2000) were used as adsorbents for heavy metal removal. However, with encouraging outcomes, marine weeds, molds, yeasts, and bacteria were screened for metal

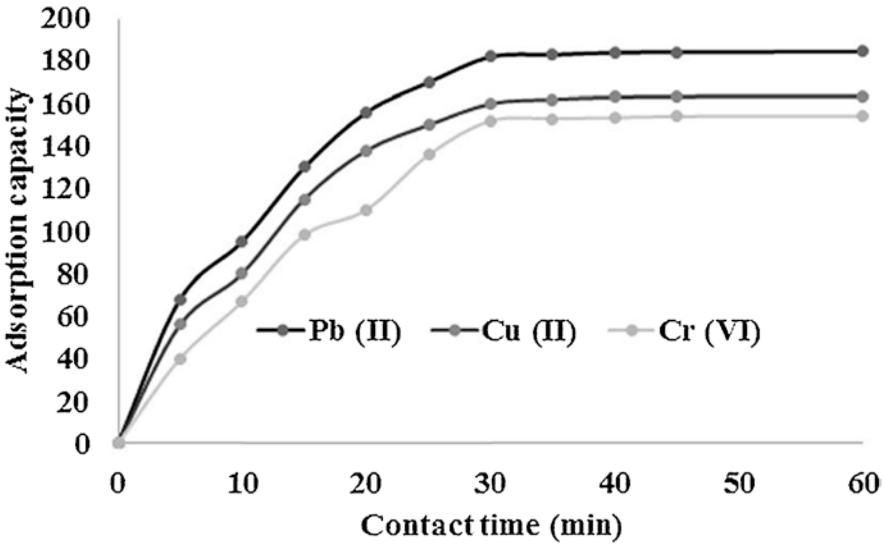

Fig. 2.4 Adsorption results of chitosan/graphene oxide (GO) nanofibrous. (Modified Najafabidi et al. 2015)

biosorption. The parameters studied to optimize the use of adsorbent in the therapy of sewage comprise:

1. Chemical behavior of sorbent and sorbate
2. Amount of toxic metals
3. Physical parameters of the aqueous solution
4. Adsorption kinetics
5. Isotherm of adsorption
6. Time of contact

Minimal or no chemical modification is required before use of these wastes. Therefore, these materials possessed weak adsorption and selection characteristics (Hegazi 2013).

2.8 Chemo-Substituted Agronomic By-Products as Adsorbent

Due to intensified industrial activity and environmental stress, the need for powerful adsorbents has appeared. Several works have been performed to solve this issue to remove efficient materials through chemical modification and treatment of these wastes. Lignified cellulosic agricultural waste materials are a plentiful source of potential metal-sorbing biomass (Sivakumar et al. 2001). As a general rule, agricultural waste products consist of lignin and cellulose constituents hemicellulose, lipids, extractives, enzymes, starches, and glucose and its simple derivatives, water, ash, and hydrocarbons and similar chemical species containing range of functional reactive groups are other elements. Cellulose and starch are the most prospective contestants with different responses and accept chemo substitution, i.e., ethoxylation, and others. The two primary methods of preparing polysaccharide-containing sorbents are:

1. Chemical bonding of OH and NH_2 groups to form water-insoluble cross-linking (gels) networks with a coupling agent.
2. Control of polysaccharide movement on surface to provide hybrid or composite materials by coupling or grafting responses. Cellulose is an abundant natural polymer on earth. It has sharp crystal structure in which sugar self-polymerizes with an intramolecular and intermolecular association of β1 4 glycosidic and hydrogen bonds. Chemical cellulose alteration has led in a huge amount of derivatives of cellulose. In this regard, cellulose, soluble, maize, and maize starch polysaccharides (PS) with varying amylopectin/amylose content were connected chemically to form polymeric adsorbents with epichlorohydrin (EPI). The characteristics of chemically bonded polysaccharides and epichlorohydrin components were designed by changing the circumstances of preparation (reagent ratios and polysaccharide) to provide adjustable-property polymer products. For sequestration of chromium VI from industrial wastewater, *Dalbergia sissoo* (Shisham) legumes were used as lignified cellulosic nitrogenous waste material. *Dalbergia sissoo* (Shisham) legumes (DSP) can be considered as a lignified cellulose agro waste product that contains sensible quantities of proteins and fibers in terms of its composition. The metal elimination capability was examined versus many variables, such as pH adsorbent dose impacts, original amount of metallic ions, stirring velocity, and time of contact. The prior job (nanoparticles of hydrogels were synthesized on carboxymethyl cellulose (CMC) acrylic acid, and N-isopropylacrylamide (NIPA) graft copolymerization. To remove aqueous solutions from copper and lead ions, the prepared nanogels were used. The impacts on metal ion removal ability of pH, moment, cross-linking agent ratio, temperature, and original metal ion concentration were explored (Mahajan and Sud 2012). In addition, the+ ve ion of metal is the adsorption mechanism of super-absorbent hydrogels based on cellulose.

Mahajun and Sud reported the prospective use of *Dalbergia sissoo* pods as a biosorbent for chromium sequestration (VI) in its different forms. This prepared biosorbent is capable of removing the chromium(VI) ions from water media along with sorption capability was heavily dependent on the adsorbent nature, the quantity used, the original metal ion concentration, and the original pH. The experimental information fits well with excellent correlation coefficients for the Freundlich and Langmuir equations. The sorption and desoption cycles have been shown in Fig. 2.5 (Mahajun and Sud 2012).

Results of sorption possessed that the percentage of ion uptake values were the peak values, i.e., 13.8, 11.5, 9.8, 9.0, and 8.7. In addition, superabsorbent hydrogels established on cyanoethyl cellulose had synthesized and utilized from aqueous solutions for Cu^{2+}ions adsorption. Metal ion removal has been discovered to be dependent on the deprotonation and protonation characteristics of basic and acidic groups, i.e., medium pH value (Dahri et al. 2014).

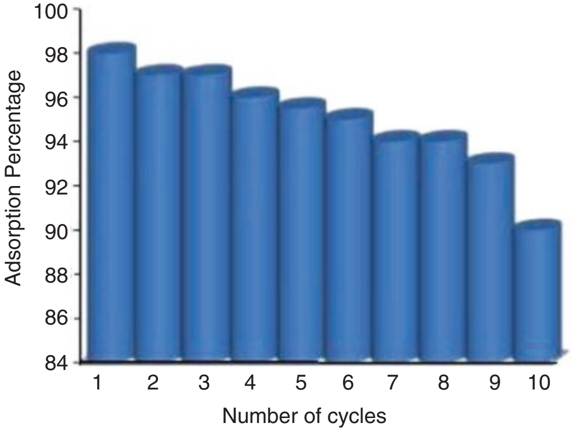

Fig. 2.5 The sorption and desoption cycles. (Modified Mahajun and Sud 2012)

In addition, to synthesize hydrogels for the purpose of sorption of metal ions, cellulose was grafted into acrylamide. The grafting conditions were explored, and the sorption by grafted cellulose of various metal ions was investigated. The cellulose derivatives were also used for the preparation of adsorbent hydrogels (O'Connell et al. 2006).

The ideal conditions for removing nickel from water using prepared copolymers were investigated by varying pH, contact time, and levels of metal ions. Starch is a natural polymeric material (primarily hydrocarbon) made up of a big amount of units of glucose joined by glycosidic bonds. Most green crops produce this polysaccharide for energy conservation. Starch is next commonly available material after cellulose carbohydrate and exists in big quantities in main foods such as maize (corn), wheat, potatoes, rice, and cassava. As it comprises two molecular types, it has a distinctive structure: straight chain or cyclic amylose and branched amylopectin. Starch usually includes 20–25% amylose and 75–80% amylopectin by weight, depending on the plant. Intensive research has been conducted to utilize in wastewater removal of heavy metals. In this regard, the initiator used ceric ammonium ion to synthesize graft copolymers of acrylonitrile and cassava starch solution made up in water. The prepared copolymer was used to absorb toxic cations from the water bodies as a sorbent. The sorption capability was assessed by evaluating the magnitude of nickel, copper, and lead metal ion sorption under circumstances of equilibrium (Liu et al. 2012).

2.9 Hydrogels as Heavy Metal Adsorbent

Hydrogels were prepared, described, and examined on the basis of saponified polyacrylonitrile and starch composites with water solubility characteristics. These hydrogels "water absorbency" characteristics were discovered to depend on factors that affect the levels of both saponification and polymerization. The hydrogels synthesized were utilized to remove certain toxic metal ions from water-based medium (Isobe et al. 2013).

2.9.1 Starch-Based Hydrogel as Adsorbent

The efficacy of removing metallic ions from their water-based solution was explored through interlinked carboxymethyl corn starch. When 1% starch was incorporated, mercury, lead, and cadmium in water were almost entirely removed. Starch could be regained by cleaning the metallic ions with weak acid from the complex (pH 2.0), although this method slightly lowered the metal bonding activity of the starch. The starch obtained from corn has been altered with natural compounds, itaconic acid, and maleic acid through esterification in a water medium, and duty of catalysis was performed by NaOH to generate sorbents for the removal of metallic cations in water bodies. The impact of single and double alteration of both acids has been explored on the swelling and solubility ability of the modified starch. In addition, the ability of itaconic acid-substituted starches to adsorb metal cations such as nickle, cadmium, zinc, and mercury has been checked, and data likened with natural corn starch (Ma et al. 2015).

The acid hydrolysis has functionalized the starch and/or oxidized to form –COOH group at six number carbon by nitrogen oxides. Copper ion sorption was researched as a purpose of composition of hydrogel and other variables. Hydrogels display a connection between structure and property in the Cu^{2+} ion sorption. The hydrogel showing the peak ion uptake was taken to analyze the impact of the concentration on sorption ability of contact moment, pH, temperature, and Cu^{2+} ions (El-Hamshary et al. 2014). In addition, carboxyl-containing anionic starch researched its use as a chelating agent. As the acrylic content improved, the sorption effectiveness of the alkali-treated samples improved. The sorption values relied on the metal ion for separate heavy metals and followed the order $Hg^{2+} > Cu\underline{2+} > Zn^{2+} > Pb^{2+}$. The removal efficiency with respect to pH has been shown in Fig. 2.6 (Kweon et al. 2001).

An innovative cross-linking at the sodium xanthate doped polyacrylamide was grafted upon starch extracted from corn, the copolymerization of acrylamide (AM) and sodium xanthate reactions by epichlorohydrin (EPI) as a cross-linking agent and ceric ammonium nitrate (CAN) as starter. In sewage therapy, the efficiency of the synthesized hydrogel was explored. Recently, metal anion adsorption mechanisms have been explored by quaternary ammonium amphoteric starch and carboxymethyl groups. The adsorption capability was discovered to be dependent on solution pH, cross-linked amphoteric starch dose, and original Pb (II) ion concentration. The proposed responses are engaged in the process of preparing (Yin et al. 2008) (Fig. 2.7).

Also used to eliminate chromium VI from aqueous solution were interlinked acid base starches (CASs). It was discovered that the adsorption method depends on original pH, Cr (VI), CAS dose, and temperature. In addition, phosphate

Fig. 2.6 Removal efficiency of heavy metals by hydrogel with respect to pH. (Modified Kweon et al. 2001)

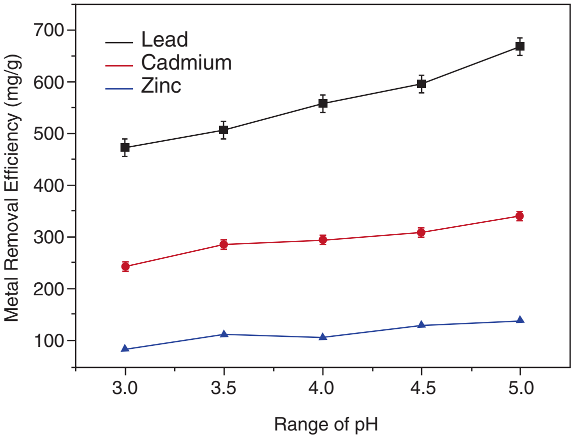

Fig. 2.7 Some sources of starch

carbamates with cross-linked starch have been prepared and used from an aqueous solution to adsorb Cu (II) ions. Batch adsorption studies were conducted based on adsorption moment, dose of adsorbents, pH, content of substitute groups, original concentrations of Cu(II) ions, and temperature (Xu et al. 2003).

2.9.2 Biopolymer Composite for Heavy Metal Removal

Despite their ultimate importance, when used in a smooth shape, biopolymers have some obstacles limiting their use, such as their small upper layer and the exertion of separating them from the medium. On the other side, in complicated multiphase structures with an external magnetic field, magnetic adsorbents have a large area upon the surface and are simple to isolate from the media and regulate (Gotoh et al. 2004).

Composites made of different polysaccharides constitute another class of naturally secure products for multiple applications in the biological and industrial fields. For instance, chitosan, gum arabic, β-cyclodextrin, and cellulose, magnetic nanomaterials functionalized with biopolymers were used to exclude poisonous metals from water medium. Very little research has been performed on starch composite preparing. The starch obtained from potato peels has been adjusted with acrylic acid in this regard. Nanoparticles were synthesized consisting of substituted starch polymer and Fe_3O_4. The nanoadsorbents prepared were used to selectively remove Pb^{2+}, Cu^{2+}, and Ni^{2+} ions from water (Zhou et al. 2016).

Because of their low price and biodegradability and therefore environmentally friendly, starch-based copolymers are highly needed in sector. Because of environmental concerns, copolymers which have grafted starch have developed the central idea for preparing hybrid superabsorbent nanocomposite. Starch has been shown to be effective in stabilizing nanoscale particles of magnetite, and starch-supported magnetite ore nanoparticles are powerful sorbents for in situ soil removal of arsenic contaminated (Carlos et al. 2013).

A freshly designed strategy to reduce the process waste left behind in the manufacturing and leachable arsenic. A fresh group of starch-linked magnetite nanoparticles for arsenate removal were prepared and tested. As an additive to depress the nanoparticle agglomeration, a cheap, green starch was used. Recently, Fe° nanoscale steadied with multiple polymers; carboxymethyl cellulose and starch were investigated and contrasted for their ability to remove arsenic (III) and arsenic (V) from water medium alternatives as the common arsenic removal iron nanoparticles (Liu et al. 2015) (Fig. 2.8).

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The most commonly occurring natural biopolymer lignocellulose has been noted for its prospective adsorption of heavy metals because its molecules contain a big amount of active hydroxyl, phenolic, carboxyl, and other working groups that can be used in electrostatic interaction and heavy metal ion coordination sites. However, it has block extensive application hard due to its bad reactivity, weak polydispersity

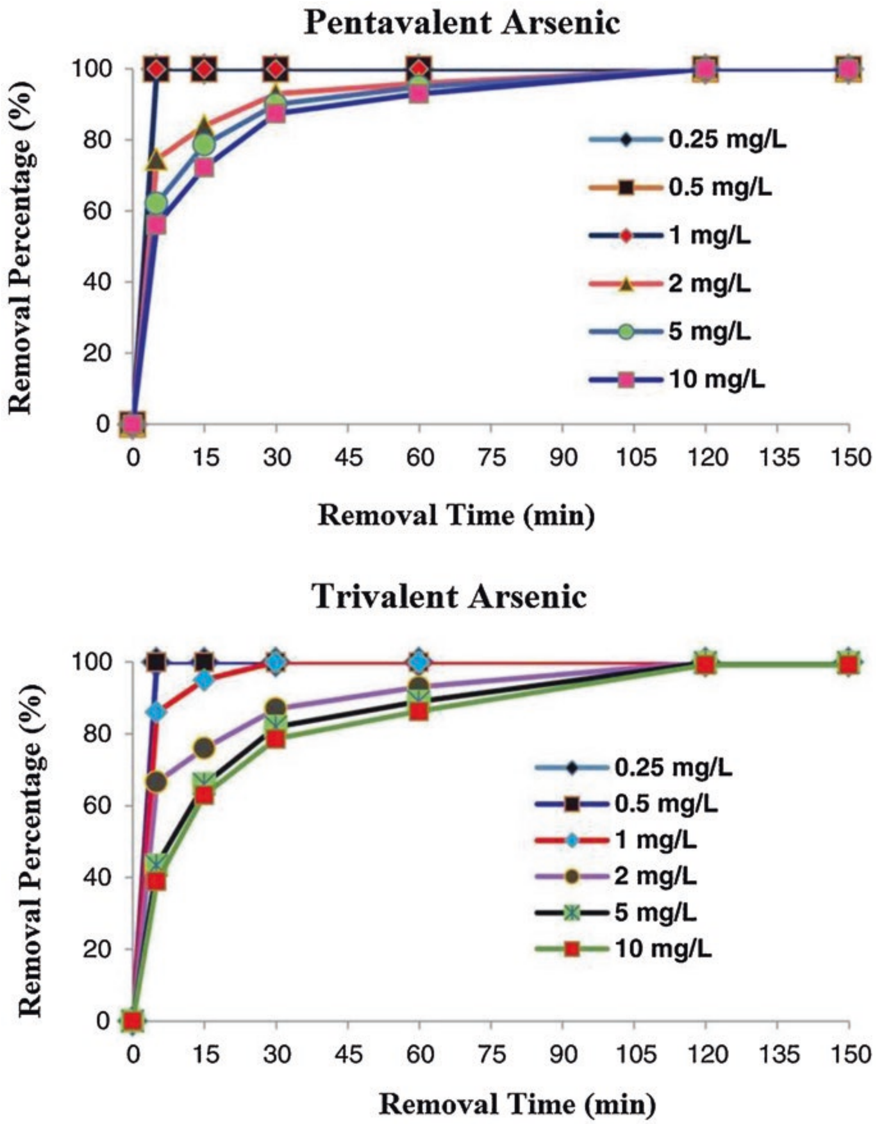

Fig. 2.8 Adsorption kinetics of As (V), (III) by S-nZVI adsorbent dosage = 0.3 g/L, pH = 7. (Modified (Liu et al. 2015)

characteristics, and low specific gravity. Therefore, particular attention was provided to derivatization by immobilizing sulfhydryl onto the LC to solve these problems and increase the adsorption impact. The sulfhydryl group site generally has elevated binding affinities with heavy metals due to its coordination and chelation. (Qi and Aldrich 2008).

In addition, a derivative of sulfhydryl–lignocellulose has many distinctive characteristics, including water solubility, controllable biodegradation, adhesive characteristics, and heavy metal selectivity. Sulfur introduction also adds to higher acidic solution stability owing to cross-link formation. It has become particularly appealing in latest times with regard to apps for adsorption. Significant recognition is currently being given to elastic layered silicates (e.g., montmorillonite clay). However, due to swelling, low affinity, and dispersed water suspension properties, montmorillonite adsorbs only very small amounts of heavy metal ions to the surface of the broken bonds on the outside. In addition, the literature showed that altered MT exhibits a greater adsorption ability than the initial clay (Salman et al. 2015).

2.10 Polymer Nanocomposites as Adsorbent for Heavy Metals

Although raw clay minerals also demonstrate sorption potential, it is also a well-established fact that unmodified natural clay particles have relatively lower adsorption capacity, so they can be altered to enhance their adsorption capacity (Ozcan et al. 2009). We need an alternative, cost-effective adsorbent to remediate heavy metal in industrial wastewater that can be recovered by desorption (Li et al. 2002).

Polymer sorbents have been acknowledged in recent centuries as a protective replacement for standard remediation methods in the form of big upper layer size, better mechanical characteristics, changing upper layer morphology gas impermeability, and achievable desorption restoration (Pan et al. 2009). As a result, polymer grafting on nanoclay particles dramatically enhances nanocomposite characteristics by enhancing surface area and sites of absorption (Ray and Okamoto 2003).

2.11 Inorganic Organic Hybrid Materials as Heavy Metal Adsorbent

Nowadays, to reduce these drawbacks, novel hybrid polymers were taken into account to remove toxic species from wastewater. The practical variant of hydrocarbons in these compounds is united with the benefits of a thermally heat resistant and robust inorganic substratum, which results in covalent bonding toward nominated metal ions and comparatively high adsorption capacity of metal ions. Functionalized polymeric hybrid materials as adsorbents are considered to be one of the most efficient methods because the organic–inorganic polymer hybrids can chemically bond metal ions. These types of products often synergistically present the finest characteristics of each of their parts and have elevated physical, chemical, and mechanical properties performance (Jiang et al. 2007). Since comprehensive research on the production of clay-based hybrid compounds by the sol–gel technique has been carried out. These compounds can be produced either directly by their precursor polymerization response (or by grafting suitable organic groups on main chain created by sol–gel methods such as silica gel) (Samiey et al. 2014).

2.12 Polymer/Clay Nanocomposite as Heavy Metal Adsorbent

Polymer/clay nanocomposites have drawn significant attention from scholarly scientists as a very promising option to expanding industrial and economic operations and satisfying progressively stringent circumstances. Polymer/clay nanocomposites are now becoming an evolving research and growth area. They are actually multiphase materials in which ultrafine clay in the range of 1–100 nm is dispersed into polymer matrix. They simultaneously demonstrate both inorganic and organic properties that assist the investigator study their apparent potential or technological material that also provides a comfortable macroscopic environment for studying main science phenomena, such as zeta potential (electrokinetic potential in colloidal systems), rheology, and young modulus. After discovering the outcomes of such different tests of these materials, it was well defined that they demonstrate enhanced characteristics such as tensile strength, traction modulus, reduced coefficient of heat expansion, enhanced solvent resistance, enhanced gas barrier characteristics, and enhanced sorption capability (Jin et al. 2011). Following are some of the materials applied for heavy metal adsorption;

For their potential application as a sorbent of metals present in aqueous media, Faizah et al. reported polymer/clay nanocomposites were performed by incorporating nanoclay into the polymer matrix. Polyacrylonitrile was chemically impregnated with sepiolite modified by 77% of vinyltriethoxysilane. The trend toward copper removal of nanocomposites was explored by spectroscopy of atomic absorption. Copper's highest adsorption was 86%, which could be accomplished with 2% initiator synthetic nanocomposites. As effective adsorbents, the findings disclosed the practical potential of the prepared PCN (Altaf et al. 2018) (Fig. 2.9).

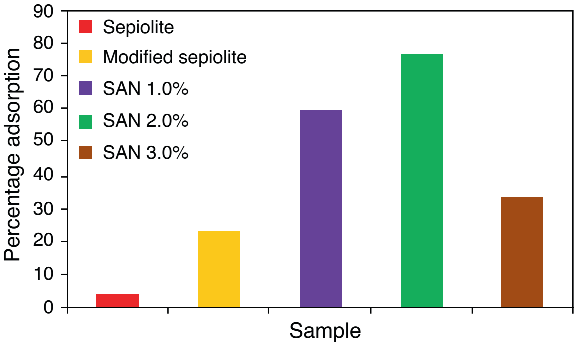

Fig. 2.9 Co removal by polymer/clay nanocomposites. (Faizah et al. 2018)

2.12.1 Amine Grafted Polymer Sorbents

Diethylenetriamine-embedded polyglycidyl methacrylate sorbent is an amine-functional sorbent obtained from diethylenetriamine attached upon micro-granules of polyglycidyl methacrylate. High amine level was discovered as an effective organic group, resulting in beneficial impacts on this adsorbent's efficacy, ability, selectivity, and reusability. The polyglycidyl methacrylate has excellent mechanical power and elevated epoxy group reactivity for upper layer grafting; it is also used in industrial column chromatography. Liu et al. indicated that a response between an NH_2 of DETA with an epoxy group of PGMA and an adsorbent showed outstanding adsorption efficiency in solution $pH > 3$ for copper ions. Ionic strength enhanced peak adsorption ability, leading in quicker adsorption kinetics. The kinetics of adsorption strongly followed the kinetic model of pseudo-second order, showing the significance of chemical adsorption in the system. The Langmuir–Freundlich isotherm model was best equipped with adsorption isotherm information. Different HNO_3 solutions were recycled in desorption, which showed that acidic circumstances significantly impacted desorption performance, and 0.1 M HNO3 solution accomplished the highest desorption effectiveness, completing 80% of desorption effectiveness in the starting minute (Liu et al. 2006).

2.12.2 Humic Acid and Bentonite Composite

Humic acid-grafted polymer and bentonite clay composite, a novel product synthesized on amine modified polyacrylamide/bentonite by directly intercalating polymer by immobilizing humic acid (HA). Anirudhan and Suchithra made polyacrylamide/bentonite amine modified. In relation to the backbone of linear or branches, cyclic units slightly acidic to fundamental medium, the multiple functional character is because of the existence of different carboxyl groups. These carboxylic and phenolic groups have improved metal ion adsorption through electrostatic interactions and surface complexation. The adsorption followed the equation of pseudo-second order, and the steady rate reduces with a rise in Cu (II) ion concentration. Thermodynamic parameters have shown that the method of adsorption is endothermic, so the impact of changes in enthalpy is prominent than changes in entropy. Large effectiveness in desorption and regeneration were reported at 0.1 M HCl. Possibility of reuse has been recorded for four consecutive cycles (Anirudhan and Ramachandran 2007).

2.13 Conclusion

Pollution of water heavy metal and metalloid bodies is an established issue, and several studies have been carried out. The polymeric materials produced so far have shown outstanding results and have the capacity to be efficiently applied to remediate heavy metal-polluted waters and have the capacity to be used in communities using mining and industrial wastewater-impacted borehole water in used water systems. The mixed polymers are produced via sol–gel procedures, self-assembly procedures, nanobuilding blocks assembly or dispersion, hierarchical structures, and interpenetration networks. The functional variety of organic materials in these compounds syndicates with the assistances of a robust and heat-resistant firm inorganic substrate. These materials have powerful binding affinities to chosen metal ions and comparatively elevated capacity to adsorb metal ions and can be used to treat wastewater and separate heavy metals from solid state. Polymer/clay nanocomposites are now becoming an evolving research and growth area. They are actually multiphase materials in which ultrafine clay in the range of 1–100 nm is dispersed into polymer matrix. They simultaneously demonstrate both inorganic and organic properties that assist the investigator study their apparent potential or technological material that also provides a comfortable macroscopic environment for studying main science phenomena, such as zeta potential (electrokinetic potential in colloidal systems), rheology, and young modulus. After discovering the outcomes of such different tests of these materials, it was well defined that they demonstrate enhanced characteristics such as tensile strength, traction modulus, reduced coefficient of heat expansion, enhanced solvent resistance, enhanced gas barrier characteristics, and enhanced sorption capability. A freshly designed strategy to reduce the process waste left behind in the manufacturing and leachable arsenic. A fresh group of starch-linked magnetite nanoparticles for arsenate removal were prepared and tested. As an additive to depress the nanoparticle agglomeration, a cheap, green starch was used.

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Chapter 3
Metal Oxyhydroxide Composites for Halogens and Metalloid Removal

Esmeralda Vences-Alvarez, Cesar Nieto-Delgado, and Jose Rene Rangel-Mendez

Contents

Abstract The occurrence of pollutants in drinking water sources has become a serious problem worldwide. Sometimes, the contamination is not even related to human activities but occurs naturally during the weathering of minerals in water reservoirs. This is the typical case for arsenic- and fluoride-polluted human consumption water sources, which is a well-documented problem that impacts millions of people worldwide. Due to the health affectation to humans, the permissible concentration limit of arsenic and fluoride in drinking water is very low, 10 μg/L and 1.5 mg/L, respectively. Therefore, purifying water to reach those levels in a cost-effective way has become a real challenge. In this chapter, we first reviewed the

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full-scale strategies for the elimination of arsenic and fluoride from water, considering only physicochemical processes. Afterward, we make emphasis on adsorption, mainly by metal oxyhydroxides as adsorbent materials. The focus of the current research on this topic is the generation of new materials with superior characteristics, including higher adsorption capacity and selectivity. Metal and bimetallic oxyhydroxides have been developed and have shown to be promising materials to remove up to 200 and 250 mg/g of arsenic and fluoride, respectively. Also, researchers have oriented their efforts to transform metal oxyhydroxides into granular materials that can be applied in full-scale drinking water operations. Among the strategies are the synthesis of polymer composites, the agglomeration of metal oxide powder with various binders, and the anchorage of particles onto granular materials such as activated carbon: the processes involved are revised, with emphasis on the interactions between the carbonaceous matrix and the anchored metal oxyhydroxides.

Keywords Drinking water · Water remediation · Arsenic · Fluoride · Adsorption · Adsorption mechanism · Metal oxyhydroxides · Granular adsorbents · Metal impregnation · Composites

3.1 Introduction to Halogens and Metalloid Water Pollution

Water is an essential liquid for living organisms and an important resource for human development. Due to the expansion of both rural and urban spaces, water supplies are being affected. The concentration of several inorganic pollutants in drinking water and water supplies is under regulation. This is because of the association of presence of contaminants in water with the increment of illnesses and diseases on human beings. Sometimes pollution has a non-anthropogenic origin, which makes the matter more challenging to solve. The World Health Organization provides international guidelines and standard settings on water quality and human health and serves as a drinking water quality parameter in most of the nations. According to the World Health Organization, the priority chemical pollutants that are considered to be regulated in drinking water are listed in Table 3.1. In this

Table 3.1 The priority chemical pollutants that are considered to be regulated by WHO

Priority chemical pollutants			
Aluminum	Cadmium	Lead	Selenium
Ammonia	Chloride	Manganese	Silver
Antimony	Chromium	Mercury	Sodium
Arsenic	Copper	Molybdenum	Sulfate
Barium	Cyanide	Nickel	Uranium
Boron	Fluoride	Nitrite	Zinc
Bromide	Iron	Nitrate	

revision, we will focus on the water pollution caused by fluoride and arsenic, being the former considered the most massive poisoning in history (Bhattacharjee 2007).

The ingestion of arsenic and fluoride is causing severe health problems worldwide (González-Horta et al. 2015; Limón-Pacheco et al. 2018). Among the affected countries are Bangladesh, India, Vietnam, Thailand, Taiwan, Mongolia, China, Argentina, Chile, Bolivia, Brazil, Mexico, Germany, Hungary, and the United States (Hossain 2006; Alemayehu et al. 2011; Chowdhury et al. 2018; Khan et al. 2019; Bhardwaj et al. 2019; Thakur 2019; Agusa et al. 2014; Tiankao and Chotpantarat 2018). Reports indicate that millions of people in different parts of the world are ingesting water with high concentrations of arsenic and fluoride (high than 300 μg/L (Smith et al. 2000) and 30 mg/L, (Dey et al. 2004), respectively). The high arsenic concentrations can cause human diseases such as arsenicosis, hyperkeratosis, keratosis, and cancer (Choong et al. 2007). On the other hand, fluoride is beneficial in a concentration of 0.7 mg L^{-1} but represents a health hazard once it exceeds a concentration of 1.5 mg L^{-1}. Chronic fluoride exposure can cause dental and skeletal fluorosis, cancer, negative effects on deoxyribonucleic acid structure, Alzheimer's disease, and kidney and neurological damage. High fluoride concentrations in water can interfere with mineral metabolism, vitamins, carbohydrates, proteins, and lipids (Ozsvath 2009).

Arsenic is a naturally ubiquitous metalloid in the earth's crust, making geological the main source of arsenic in water. Arsenic exists in three main oxidation states, +5, +3, and −3, known as arsenate, arsenite, and arsine, respectively. Arsenic pollution of drinking water can be caused by naturally ocurring minerals or can be related to anthropogenic activities, such as mining (since about 245 minerals contain arsenic), the use of fossil fuels and pesticides (Bissen and Frimmel 2003). Arsenic is one of the 20 most abundant elements in nature, and we can also find it in the human body and in seawater (Mandal and Suzuki 2002). Arsenic appears in natural waters commonly as oxoanion, being the arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}) the most common oxidation states. Figure 3.1 shows the -Log [H^+] vs. -Log concentration diagram for those chemical species. The predominant chemical speciation of arsenate in the pH of natural waters (6–8) is as mono- and dianion, while for arsenite, the predominant chemical form is the neutral oxo-complex.

On the other hand, fluoride occurs in the environment mainly associated with metals, including sellaite (MgF_2), fluorite (CaF_2), cryolite (Na_3AlF_6), and fluorapatite ($Ca_{10}(PO_4)_6F_2$). When a suitable chemical environment surrounds the fluoride-containing minerals, the minerals dissolve, and the fluorine becomes part of the dissolved components of the water reservoir. Additional fluoride sources are related to industrial activities, including metal casting operations (iron, steel, and aluminum), production of ceramics, and the production of phosphate-based fertilizers. Besides, many sources of fluoride for human include food, medicaments, cosmetics, and organofluorine compounds, among others (Council 2006). The chemical speciation of fluoride in groundwater appears in Fig. 3.2. Arsenic can be seen, and the predominant chemical species of fluorine in groundwater is the anionic form. Interesting, the presence of metal alkaline cations promotes the formation of fluorine ionic pairs with a positive charge (i.e., MgF^+, CaF^+).

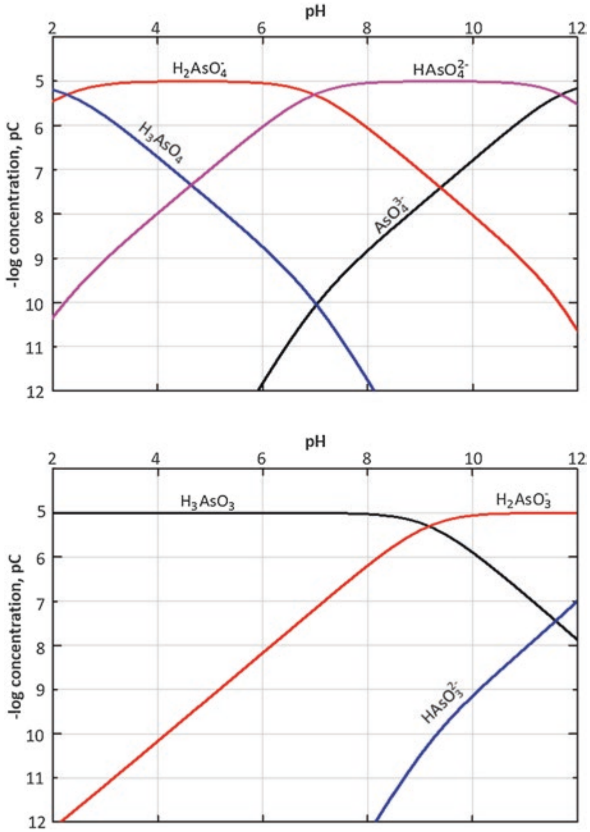

Fig. 3.1 pC–pH diagram for arsenate (top) and arsenite (bottom) in pure water. Total arsenic concentration 5 µM, 25 °C. Around neutral pH (6–8), the chemical form of arsenate is as a negative ion, 1 or 2 negative charges. In contrast, arsenite appears as a neutral species

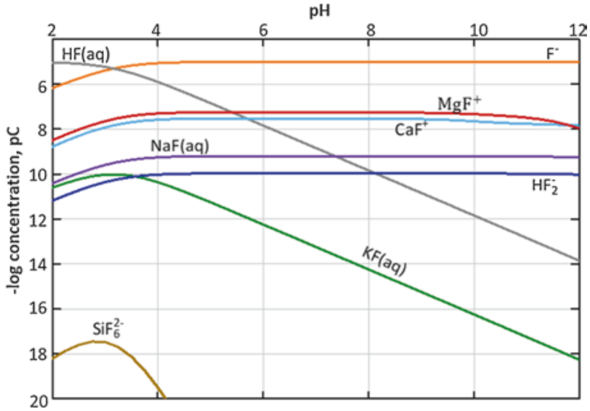

Fig. 3.2 pC–pH diagram for fluoride in water with the main components in typical ground water. Total concentration (mg/L) F^- (5), Ca^{2+} (10), Mg^{2+} (2), Na^{1+} (1.5), K^{1+} (1), CO_3^{2-} (45), H_4SiO_4(15), 25 °C. Around neutral pH, the predominant chemical species is the single atom anion (F^-). However, in the presence of metal cation such as calcium and magnesium, the concentration of the positive ionic pair becomes significant

To abate the arsenic and fluoride effect to human health, international organizations have lowered the maximum allowable limits of these pollutants in drinking water. The World Health Organization suggests a maximum permissible limit of arsenic and fluoride in water of 10 μg/L and 1.5 mg/L, respectively. Reaching a low arsenic and fluoride concentration requires the application of low-cost and efficient technologies to allow safe drinking water supply for human consumption. In the following section, we review the most relevant technologies for the elimination of these pollutants from drinking water, making emphasis in its fundamentals.

3.2 General Strategies for Arsenic and Fluoride Removal from Water

Currently, there are full-scale technologies for the elimination of arsenic and fluorine from drinking water. The efficiency of any treatment strategy depends on the raw water composition, the volume of water to be treated, and the final target concentration of the pollutants. In addition, the selection of the most suitable treatment depends strongly on cost-effectiveness during implementation and use. For drinking water supply, physicochemical treatments are the methods of choice, being the most relevant coagulation/precipitation, membrane processes, ion exchange, membrane filtration, and adsorption. In the following section, we briefly review the fundamentals of these technologies, including the specifics for fluorine and arsenic removal from water.

3.2.1 Coagulation and Flocculation

Coagulation and flocculation process includes the addition of chemicals to remove stable colloidal particles from water, including natural organic matter. This process typically takes place in two stages: coagulation followed by flocculation. Figure 3.3a represents the typical configuration of a water clarification system. During coagulation, chemicals are added to neutralize the charges of the colloidal particles, creating neutral particles that can be attached. Each particle carries a similar charge, and almost all the colloidal impurities in the water are negatively charged. Generally, the size of the colloidal particles is around 0.01–1μm; therefore, the attractive forces between the particles are less than the repelling forces of the electric charges (Teh et al. 2016).

The colloids present in the aqueous solution attract ions from the opposite charges, named counterions. The counterions, attracted by electrostatic forces and van der Waals forces, will form a compact layer around the charge of the colloid (Fig. 3.3B). Therefore, the counterions tend to remain discrete and dispersed in the suspension. The stability of the colloidal particles can be explained quantitatively by the estimates of the attractive energy such as van der Waals forces and the repulsion energy. Another estimate attractive energy is the superposition of electric double layers, in terms of the distance between particles (Fig. 3.3C). Once the colloidal

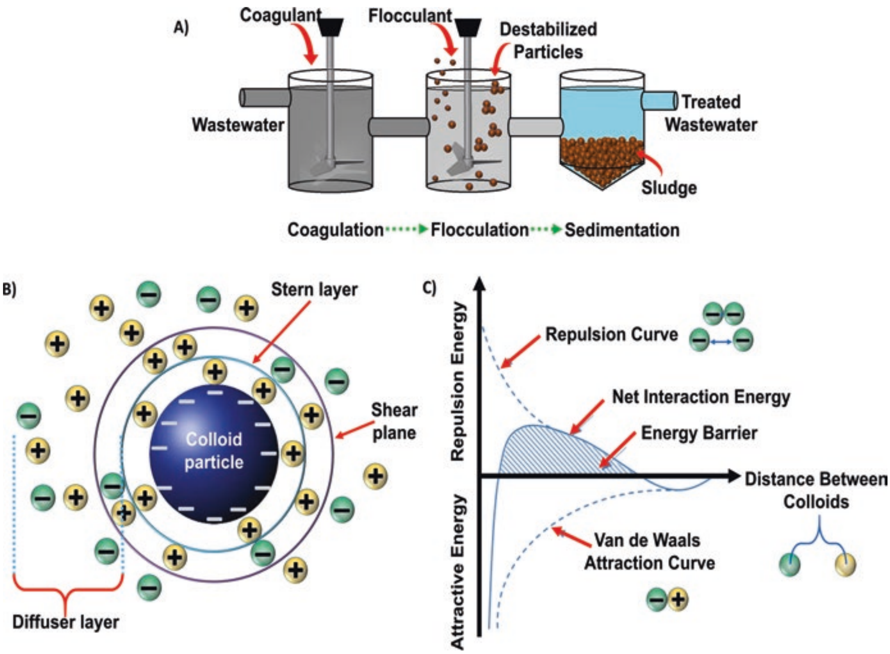

Fig. 3.3 Schematic representation of a typical coagulation/flocculation process **(A)**. Representation of charges around colloidal particles. Coagulant addition into water neutralizes these charges to destabilize the colloids **(B)**. Representation of interparticle forces as function of the particle distance **(C)**

particles are unestablished or neutralized, the particles start to agglomerate under gentle stirring. The addition of chemicals promotes the collection of particles, until reaching a mass high enough to settle or to be removed during filtration.

The most common chemicals used during coagulation are hydrolyzed metals, including ferric sulfate ($Fe_2(SO_4)_3$ xH_2O), aluminum sulfate ($Al_2(SO_4)_3$ $14H_2O$), and ferric chloride ($FeCl_3$ xH_2O) (Edzwald 2010). These metals hydrolyze in water, to form iron and aluminum hydroxo/aquo complexes with positive charges (e.g., $Al(H_2O)_6{}^{3+}$) that neutralize the negative charge of the colloids in water. Polymers can achieve the same task, including biopolymers such as chitin, among others (Kartinen and Martin 1995).

In this way, the clarification process which includes coagulation, flocculation, and sedimentation is a specific operation for the removal of colloidal particles from water. However, these processes can also remove arsenic and fluorine indirectly. According to the chemical speciation of arsenic (arsenate) and fluorine, the predominant chemical form is a negatively charged ion, also known as anion (see Figs. 3.1 and 3.2). Since coagulant bears a positive charge, arsenic and fluorine can be attracted to coagulant chemicals by electrostatic interaction and removed from the solution as adsorbed anions in the sludge. A study of the arsenic removal during conventional water treatment at a full scale with aluminum-based coagulants confirmed that most of the soluble arsenate is converted to particulate arsenic. This formed by adsorption during rapid mixing coagulation, removing near to 95% of soluble arsenate.

In contrast, arsenite with a neutral charge remains in solution due to the lack of interaction with positive coagulants (Gregor 2001). Thus, the ability to remove arsenic from water during clarification depends on the proportion of arsenate to arsenite in the water source. The results are similar when iron-based coagulants are employed, having a similar removal mechanism (Hering et al. 1996). Additional strategies can be implemented to increase the arsenic removal during coagulation and flocculation, including the aeration of the water source to transform all arsenite to arsenate, pH control, and optimal coagulant dose. Further information can be found elsewhere (Mondal et al. 2013).

A similar mechanism applies for fluoride removal from water during coagulation, being mostly aluminum salts employed for this purpose (Bhatnagar et al. 2011; Loganathan et al. 2013). The efficiency of fluoride removal by aluminum salt depends on water composition, pH, and other solution characteristics (Hao Oliver and Huang 1986). The most appropriate pH for defluorination during coagulation is between 5.5 and 6.5 (Shen et al. 2003).

3.2.2 Ion Exchange

The ion exchange is an adsorption process that employs granular materials, characterized by having exchangeable ions in the material surface. These ions can be exchanged by ionic pollutants, lowering the contaminant concentration in the treated water (Fig. 3.4). The ion-exchange materials are usually cross-linked polymeric resins with chemical functionalities linked to the main polymeric chain. The chemical functional groups are characterized by having a stable positive or negative charge when equilibrated in water. The common functional groups are strong acid such as sulfonate, $-SO_3^-$; weak acid such as carboxylate, $-COO^-$; strong base such as quaternary amine, $-N(R)_3^+$; and weak base such as tertiary amine, $-N(R)_2$ (Edzwald 2010).

For the removal of arsenate and fluoride anions, the anionic exchange materials are appropriate. In the process, the pollutants are exchanged for the negative ions that balance the charge in the ion exchanger, generally hydroxide or chloride. Resins have been reported that can interchange arsenic for more than 4000 equivalent bed volumes before becoming exhausted (DeMarco et al. 2003). In particular, for arsenic removal, there are hybrid resins that incorporate metal hydroxides in addition to the anionic exchange functional groups. Iron is the metal often used for the hybrid ion-exchange resins and represents some of the more successful materials for arsenic removal from water. Cumbal and SenGupta reported the treatment of up to 15,000 bed volumes of arsenite or arsenate polluted groundwater (Cumbal and SenGupta 2005).

On the other hand, some examples of materials that have been used as ion exchangers to remove fluoride from water are zeolite and activated carbon. Zeolites are often used as a cation exchanger material; hence its arsenic and fluoride removal is negligible. However, by means of the anchorage of high-valence cations such as

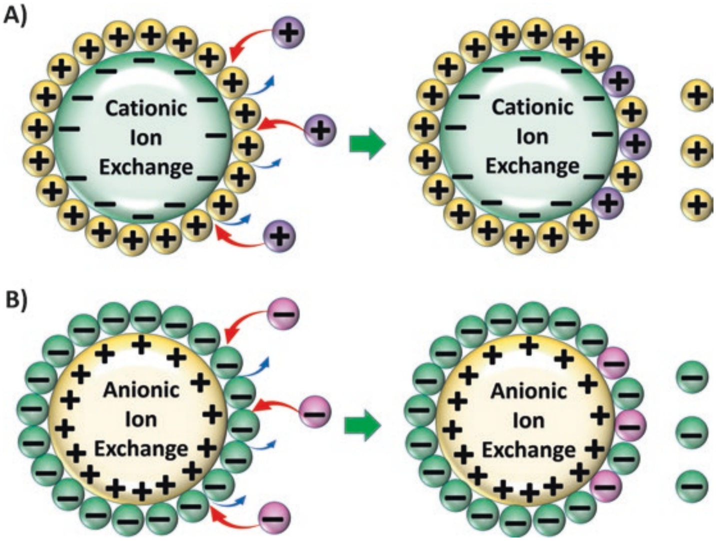

Fig. 3.4 Schematic representation of the ion-exchange process in a cationic (**A**) and an anionic exchange resin (**B**). Cationic exchange resin often balances the polymer fixed charge with protons (H^+) that can be exchanged for cations in the solution. An anionic exchanger has positive charges fixed to the resin that are balanced with negative ions, commonly Cl^- or OH^-. Those anions can be exchanged for anions in the solution, such as $H_2AsO_4^-$ or F^-

Al^{3+} or La^{3+} in a low-valence zeolite site such as Na^+ site, the surface of the modified zeolite acquires a positive charge and is able to remove fluoride from water (Onyango et al. 2004). Regarding to polymeric resins, zirconium and alum have been successfully incorporated into the polymer matrix to generate hybrid resins (Pan et al. 2013; Viswanathan and Meenakshi 2009). For example, the commercial resin (FR 10) with Na^+ and Al^{3+} increased the fluoride adsorption significantly to capacities around 450 mg F^-/kg. Despite the efficiency of the ion-exchange resins for the removal of arsenic and fluoride from water, the material cost and the disposition or regeneration of exhausted resins make its application difficult. The economic factor is something to take into consideration since most of the population exposed to arsenic and fluorine polluted water belongs to marginalized communities.

3.2.3 Membrane Filtration

Membrane filtration is a technology in which the water pollutants are removed from water utilizing the size exclusion provided by a semipermeable thin layer of polymer, known as membrane (Singh 2015). The membrane filtration is classified by the average pore size of the membrane, and hence, this establishes the pollutants that could retain (Fig. 3.5). Microfiltration with a pore size between 0.1 and 1.0 µm is capable of retaining colloids and bacteria. Ultrafiltration with a pore size between 0.01 and

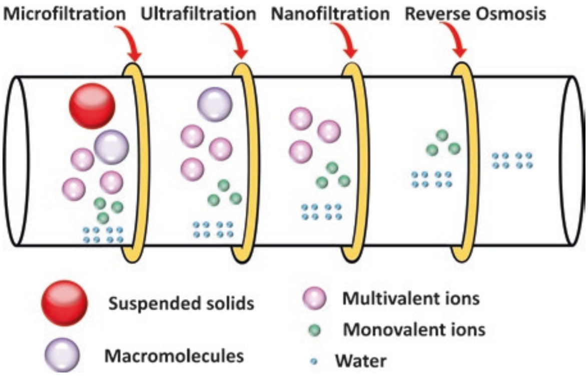

Fig. 3.5 Size exclusion of different water component for different kinds of membranes. Microfiltration retains suspended solids, ultrafiltration retains macromolecules, nanofiltration retains multivalent ions and reverse osmosis monovalent ions (Modified after Mashallah et al. 2017)

1.00 μm retains the virus in addition to colloids and bacteria. Nanofiltration with pores between 0.001 and 0.01 μm can retain some inorganic multivalent ions. Finally, reverse osmosis that uses membranes with pores lower than 1 nm allows only the pass of water molecules, retaining all other water components (Najafpour et al. 2007).

The arsenate and fluoride anions have an ionic radius of 0.248 and 0.133 nm, respectively (Regenspurg and Peiffer 2005; Chowdhury et al. 2018). Hence, nanofiltration and reverse osmosis are the membrane technologies capable of removing arsenic and fluoride from water. However, removing arsenic and fluoride depends on factors such as pore structure of the membrane, material composition and chemistry, system configuration, and water composition. For instance, the removal of fluoride was reported using a nanofiltration/reverse osmosis system, obtaining a removal efficiency higher than 96% with reverse osmosis and higher than 90% with tight nanofiltration and up to 50% with loose nanofiltration membranes (Ayoob et al. 2008b; Dolar et al. 2011). Nunes-Pereira et al. 2018, obtained a maximum fluoride rejection of 68% after six filtrations for composite membranes of hydroxyapatite and poly(vinylidene fluoride-hexafluoropropylene). The membranes presented an homogeneous porous structure with degrees of porosity ranging between 20 and 76% and average pore size in the micron range.

On the other hand, arsenic removal studies showed the reduction of arsenate in a range from 88 to 96% but only 5% for As(III), with reverse osmosis membranes (Ning 2002). The rejection of As(V) by the nanofiltration membrane was found to be between 90 and 100% (Xia et al. 2007). Hubadillah et al. (2019) prepared a hollow fiber membrane of hydrophobic kaolin (0.32 μm of average pore size), and reported an arsenic rejection efficiency of 100% at 60 °C and met the maximum required limit of 10 μg/L.

Even though membrane filtration can reduce the arsenic and fluorine concentration to levels below the permissible concentration for drinking water, its implementation remains limited. Under operation, reverse osmosis can have a percentage of water loss, calculated as the water that does not pass through the membrane, that ranges from 35 to 65% (Ingallinella et al. 2011). The refused water often bears a high concentration of pollutants and requires additional treatment before its discharge, increasing the water treatment cost.

3.2.4 Adsorption

Adsorption is an interfacial process that involves the attachement of molecules from a gaseous or liquid phase onto the surface of a solid (see Fig. 3.6). This attraction between the molecules (also known as adsorbate) and the solid (known as adsorbent) is caused by different forces. The main attraction forces in the adsorption process are van der Waals-like and columbic forces, polar interactions, and specific bond formation. Both shorter range that are often repulsive and more extended range that are often attractive forces are balanced when the adsorption equilibrium is reached (Thomas and Crittenden 1998; L. G. Wader 2011). The schematic representation of this interaction appears in Fig. 3.7.

Adsorption is probably the most sustainable technique that can be applied to the arsenic and fluoride removal from aqueous solutions (Khan et al. 2000; Sarkar et al. 2008; Nabbou et al. 2019). The principal advantages of the adsorption process

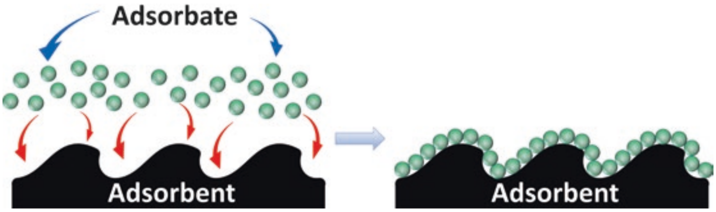

Fig. 3.6 Schematic representation of the adsorption process. Adsorption is a mass transfer process in which one or more adsorbents present in a fluid, whether liquid or gas, accumulates in the adsorbent and are removed from the effluent

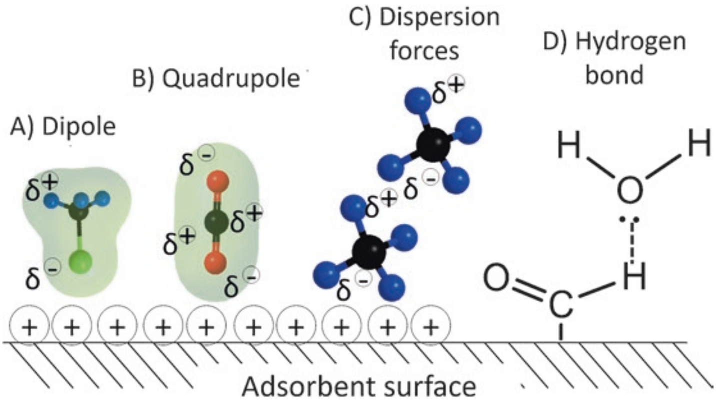

Fig. 3.7 Schematic representation of interactions between adsorbent surface and adsorbate. The surface of the adsorbent can be charged (positive charges) and interact with permanent **(A and B)** or induced **(C)** charges of the adsorbates. The adsorbate can also interact with specific functional groups on the adsorbent surface, e.g., aldehyde, by means of a specific bonding interaction (hydrogen bond, **D**)

include the ability to remove the pollutants even at a very low concentration, low energy consumption, and the availability of different adsorbent types (Ali 2012). Numerous studies and reviews have reported the benefits of the adsorption process during arsenic and fluoride removal (Bhatnagar et al. 2011; Gallegos-Garcia et al. 2012; Velazquez-Jimenez et al. 2015; Jadhav et al. 2015; Lata and Samadder 2016). This technology offers satisfactory results at low cost with a simplicity of design and operation.

Adsorption is a highly efficient technique for arsenic removal due to its numerous advantages already mentioned, which also include relatively high arsenic removal efficiencies (Singh and Pant 2004; Mohan and Pittman 2007). However, arsenic adsorption capacity strongly depends on the concentration and pH of the system. The pH of the solution changes the predominant chemical species in water. At the same time, pH alters the activity of functional groups on the surface of adsorbents. According to the study conducted by Lenoble et al. (2002), arsenate adsorption is favored at low pH, whereas at pH between 4 and 9, maximum arsenite adsorption capacity is reached. Table 3.2 shows several adsorbent materials to remove arsenic and fluoride from water.

Table 3.2 Several adsorbent materials to remove arsenic and fluoride from water

Contaminant	Adsorbents	References
Arsenic	Titanium-based nanocomposite: titanium-based nanocomposites are TiO_2–αFe_2O3, hydrous TiO_2, crystalline hydrous titanium oxide, titania impregnated chitosan bead, titania nanotubes, Ce–Ti oxide, Zr–TiO_2	Ashraf et al. (2019)
	Modified-natural adsorbents	Asere et al. (2019)
	Nanomaterials and composites.	Siddiqui et al. (2019b)
	Fe–carbon, Zr–carbon, Fe:Mn– carbon	Arcibar-Orozco et al. (2014), Velazquez-Jimenez et al. (2018), Nieto-Delgado et al. (2019), Kalaruban et al. (2019)
Fluoride	Alumina and aluminum, activate carbon, alumina impregnated calcium alginate beads, oxide calcium, hydroxyapatite	Yadav et al. (2018)
	Monometallic oxides: lanthanum hydroxide, granular ferric hydroxide, zirconium oxide	Kumar et al. (2009), Na and Park (2010), Dou et al. (2012)
	Bimetallic oxides: Al–Zr, Al–Mn, Cu–Al, Mn–Ce, Fe–Ti, Ti–Ce, Ti–La, Fe–Zr, Fe–Al, Li–Al	Maliyekkal et al. (2006), Biswas et al. (2007a, b), Bansiwal et al. (2010), Liu et al. (2010), Li et al. (2010), Deng et al. (2011), Chen et al. (2012), Zhang et al. (2012)
	Trimetallic oxides: CeO_2/Mg–Fe, Fe–Al–Cr	Biswas et al. (2010), Zhang et al. (2013)
	Carbon modified with metallic oxides: carbon–La, carbon–Ce, carbon–Zr, carbon–Al–Fe	Velazquez-Jimenez et al. (2014, 2018), Arcibar-Orozco et al. (2014), Vences-Alvarez et al. (2015)

The materials studied show an outstanding efficiency to remove fluoride from water. However, it is essential to consider that the contaminate concentration, solution pH and temperature, surface area of adsorbent, and the contact time are parameters that affect the fluoride adsorption capacity (Yadav et al. 2018). The pH is an essential factor affecting defluorination (Ma et al. 2009), for instance, the adsorbent surface at alkaline pH has a negative charge while at acid pH is highly protonated. Therefore, the high fluoride adsorption capacity at acid pH can be attributed to an increase in attractive forces between the adsorbate and adsorbent (Rajan and Alagumuthu 2013; Vences-Alvarez et al. 2015).

As for the adsorption capacity, this can vary depending on the adsorbent material. In general terms, the arsenic adsorption capacity is between 2 and 200 mg/g using metal and bimetallic oxyhydroxides (Zhang et al. 2003; Dou et al. 2011b; Basu and Ghosh 2013; Chaudhry et al. 2017; Dou et al. 2018). Chen et al. 2014 synthesized iron–cerium alkoxide with a high surface area and abundant surface functional groups. The bimetallic oxide produced by using a molar ratio of 5:1 for Fe:Ce, respectively, exhibited the highest adsorption capacities for both As(V) and As(III) (206 and 266 mg/g, respectively). As for the fluoride adsorption capacity, it is between 2 and 250 mg/g (Bhatnagar et al. 2011; Loganathan et al. 2013; Velazquez-Jimenez et al. 2015). Lv et al. (2007) employed MgAl–CO_3 layered double hydroxides to treat high fluoride concentration solutions. The MgAl–CO_3 maximum adsorption capacity was 319.8 ± 5.7 mg/g at an initial fluoride concentration between 1000 and 1500 mg/L, and in a pH range of 5–7.

An example of the application of alumina in the simultaneous arsenic and fluoride removal from water is the system called ArCIS-UNR. This is a hybrid process that integrates adsorption, coagulation and filtration: using poly-aluminum chloride as a coagulant, followed by two filtration units (upflow coarse gravel filtration and rapid sand filtration). This process has been successfully implemented in large-scale plants in Argentina, and has treated groundwater with arsenic concentrations of 100–150 μg/L and fluoride concentrations of 1.7–2.5 mg/L. The results of this research indicate that the optimum pH range for the removal of arsenic and fluoride was 6.3–7.3 and 5.2–6.2, respectively. The efficiencies reached ranged between 75 and 85% for arsenic and between 50 and 55% for fluoride. However, the disadvantage of this process is that at pHs below 7.0, the residual aluminum begins to increase (Ingallinella et al. 2011).

Other material that has been succesfully employed for the removal of asernic from water is iron based ion exchange resin. German and coworkers (German et al. 2019) reported the performance of a community scale hybrid anion exhange system as a long-term solution for arsenic contaminated growndwater. The hybrid ion-exchange materials are composed of cerium or zirconium oxide nanoparticles dispersed in an anionic exchange polymer resin (Cumbal et al. 2003; German et al. 2014). Three of the arsenic mitigation systems were monitored during 24 months of long-term self-sustainable operation to assess the efficiency and profitability of the systems. The systems were designed to provide high-quality water to 200 families, that is, between 500 and 1000 people. Hybrid ion-exchange materials can be regenerated efficiently compared to activated alumina (German et al. 2019).

Finally, the majority of the current research in arsenic and fluorine adsorption is directed towards the development of new adsorbent materials with advanced characteristics. High adsorption capacity or high selectivity is a valuable characteristic presented by the new developed adsorbent materials. Particularly, the adsorbent materials with the most elevated adsorption capacities of arsenic and fluorine are based on metal oxyhydroxides (Jadhav et al. 2015), which is described in the following sections.

3.3 Metal Oxyhydroxides for Adsorption

The metal oxides are solid materials with a chemical structure formed by the alternation of metal cations and oxygen or hydroxide anions. The cohesion between the metal and oxygen or hydroxide is achieved by electrostatic interactions that generate covalent bonds with different levels of cohesion depending on the metal electronegativity (Pawelec 2005). In the surface of the metal oxide, the coordination of the metal cation is lost, creating unsaturated sites that can be compensated with the adsorption of ions and molecules. The primary reaction in the metal oxide and water interface is the hydroxylation of the metal surface to form a metal oxyhydroxide (see Fig. 3.8). These hydroxyl surface groups follow similar reactions to the

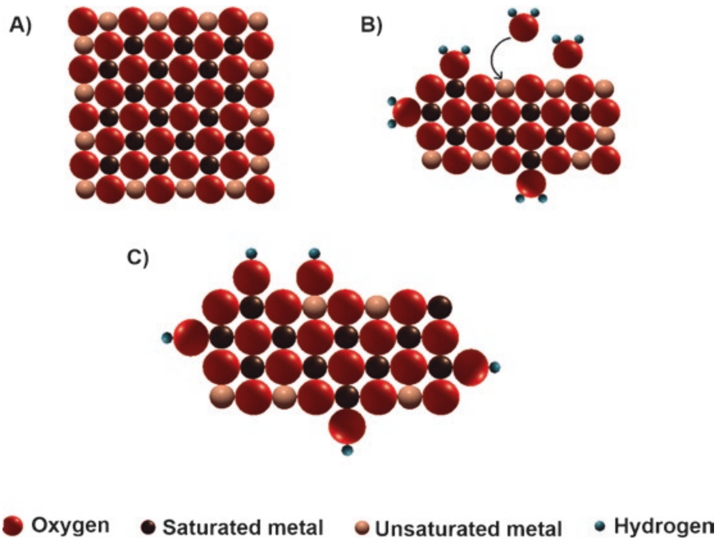

Fig. 3.8 Schematic representation of the cross section of a metal oxide and the hydroxylation of its surface. The metal cations in the surface layer are unsaturated (Baeige atom color in **(A)** and can react as a Lewis acid with water molecules **(B)**). The further dissociation of the coordinated water molecule generates the hydroxylated water surface **(C)**. (Modified after Stumm and Morgan 1996)

aqueous complexes generating a local surface charge that can be negative, neutral, or positive as a function of the solution pH, as illustrated in the Eq. 3.1.

$$\mathrm{M-OH_2 +{}^{-}\,OH \overset{pka_1}{\rightleftarrows} \equiv M-OH+H_2O \overset{pka_2}{\rightleftarrows} \equiv M-O^{-}+H_2O} \tag{3.1}$$

The symbol ≡M indicates that the metal is attached to a solid surface. The chemical form of the surface groups in the metal oxyhydroxides depends strongly on the solution pH and the chemical nature of the metal cation. A useful indicator for the transition between a positive surface charge and a negative surface charge in a metal oxyhydroxide is the pH of the point of zero charge. This is the pH at which the net charge of the metal oxyhydroxides is zero. The point of zero charge of selected metal oxides is presented in Table 3.3. When the solution pH is lower than the point of zero charge, the net charge of the metal oxyhydroxides is positive. Hence the material can adsorb anionic pollutants such as arsenate and fluoride. In this sense, Fe-, Ti-, Mn-, Al-, Cu-, Mg–Zn-, Zr-, and Ce-based metal oxides are good candidates for the removal of arsenate and fluoride from water through electrostatic interactions. The specific adsorption mechanism is discussed in the following sections.

Table 3.3 Point of zero charge of selected metal oxides

Substance	Point of zero charge (pH_{PZC})
SiO_2	2–4
Albite (Na feldspar)	2.0
Feldspars	2.0–2.4[a]
Montmorillonite (clay)	2.5
™-MnO_2	2.8
Kaolinite (clay)	4.6
α-$Al(OH)_3$	5.0
TiO_2	3.5–6.5[a]
Fe_3O_4	6.5
CeO2	6.8
β-MnO_2	7.2
α-FeOOH	7.8
ZrO2	7.8[b]
©-AlOOH	8.2
α-Fe_2O_3	5.5–9[a]
$Fe(OH)_{3(am)}$	8.5
α-Al_2O_3	6.5–10[a]
CuO	9.5
ZnO	9–10[a]
MgO	12.5

Data from Brezonik et al. unless otherwise indicated (Brezonik and Arnold 2011)

[a] Data from Jolivet et al. (2000)

[b] Measured by potentiometric titration

Many of the chemical properties of the metal oxides depend on the crystallographic structure, related to atom arrangement, and the crystal habit which is the characteristic external shape of a crystal group. Not all the crystalline planes offer the same amount and type of active sites, e.g., gibbsite particles have a hexagonal platelet habit (see Fig. 3.9). The (001) faces have only Al_2OH uncharged sites, with a group's density of 13.8 groups/nm^2, obtained by crystallographic data. In contrast, the (hk0) faces have two kinds of groups, Al_2OH and $AlOH^{-1/2}$, with a theoretical concentration of 9.6 and 4.8 groups/nm^2, respectively (Jolivet et al. 2000). Hence, the reactivity of specific crystalline planes is different. It is worth mentioning that the charge compensation by coordinate cations in the metal oxyhydroxides surface is not always complete, according to the multisite complexation model. Further information of the model and how it can be applied to the study of adsorption on metal oxides can be revised elsewhere (Hiemstra et al. 1989a, b).

The reactive nature of the unbalanced metal cations in the surface of the metal oxyhydroxides represents significant advantages for the adsorption of ionic pollutants from water. The polar nature of the atoms in the metal oxyhydroxides surface needs to be balanced by surrounding molecules. Noguera and coworkers reviewed the advances in the understanding of the polar electrostatic surface of different metal oxides and its compensation by external molecules (Noguera 2000; Goniakowski et al. 2008). This polar interaction can promote diverse mechanisms of pollutants adsorption. The main adsorption mechanisms are numbered below:

1. The ion exchange of surface groups, such as the hydroxyl adsorbed molecule.
2. Adsorption of charged species by means of electrostatic attraction with the metal oxide charged sites ($\equiv M\text{-}OH_2^+$ or $\equiv M\text{-}O^-$).
3. The adsorption of metal cations by means of Lewis acid–base complex formation.
4. The exchange of ligand between the metal oxyhydroxides surface and polyatomic ions (i.e, oxocations).

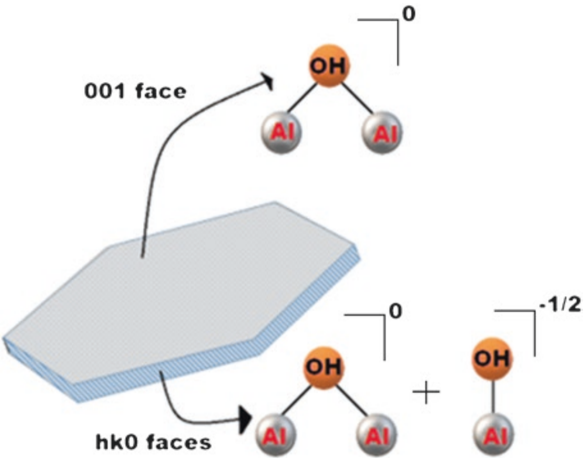

Fig. 3.9 Gibbsite particle and the different active sites in the characteristics crystalline faces. Gibbsite particles have a hexagonal platelet habit (Modified after Jolivet et al. 2000)

5. The dissociative adsorption of Bronsted acids such as alcohols, in which the oxygen in the metal oxyhydroxides surface acts as proton acceptor and the deprotonated molecule binds to the metal cation (Parkinson and Diebold 2016). In the following section, we revise the adsorption mechanism of arsenic and fluorine in selected metal oxyhydroxides.

3.3.1 Fluoride Adsorption on Metal Oxyhydroxides

Due to the chemical characteristics of fluoride, the most relevant adsorption mechanism implies the coordination of fluoride anions in the metal surface. Fluoride has a negative charge and bears eight free electrons that can be easily donated to unsaturated cations in the metal oxide surface. The fluoride has a small size (0.133 nm), so it can be easily accommodated in the coordination geometry of transition metals. There are scientific reports that provide experimental evidence to support this adsorption mechanism. Tang and coworkers studied the adsorption of fluoride on granular iron hydroxide using X-ray photoelectron spectroscopy and infrared spectroscopy (Tang et al. 2009). The results indicated the complexation of fluoride anions in the surface of the metal oxide. In addition, it was possible to detect hydrogen bonding between the surface hydroxides and fluoride.

On the other hand, Shao-Xiang Teng and coworkers reported the adsorption of fluoride in hydrous-manganese-oxide-coated activated alumina (Teng et al. 2009). The authors evaluated the solution pH change during the adsorption process, noticing that the pH increases with the adsorption of fluoride. The author associates this process with an ion-exchange mechanism in which the surface hydroxides in the material surface are exchanged by fluoride anions that become part of the inner-sphere complexes. Similar results were obtained by Ayoob and coworkers using alumina granules (Ayoob et al. 2008a). Therefore, OH groups play an essential role in the adsorption process of fluoride ions (Jin et al. 2016; Yu et al. 2018; Wang et al. 2018; Kang et al. 2018). However, the interactions between fluoride and the surface of adsorbent do not lead to chemisorption since, in several studies, it has been shown that fluoride adsorption is reversible (Medellin-Castillo et al. 2014).

Conventionally, aluminum and iron oxyhydroxides have been used for the fluoride adsorption; however, recent research has reported the use of rare earth metal for the fluoride adoption, including lanthanum and cerium (Huo et al. 2011; Vences-Alvarez et al. 2015, 2019; Zhu et al. 2017; Hernández-Campos et al. 2018; Chigondo et al. 2018; Zhang et al. 2019). Rare earth-based metal oxides provide a slightly different adsorption mechanism. Zhang and coworkers recently reported that lanthanum oxide (La_2O_3) could bond fluoride anions without the exchange of hydroxy ligands (Zhang et al. 2019). Results of X-ray photoelectron spectroscopy showed no change of the peak attributed to M–OH after the fluoride adsorption. However, the relative area of the peak attributed to M–OH_2 decreased considerably. Magnetic resonance spectroscopy analysis and theoretical calculations demonstrated the configuration of the adsorbed fluoride. A study on the coordination chemistry of lanthanides demonstrated that lanthanum could coordinate up to nine aquo complexes. However, in the presence of fluoride ions, the water molecues can be displaced, apparently because the bounded fluoride generates a more stable configuration (Parker et al. 2002).

3.3.2 *Arsenic Adsorption on Metal Oxyhydroxides*

As revised in Sect. 3.1, the predominant chemical forms of arsenic in water are arsenate and arsenite. The arsenate is in the water as hydroxide-anion and the arsenite is a reduced species that predominates as an uncharged molecule. In consequence, the adsorption mechanism of arsenate and arsenite has some differences.

The metal oxides often studied for arsenic adsorption are iron and aluminum oxyhydroxides. Goldberg and Johnston studied the adsorption mechanism of arsenate and arsenite in amorphous aluminum and iron oxides. Accordingly, arsenate is adsorbed through ligand exchange reactions with the surface coordinated molecules such as water or hydroxyl, to form inner-sphere surface complexes on both metal oxides. In contrast, arsenite can adsorb on iron oxide by the formation of both inner and outer surface complexes and only by outer-sphere complexes in aluminum oxides (Fig. 3.10) (Goldberg and Johnston 2001). The formation of inner-sphere complexes between arsenate and both metal oxides has been confirmed by other authors using advanced spectroscopic techniques such as extended X-ray absorption fine structure (Manceau 1995; Arai et al. 2005). With regard to arsenite adsorption, Jain A. et al. evaluated the H^+ and OH^- release during the arsenite adsorption on ferrihydrite. The authors showed that the adsorption of neutral arsenite (H_3AsO_3) can be carried out as an outer-sphere complex at low pH (Jain et al. 1999).

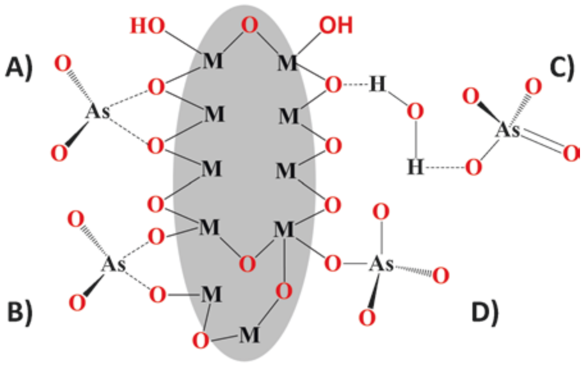

Fig. 3.10 Schematic representation of the different configurations in which arsenate can be adsorbed on metal oxyhydroxide: **(A)** mononuclear bidentate inner-sphere complexation; **(B)** binuclear bidentate inner-sphere complexation; **(C)** outer-sphere surface complexation; and **(D)** mononuclear monodentate inner-sphere complexation. Arsenite binds on metal oxide surfaces in a similar way

Due to the chemical charge of arsenate and arsenite ions at different solution pH, the adsorption mechanism could change, including electrostatic interactions (Chen and Huang 2012), coordination (Jun et al. 2015), and hydrogen bonds (Liu et al. 2014). The electrostatic interactions occur mainly by attraction–repulsion between the adsorbate and the adsorbent. When the solution pH is below the point of zero charge of the adsorbent material, its surface is positively charged due to hydroxyl groups on the protonated surface to form OH_2^+ (Sarkar et al. 2008). The positive charge of adsorbent material favors the adsorption of the arsenate anion. On the other hand, when the pH is above the point of zero charge of the adsorbent material, the hydroxyl groups of the surface are deprotonated, whereby the material will be negatively charged. In these conditions, the arsenate adsorption becomes unfavorable due to electrostatic repulsions (Zhang et al. 2010).

In recent studies, zirconium oxyhydroxides have been tested for the arsenic adsorption. He et al. 2019 used organic zirconium metal structures for the removal of As(III) and As(V). The authors demonstrated through extended X-ray absorption fine structure studies the formation of a bidentate mononuclear and bidentate binuclear complex for As(V) and As(III), respectively, as shown in Fig. 3.11.

Studies currently conducted by various research groups agree that the arsenic adsorption process can be summarized as follows: arsenic diffuses from the solution to the interface of the adsorbent material. In the interface of the adsorbent, a fraction of arsenic(V) is adsorbed on the adsorbent surface, for example, metal oxide (≡M-OH or ≡M-O). Some of them can be adsorbed by ligand exchange (OH^-) with the adsorbent material and form monodentate or bidentate complexes. The remaining parts of As(III) react with M–O to form an M–O⁻As complex. In the adsorption process, two electrons are transferred to As(III) oxidizing to As(V) through the reduction of the metal (Yin et al. 2019). However, the most common mechanism is though the ligand exchange with the hydroxyl groups of the adsorbent material (Santra and Sarkar 2016; Xi et al. 2019).

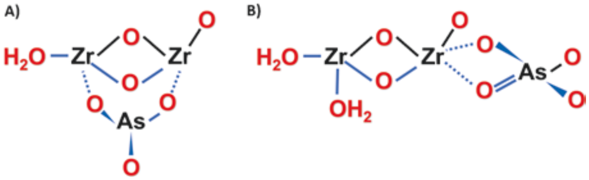

Fig. 3.11 Binding modes of (**A**) As(III) and (**B**) As(V) onto the hexanuclear zirconium. The As(V) and As(III) form bidentate mononuclear and bidentate binuclear complex with the zirconium, respectively. (Modified after He et al. 2019)

3.4 Synthesis of Metal Oxyhydroxide-Based Materials for Adsorption

As reviewed in Sect. 3.3, metal oxyhydroxides have ideal chemical properties for the arsenic and fluoride adsorption from water. Currently, several research groups that are working on the development of new adsorbents based on metal oxyhydroxides that can be ultimately applied in the elimination of arsenic and fluoride purification of drinking water. The efforts are oriented in two main areas: the increment of the adsorption capacity of the metal oxides and the conformation of granular materials. For the increment of adsorption capacity, authors have developed new synthesis methodologies in which the particle size and specific crystalline structures (crystalline habit) can be controlled. Also, the development of binary and ternary metal oxide is a strategy already tested to increase the reactive surface of the metal oxyhydroxide. Regarding the formation of granular materials, the agglomeration of the metal oxyhydroxides with binders and the anchorage of the metal oxides to granular materials are the most relevant strategies. In the following sections, we review the recent advances in both areas.

3.4.1 Natural Metal Oxyhydroxides

There are natural materials with a high potential to be used as adsorbent due to its physical properties. Giménez et al. (2007) evaluated the arsenic adsorption capacity in natural hematite, magnetite, and goethite. Within the physicochemical characteristics of natural oxides, the surface area was determined. The natural oxides have a relatively low surface area, between 0.381 and 2.009 m^2/g, compared to synthetic oxides: 11–140 m^2/g for goethite, 2–14 m^2/g for hematite, and 60 m^2/g for magnetite (Grossl and Sparks 1995; Singh et al. 1996; Matis et al. 1997; Manning et al. 1998; Dixit and Hering 2003; Yang et al. 2010). The points of zero charge for magnetite, goethite, and hematite are very similar (6.5, 6.8, and 6.7, respectively), so the oxides tend to have a positive surface charge at acidic pH and a negative charge at alkaline pH. The adsorption capacity of natural oxides is usually low ~ 1.31 mg/g (Ramirez-Muñiz et al. 2018).

Another natural granular material studied for the removal of arsenic is volcanic rock. The soils and volcanic rocks are composed mainly of silicon, iron, and aluminum oxides (Alemayehu and Lennartz 2009). Therefore, arsenic removal by soils and volcanic rocks such as pumice and slag can be considered as low-cost adsorbents (Yazdani et al. 2016). However, both slag and pumice have quite low adsorption capacity of As(III and V) (Kwon et al. 2010; Turan et al. 2014).

Hybrid adsorbents composed of iron–polymer oxide have been developed (Rahim and Mas Haris 2015). Within these materials, we find iron oxyhydroxide nanoparticles contained in polyvinyl alcohol microspheres with an adsorption capacity of 87.18 mg/g in the pH range 2–5 (Santos et al. 2012). Ramirez-Muñiz et al. (2018) used a composite formed by natural goethite and polyacrylamide hydrogel, which has mechanical properties and chemical stability for its application in continuous systems. However, the authors observed that the content and dispersion of goethite in the hydrogel are variable and reduce the specific surface area of the composite, compared to goethite powder, affecting its adsorption capacity.

In the case of fluoride removal, zeolite has been used primarily as a natural adsorbent material (Přech et al. 2019; Suárez et al. 2019). Zeolites are highly crystalline hydrated aluminosilicates with a porous structure with pore diameters between 3 and 10 Å. The zeolites are widely used in ion-exchange processes, because of their low-cost and large internal and external surface (Lindlar et al. 2001). The structure of the zeolites consists of a three-dimensional framework formed by tetrahedra of SiO_4^{4-} and AlO_4^{5-} that give a negative charge to the structure (Doong 2012; Siddiqui et al. 2019a). This charge can be neutralized by interchangeable cations like Na^+, Ca^{2+}, K^+, Mg^{2+}, and NH^{4+}. The fact that the exchangeable cations of the zeolites are practically harmless makes them suitable for application in the processes of removal of undesirable heavy metals from water (Motsi et al. 2009). The zeolites have been modified with various metal oxides (iron, lanthanum, zirconium, and manganese) for fluoride removal (Sun et al. 2011; Lai et al. 2018).

Velazquez-Peña et al. (2017) modified zeolites with oxides of iron, zirconium, and iron–zirconium to evaluate their fluoride removal efficiency from aqueous solutions. The fluoride adsorption capacities of the zeolites modified with zirconium and iron were 2.5 and 1.6 mg/g, respectively. Zirconium–iron-modified zeolite had the highest adsorption capacities as high as 3.5 mg/g. In addition, the authors determined by thermodynamic studies that fluoride adsorption is carried out by an exothermic process.

3.4.2 Bimetallic Oxyhydroxides

In recent years, there has been a particular interest in applying bimetallic oxides to remove fluorides and arsenic from water. This is because the bimetallic oxides inherit the advantages of pristine oxides, such as considerable high surface area, adsorption capacity, and selectivity. Also, the bimetal oxides show a synergistic effect, high specific area and high concentration of active groups, which results in an improved adsorption capacity (Mandal et al. 2011; Yamani et al. 2012; Xu et al. 2013). For example, to increase fluoride adsorption capacity, alumina (Liu et al. 2010) has been modified with different types of oxides, including cerium, titanium, lanthanum, and zirconium. Hybrid oxides, alum–lanthanum and alum–zirconium have an adsorption capacity by around 6.6% and 33%, respectively. On the other hand, alum modified with manganese and cobalt has also shown a high adsorption capacity

Table 3.4 Other bimetallic oxides studied for the removal of arsenic and fluoride

Bimetal oxide	Ref.
Mn–Ce	Deng et al. (2011)
Fe–Ti	Chen et al. (2012)
Sn(IV)–iron (III) oxide, hydrous Fe(III)–Zr (IV)	Biswas et al. (2007a), Dou et al. (2011a)
Ti–Ce and Ti–La	Zhijian et al. (2010)
Iron(III)–aluminum(III)	Biswas et al. (2007b)
Fe_2O_3@$Al(OH)_3$	Zhao et al. (2010), Chai et al. (2013)
Mg–Al	Kim et al. (2013)
Mg–Fe	Lv et al. (2007), Kang et al. (2013)

(Maliyekkal et al. 2006; Tripathy and Raichur 2008; Bansiwal et al. 2010). Other important bimetallic oxides studied for the arsenic and fluoride removal are shown in Table 3.4.

Cerium–iron bimetallic oxides were used for the removal of fluorides and arsenic. The bimetallic oxide has a surface area between 127 and 165 m^2/g and pore size of 1.68–9.54 nm, and particle size was found in a range of 290–300 nm. The bimetallic oxides showed a high adsorption capacity for arsenic and fluorides of 32 and 61 mg/g, respectively. This high adsorption capacity is attributed to the increment of accessible active sites due to the distortion of the crystalline network caused by the intercalation of metal cations of different sizes. For example, the individual oxides have a fluoride adsorption capacity of only 10 and 5 mg/g, for Ce and Fe, respectively. Also, cerium–iron oxides may have high adsorption capacity in a pH range of 3–10 (Tang and Zhang 2016; Sahu et al. 2016).

3.4.3 Anchorage of Metal Oxyhydroxides onto Granular Carbon Materials

Carbon-based adsorbents have a poor adsorption capacity of fluoride and arsenic. However, materials such as activated carbon have been used as granular support for the anchorage of the metal oxyhydroxide. For the fluoride adsorption, activated carbon has been recently modified with transition metal oxides and rare earth oxides. Among the oxides used to modify the activated carbon are cerium (Sivasankar et al. 2013), aluminum, iron (Leyva Ramos et al. 1999; Tchomgui-Kamga et al. 2010), manganese (Ma et al. 2009), zirconium (Janardhana et al. 2007; Sathish et al. 2008), and lanthanum (Vences-Alvarez et al. 2015).

Our research group has used commercial activated carbon modified with zirconium and oxalic acid (Velazquez-Jimenez et al. 2014). The activated carbon modified with zirconium–oxalic acid has a fluoride adsorption capacity of 5.94 mg/g at pH 7, Ce = 40 mg/L and 25 °C. Bituminous coals and coconut fibers modified with zirconium increase the fluoride adsorption capacity with respect to unmodified materials (Sathish et al. 2008). The calcium impregnated on the carbon surface also increases the adsorption capacity with respect to the unmodified material (Hernández-Montoya et al. 2012). In our study, it was found that the presence of oxalic acid contributes to the increase in adsorption capacity, since it increased by only 32%. On the other hand, kinetic studies showed that in the first 15 minutes, carbon–zirconium removed 71% of the initial fluoride concentration, and 50 minutes are required for the modified material to reach equilibrium.

We have also developed activated carbon with lanthanum. Lanthanum uses carboxyl and phenolic groups as nucleation centers to anchor on the activated carbon surface. At pH below to 9, the activated carbon–lanthanum surface has a positive charge (Vences-Alvarez et al. 2015). In this study, the fluoride adsorption capacity (9 mg g^{-1}) was 1.8 times higher with respect to the modified carbon with zirconium and oxalic acid.

In the arsenic removal from water, different activated carbons modified with oxyhydroxide were studied. The granular activated carbons used in this study were bituminous carbon (F400), and agave bagasse was used as maternal precursor to produce activated carbon, and they were chemically activated with $ZnCl_2$ and H_3PO_4. The adsorption capacity of the carbons at arsenic concentrations in a range of 370 μg/g at 1250 μg/g was determined. Analyses showed that the temperature did not have a significant effect on the arsenic adsorption; however, at pH 8, arsenic adsorption decreased 32%. In addition, the presence of SO_4^{2-}, Cl^-, and F^- co-anions in the solution induce a decrement in the arsenic adsorption capacity, because these anions compete for the active sites in the adsorbent surface (Vitela-Rodriguez and Rangel-Mendez 2013).

On the other hand, the influence of iron content on the arsenic adsorption capacity on granular activated carbons has also been studied. Characterization analysis has shown that iron content varies from 0 to 2%; thus the point of zero charge can be found in a range of 3–11 depending on the iron content. The surface area of the materials varies from 388 to 1747 m^2/g. This study shows that the point of zero charge is the main parameter that affects the adsorption capacity of activated carbon for the As(V) removal from water with a contribution of 52%. Thus, it was determined that the presence of iron is essential in 36% to improve the arsenic adsorption capacity. Therefore, the optimal iron content of activated carbon to effectively remove arsenic is about 1%, with an arsenic adsorption capacity of 2.5 mg/g (Arcibar-Orozco et al. 2014).

An example of the metal oxide anchoring mechanism on activated carbon is presented in Fig. 3.12. The positive lanthanum species were charged to the periphery of the graphite sheets by electrostatic interactions with oxygenated groups to form O–La bonds. The oxygens of the oxygenated groups become nucleation centers for the growth of the crystal of $La(OH)_3$ by H^+ ions displacing to form a tetrahedral structure (Vences-Alvarez et al. 2015).

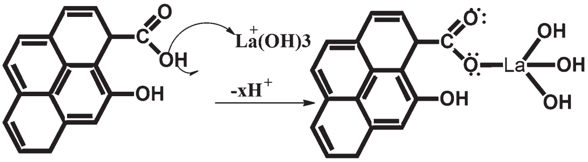

Fig. 3.12 Schematic representation of the lanthanum anchor mechanism in activated carbon. The oxygens become nucleation centers for the growth of the crystal of La(OH)$_3$ by H$^+$ ions displacing. (Modified after Vences-Alvarez et al. 2015)

3.4.4 *Particle Size Control of Metal Oxides Using Capping Agents*

The modification of activated carbon with metal oxides has led us to consider the physicochemical properties of both materials (Fierro et al. 2009), since the incorporation of metal oxides on activated carbon reduces the activated carbon surface area. The reduction in the area of activated carbon can be attributed to the formation of clusters that block the pores of activated carbons, thereby reducing the adsorption capacity of the hybrid material. Therefore, the particle size of the metal oxides incorporated onto activated carbon is a critical factor in the adsorption capacity of the material. Studies have proven that smaller particles are more likely to adsorb other molecules to become more stable (Zhang et al. 2013). Besides, a notable increase in adsorption capacity has been observed when the particle size is ≤20 nm (Yean et al. 2005).

Forced hydrolysis has been considered as one of the appropriate methods to synthesize iron oxyhydroxide nanoparticles (Meyer et al. 2000; Musić et al. 2003; Kandori et al. 2006). Studies have shown that the nanoparticles have a significant change in morphology, size, and crystallinity by adding a capping agent. Some examples of chemical agents to modify the particle size of iron oxides are polymers, heavy metals, surfactants, phosphates, amino acids, polymers, and silicon (Ishikawa et al. 2002; Musić et al. 2003; Kandori et al. 2005, 2006; Kwon et al. 2007). For example, phosphate can decrease the particle size of iron oxyhydroxides to less than 5 nm (Ishikawa et al. 2005).

In our research group, phosphate, oxalic acid, and manganese were used as capping agents, with the aim to controlling the particle size of the metal oxides incorporated in activated carbon. Arcibar-Orozco et al. (2012) used phosphate (PO$_4$) as a protective agent in the incorporation of iron particles on the activated carbon surface. By characterization analysis, it was observed that the iron nanoparticles had a size between 2 and 300 nm. Therefore, Fe–PO$_4$-modified carbons with a molar ratio of 1.5 showed a 40% increase in the As(V) adsorption capacity. Carbon modified with iron oxides and phosphate has a high As(V) adsorption capacity of 5 mg/g compared to carbon modified with only iron oxides (3.4 mg/g).

On the other hand, the mechanism indicates that during the olation reactions, iron particles start to grow up and condensate taking the oxygen groups in activated carbon as nucleation center (See Fig. 3.13). In the presence of the capping agent, some HPO_4^{2-} and $H_2PO_4^-$ adsorb over the surface of the growing nanoparticles by interchanging an OH ligand. Therefore, the capping agent avoids the excesive growth of the iron oxide particle, stabilizing its surface, allowing the formation of small particles with enchanced surface area. However, the presence of phosphate in the final material was not detected. The absence of phosphate indicates that phosphate species only adsorb over the surface of the iron and are removed during the materials rinsing with double deionized water.

In another research work, the presence of manganese is studied in the hydrolysis of iron nanoparticles on activated carbon. Manganese (Mn) acts as a capping agent during the iron precipitation in the activated carbon surface. Manganese modulates the growth and morphology of iron oxyhydroxide particles. The presence of manganese in the formation of iron oxyhydroxide generates interconnected fibrils on activated carbon. This new morphology of iron oxyhydroxide anchored onto activated carbon surface significantly increased the iron content without affecting

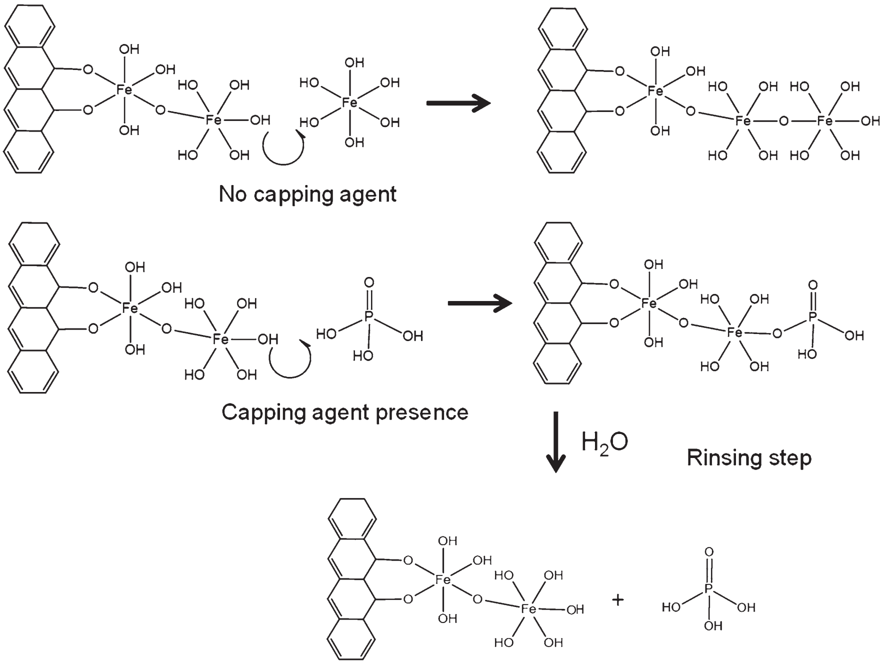

Fig. 3.13 Adsorption of phosphate anions on the surface of the growing iron oxide nanoparticles. The capping agent (in this case the phosphate) stabilizing the surface of the nanoparticles, allowing the particle to condensate into smaller sizes

the pore structure of activated carbon. The As(V) adsorption capacity of modified material was 4.9 mg/g, this being greater than the reported by activated carbon modified with iron (2.9 mg/g) under similar conditions (Nieto-Delgado et al. 2019).

Velazquez-Jimenez et al. (2014) used oxalic acid as a capping agent to maximize the zirconium dispersion on activated carbon. The presence of oxalic acid and zirconium on the activated carbon surface at a molar ratio of 1.05 increased the fluoride adsorption capacity to a factor of 3 on activated carbon modified only with zirconium. Our work suggests that oxalic acid limits the growth of ZrO_2 crystals. The above is attached to the complexation of oxalic acid with zirconium ions. The reduction in the particles size of zirconium increases the active surface area favoring the fluoride ion adsorption.

3.5 Conclusions

Arsenic and fluoride are considered as priority pollutants, due to the high toxicity they present in living organisms. Therefore, they must be removed from the water for human consumption in such a way that they comply with the recommended concentrations established by the World Health Organization. The technologies currently implemented for this purpose have several disadvantages, such as low efficiency and high costs. Since water with high arsenic and fluoride concentrations is mainly found in low-income communities, the development of new materials for the removal of these pollutants is of great interest in the scientific community. Metal oxyhydroxides have shown to have high levels of arsenic and fluoride removal from water. Metal and bimetallic oxides have proven to be highly efficient materials with adsorption capacities in the range of 2–200 and 2–300 mg/g for arsenic and fluoride, respectively.

Regardless of the chemical nature of the metal oxyhydroxides, the adsorption mechanism reported for fluoride is the ligand exchange to form an inner-sphere complex. Interestingly, rare earth metal oxides like La_2O_3 have a superior adsorption capacity, due to their capability to accommodate more than one fluorine ligand per metal cation. In contrast, the arsenic adsorption mechanism depends on the chemical nature of the metal oxyhydroxides.

There is a significant effort in the development of experimental procedures for the synthesis of monometallic and bimetallic oxyhydroxides, with small particle size, high reactivity, and selectivity for the target pollutants. Studies suggest that the synthesis solution chemistry should be considered when thermal hydrolysis is employed for the precipitation of metal oxyhydroxides: an adequate selection of the synthesis condition ensures the growth of specific crystalline structures. On the other hand, it is essential to consider the chemical and physical properties of the metal oxyhydroxide support. For instance, the activated carbon functional groups have an indispensable role during the precipitation of oxyhydroxides by thermal hydrolysis, leading the condensation reactions of the metal hydroxides. In addition, the addition of surface modifiers allows the growth of specific crystalline planes during the metal oxide precipitation, generating metal oxides with enhanced properties for the arsenic and fluoride removal from water. We hope that the concepts revised herein motivate further research in adsorbent materials science to remove different pollutants. In this respect, we hope that the mechanisms suggested here serve as a starting point for future research.

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Chapter 4
Montmorillonite Clay Composite for Heavy Metal Removal from Water

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Contents

Abstract Heavy metals are the most important pollutants due to their adverse effects on ecology, genetic, nutrition, and environment. They are essential for organism in trace amounts, but become toxic and hazardous when they exceed certain threshold concentrations. Various water treatment methods have been applying heavy metal removal from wastewater effluents. But, the adsorption process stands out due to cost-effectiveness and easy applicability of adsorption. On the other hand, clays and clay minerals such as montmorillonite, kaolinite, clinoptilolite, and zeolite are convenient adsorbents for heavy metals as regards their low cost, environment-friendly nature, abundancy, high specific surface area, small particle size, high cation exchange capacity, applicability in a wide pH range, and high chemical stability. Recently nanocomposites have been preferred because of their improved thermal, mechanical, magnetic, and electric properties. The addition of low amount of clay into polymers results in enhancing optical, flammability and barrier properties.

The aim of this review is to introduce removal efficiency and environmental remediation capability of different types of composites of montmorillonite for heavy metal ions. In this review, montmorillonite was specifically considered in terms of high affinity to adsorb heavy metals and excellent ion-exchange properties.

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Further investment about the adsorption properties of polymeric, metal oxide, and biosorbent composites of montmorillonite was performed as regards possible interaction mechanism and the latest environmental application.

Keywords Adsorption · Montmorillonite · Nanocomposite · Heavy metal · Permanently negative charge · Edge sites · Adsorption isotherms · Heavy metal removal · Surface acidity · Biosorbent

4.1 Introduction: Montmorillonite as a Clay and an Adsorbent

The clay minerals occur as a result of chemical weathering of rocks and are differentiated from soil with crystallographic arrangements of Al^{3+}, Si^{4+}, and oxygen atoms. Clay minerals form from octahedral and tetrahedral structures involving oxygen or hydroxyl groups. Regarding the tetrahedral to octahedral ratio, two types of clay mineral exist in nature: 1:1 structures and 2:1 structures. The 1:1 kaolin structures consist of tetrahedral sites, which are occupied by silicon, and octahedral sites are occupied by aluminum (Hızal and Apak 2006a, b). In 2:1 type of clays named as smectite-type clays, octahedral alumina sheets are constructed between two tetrahedral silica sheets.

The isomorphic substitution of Si(IV) by Al(III) between adjacent octahedral and tetrahedral lattice results in accumulation of negative charge throughout tetrahedral surface. While the tetrahedral surface permanently carries negative charge, which enables to interact with positively charged ions, the tetrahedral surface also carries pH-dependent variable charge because of protonation/deprotonation of surface hydroxyl groups. On the other hand, alumina surface has pH-dependent sites called edge sites.

In aqueous solution, silanols and aluminols convert to hydrated form to generate donor and proton-releasable hydroxyl groups. These edge sites on alumina and silica surfaces have acidity constant sourced from acidic character of hydrated oxygen. This property is majorly responsible for the interaction between clay and environmental contaminants as heavy metal ions.

The adsorption of positively charged ions mainly occurs on proton-releasable functional groups having donor character via covalent binding. Additionally, heavy metal ions may bind to the organic components of clay having many functional groups such as carboxyl, phenol, or amine.

The primarily construction components of montmorillonite are SiO_2 and Al_2O_3. Other oxides as Fe_2O_3, TiO_2, and oxides of alkali and alkaline earth metals can exist in montmorillonite with variable percentage. The predominant species in nature is calcium montmorillonite (Uddin 2018). Erçağ et al. declared that the diameter of 50% of montmorillonite particles and a mean particle diameter of montmorillonite are 9.24 and 12.30 μm, respectively.

4.2 Heavy Metal Removal by Clay Minerals

Heavy metals have serious adverse effects on ecology, genetics, nutrition, and environment. Heavy metal cations discharge from many industrial processes as a waste and accumulate in soil and/or water basin and mobilize by the aid of groundwater stream. Thus, heavy metals may be consumed by humans feeding by plant and animal. The most commonly found heavy metals in wastewater are arsenic, cadmium, chromium, copper, lead, nickel, zinc, and other heavy metals of the periodic table (Jaishankar et al. 2014). The usage of As(III, V), Sb(III, V), Pb(II), Cd(II), Hg(I, II), and Cr(VI) metals is restricted by The European Union Restriction of Hazardous Substances Directive and The European Union End of Life Vehicles Directive (European Union Directive 2000/53/EC; European Union Directive 2002/95/EC).

Many water treatment methods have been applied for removal of heavy metals from wastewater effluents. But, the adsorption process stands out due to cost-effectiveness and easy applicability of adsorption. Especially, the adsorption onto clay is widely used for the purpose of heavy metal removal and environmental remediation. Heavy metal adsorptions are performed onto natural or modified clay, or clay nanocomposite. Clays are economically and technically convenient to be an adsorbent, and additionally, clays are good and effective sorbents for radionuclides. Sr^{2+}, Cs^{+}, and UO_2^{2+} are readily adsorbed by clay minerals as illite, kaolinite, and montmorillonite (Arda et al. 2006; Abdel Karim et al. 2016; Siroux et al. 2017).

The studies, dealt with inspection of the types of surface sites having different functional groups on clay minerals as kaolinite and montmorillonite and the individual and competitive heavy metal adsorption on those surface sites, showed that three types of surface site are mentioned considering surface acidic functional groups of adsorbent: (i) silanol sites and/or carboxyl group having close pKa values to that of silanol, (ii) aluminol sites and/or phenolics having compatible pKa values with that of aluminol, and (iii) permanent negatively charged sites. The electrostatic interaction between heavy metal ions and permanent negatively charged surface of clay minerals has indirect pH dependency and is dominant at low pH because of positively charged silica and alumina groups (Hızal and Apak 2006a, b; Hızal et al. 2009, 2016).

While pH of solution increases, at first, silica groups start to lose H^{+} ions and become negatively charged upon zero acidity constant of silica groups. In this pH interval, heavy metal cations mostly bind to negatively charged silica surface. Because alumina groups have more basic character than silica groups, alumina groups lose their proton at higher pHs (Tombacz and Szekeres 2004). Between two pH points, corresponding to the surface acidity constant of silica and alumina surfaces, silica sites have lost releasable hydrogen, and alumina sites are still in protonated form. Thus, heavy metal–silica surface complexation is dominant. At higher pHs, alumina surfaces become activated and then metal–alumina surface complexation gets dominant (Hızal and Apak 2006a, b).

The clay minerals prefer to behave as if they were chelating ion-exchange sorbent for heavy metals in the presence of strong Lewis base such as humic acid by forming ternary surface–Lewis base–heavy metal complexation. The adsorbed amount of particular heavy metal from metal cations and humate mixture solutions is generally lower than the adsorbed from individual metal ion solutions. Competition among metal cations reduces the maximum adsorption capacity. But the competition does not affect the adsorption characteristic (Hizal et al. 2016).

The studies showed that the metal ion, having high affinity for permanently negatively charged sites, such as Cd(II), is nearly not affected from competitive adsorption at low pH (Hızal et al. 2009). Hence, Hizal et al. explained the significant enhancement adsorption of Cd(II) on montmorillonite, comparing the adsorption on kaolinite, by 2:1 smectite-type structure of montmorillonite (Hizal et al. 2016).

On the other hand, montmorillonite has high affinity for cationic organic dyes. The adsorption of cationic/basic organic dyes occurs as a result of electrostatic interaction of positive charges on nitrogen atoms of five-membered cyclic rings with permanent negatively charged surface of montmorillonite. Because the interaction between montmorillonite surface and cationic organic dye does not include hydrogen ion exchange, the adsorbed amount of the basic organic dye is not effected from deprotonation of surface occurred by increasing pH. Erçağ et al. declared that while the maximum adsorption capacities of dyes on montmorillonite significantly decreased in the presence of other basic dyes, the Langmurian character of adsorption was maintained as expected (Erçağ et al. 2015).

4.3 Polymer Composites of Montmorillonite

Montmorillonite is the basic and most commonly used clay in production of polymer nanocomposites due to high abundancy and high surface area allowing interfacial interaction between montmorillonite and polymer matrix in nanoscaled size, besides reduced cost (Sani et al. 2017; Uddin 2018). Generally, two types of polymeric nanocomposites occur: (i) when clay nanoparticle is used, the intercalated clays form by replacement of polymeric chains into the clay platelets, (ii) or clay particles can randomly disperse all over polymeric structure, and in this situation, clay exfoliation occurs.

Montmorillonite particles and polymer matrix interact with each other via hydroxyl group and permanent negative charge of clay, and the higher interaction between polymer and clay means stronger mechanical and thermal properties. Copolymerization and grafting reactive groups or clay organophilization methods are used in order to enable the interaction of clay and polymer matrix. Generally, amino acids, alkylammonium, and other organic compounds are used as organophilization agents.

Polymeric composites of montmorillonite have been widely used for heavy metal removal (Say et al. 2006; Anirudhan and Rijith 2012; Zauro and Vishalakshi 2018). The composite of extracellular polymeric substances, which was extracted from *Pseudomonas putida* X4, with montmorillonite showed high adsorption affinity for Cu(II). It was suggested by the authors that inner-sphere Cu(II) adsorption onto composite occurred as a result of the interaction between Cu(II) ion and carboxyl and phosphoryl groups of extracellular polymeric substance–montmorillonite composite (Fang et al. 2010). The adsorption of Th(IV) ions on polyacrylamide–montmorillonite and polyacrylamide–phytic acid-modified montmorillonite composites was studied by Baybaş and Ulusoy. The results were compared with those of obtained for unmodified montmorillonite. The increase in Th(IV) adsorption on composites was explained by increase in available sites for adsorption due to fine dispersion of the mineral particles beyond polyacrylamide chain (Baybaş and Ulusoy 2011).

Zhu et al. studied Ni(II), Pb(II), and Cu(II) adsorption onto 2-acrylamido-2-methyl-1-propane sulfonic acid–montmorillonite intercalated composite for the purpose of heavy metal removal from aqueous solution and exhibited that Pb(II) ions showed high adsorption affinity onto intercalated composite, while Ni(II) and Cu(II) adsorbed with lower affinity. When heavy metal-loaded composite was eluted with strong acid, 96% of loaded Cu(II) was recovered (Zhu et al. 2012). Afterward, Urbano and Rivas used same composite for the purpose of Cu(II), Cd(II), Pb(II), and Al(III) adsorption at different pHs. It was determined that the composite showed high affinity to adsorb all heavy metal ions at pHs 3 and 5. But the highest adsorption capacity was obtained for Al(III) (Urbano and Rivas 2013).

As a natural polymer, chitosan, which is an excellent adsorbent for heavy metals, is also intercalated into montmorillonite. Chitosan to montmorillonite ratio effects on heavy metal adsorption due to forming different chemical environment (Ngah et al. 2011). The chitosan intercalated montmorillonite has two active functional groups: (i) amine groups which come from chitosan chain and (ii) permanent negatively charged surface and hydroxyl sides which come from montmorillonite. These active sites allow electrostatic interaction and chemisorption (Ngah et al. 2011). At low pH both amine groups and hydroxyl sites are in protonated form. In acidic medium oxoanions of heavy metals can be adsorbed. Increase in pH causes withdrawing of H^+ ions from amine groups, while hydroxyl sites become deprotonated form which allows electrostatic interaction and chemisorption of heavy metal cations.

Epichlorohydrin cross-linked chitosan–clay composite beads were fabricated by Tirtom et al. Ni(II) and Cd(II) removal was performed onto fabricated composite. It was mentioned that the maximum adsorption for Ni(II) and Cd(II) occurred at pHs 6 and 4.5, respectively, and Ni(II) adsorption was higher than Cd(II) adsorption (Tirtom et al. 2012). On the other hand, Cr(VI) chemisorption was performed onto chitosan/montmorillonite–Fe_3O_4 microsphere (Chen et al. 2013). The adsorption capacity of this microsphere was higher than those of individual chitosan and montmorillonite. That the fabricated microspheres were efficient adsorbent for Cr(VI) was declared by the authors (Chen et al. 2013).

Irani et al. used the waste linear low-density polyethylene-g-poly(acrylic acid)-co-starch-organo–montmorillonite hydrogel composite, which was synthesized by emulsion polymerization, for Pb(II) removal. It was determined that the prepared composite had high adsorption capacity for Pb(II) ions. The adsorption showed Langmuir character, and the kinetics of the adsorption fitted pseudo-second-order model (Irani et al. 2014). Kinetic and thermodynamic properties of Co(II) adsorption onto chitosan–montmorillonite composite were searched by Wang et al. (Wang et al. 2014). It was mentioned that the maximum Co(II) adsorption was obtained for chitosan–montmorillonite composite having 1:4 chitosan–montmorillonite ratio, and it was concluded that the multilayer Co(II) adsorption onto composite is endothermic chemisorption (Wang et al. 2014).

Vieira et al. used the chitosan/acid-activated montmorillonite composite hydrogel for the removal of Pb(II) and Ni(II) ions by adsorption process (Vieira et al. 2018). The chitosan hydrogel was synthesized by using acrylic acid and N,N′-methylenebisacrylamide. The presence of montmorillonite did not significantly change the adsorption capacities of chitosan hydrogel. This situation was attributed to the increase in hydrogen bonds and cross-linking points after incorporating montmorillonite (Vieira et al. 2018).

4.4 Metal Oxide Composites of Montmorillonite

Many types of iron and iron oxides such as Fe_2O_3 or Fe_3O_4 have been widely used as a part of montmorillonite composite (Wang et al. 2010; Hua et al. 2012; Egirani et al. 2019). Zn(II), Cd(II), and Ni(II) adsorption onto bentonite and magnetic iron oxide–bentonite composite was studied by Mockovčiaková et al. The studied composites were obtained at different bentonite–iron oxide ratios and at different temperatures. As a result, obtained composites had higher specific surface area and pore volume comparing those of natural bentonite. It was determined that the zeta potential of composite suspension was negative at all pHs. Heavy metal adsorptions did not significantly change with respect to adsorption onto natural bentonite. Zn(II) and Cd(II) adsorptions showed Langmuir character, while the Freundlich model better described the Ni(II) adsorption on bentonite–iron oxide composites better (Mockovčiaková et al. 2010).

The composite, obtained by N-[3-(trimethoxysilyl)propyl]ethylenediaminetriacetic acid sodium salt addition after mesoporous silica and ferric oxide–montmorillonite composite was formed, was used to adsorb Cu(II), Ni(II), Cd(II), Zn(II), Fe(III), and Pb(IV) ions. Because N-[3-(trimethoxysilyl)propyl]ethylenediaminetriacetic acid is a EDTA-like chelating agent for heavy metals, adsorption capacities for all metal ions enhanced. Although clay minerals cannot adsorb unhydrolyzed metal cations from acidic solution because of positive charge, chelating agent grafted composite retained the heavy metals at low pH. The authors declared that the fabricated composite was successfully used to uptake heavy metals from individual and mixture solutions and showed preferable adsorption for Fe(III) cations (Addy et al. 2012).

Another iron source for formation of composite is nanoscale zero-valent iron. The nanoscale zero-valent iron has been widely used for environmental remediation due to having many advantages such as controllable particle size and abundant surface sites (Zou et al. 2016) It is known that the composite shows high affinity to adsorb inorganic species of As(III) and As(V) (Bhowmick et al. 2014). It was mentioned by Bhowmick et al. that montmorillonite-supported nanoscale zero-valent iron retained As(III) and As(V) inorganic species via ligand-like adsorption with fast kinetic, and the adsorption capacity decreased above pH 8 (Bhowmick et al. 2014).

In a study, montmorillonite–iron oxide composite was used to remove Cs^+ from aqueous solution. It was observed that prepared nanoadsorbent had high affinity to Cs^+ and that the removal efficiency decreased in the presence of Sr^{2+} (Ararem et al. 2013). When montmorillonite was modified with iron oxide, the zeta potential was changed to positive from the negative below pH 6.5, which is point of zero charge of iron oxide–montmorillonite composite (Cottet et al. 2014). The change in zeta potential can be explained by the fact that the maximum adsorption of heavy metals onto Iron oxide–montmorillonite composite is achieved above pH 6.5 via interacting to negatively charged surface of composite..

Kalantari et al. used Fe_3O_4–montmorillonite nanocomposite for the Cu(II), Ni(II), and Pb(II) removal from aqueous system. The diameter of composite was 8.4 nm, and the adsorption efficiencies were yielded between approximately 76% and 90% depending on the solid to liquid ratio used in the experiments. The magnetic nanocomposite was found to be an efficient adsorbent for removing heavy metals from aqueous solutions by the authors (Kalantari et al. 2015).

Pb(II), Cu(II), Zn(II), and Cd(II) removal from highly acidic solution was performed by adsorption process using montmorillonite–kaolinite–TiO_2 composite as an adsorbent. The optimal amount of TiO_2 as an additive was determined 20% to achieve improved adsorption ability. The results showed that fabricated composite had high affinity at whole pH range from pH 2 to 6. Especially, 96% removal was obtained for Pb(II) ions at pH 2, while the maximum removal for other ions was 41%. The dramatic enhancement of heavy metal adsorption at low pHs was explained by the changes in microstructural and morphological characteristics of composite in the presence of TiO_2 with different crystalline forms and by well dispersion of TiO_2 on the surface of the clay matrix (Đukić et al. 2015).

Zheng et al. fabricated ammonium-pillared montmorillonite–$CoFe_2O_4$ composite caged in calcium alginate beads which has magnetic character and investigated Cs^+ adsorption in terms of adsorption properties, mechanism, and capacity. As a result, Zheng et al. expressed that fabricated composite showed high Cs^+ adsorption efficiency with the high selectivity, and this composite might be used to removal of Cs^+ from Cs-contaminated environments (Zheng et al. 2017).

Pb(II) and Cu(II) adsorptions on zinc oxide–montmorillonite nanocomposite were investigated by Sani et al. It was determined that the composite showed high adsorption efficiency in a wide pH range. As a result of regeneration experiments, it was decided the composite could be used for three adsorption–desorption cycles. The kinetics of adsorptions was well explained by pseudo-second-order model, while the equilibria of adsorptions were described by Langmuir isotherm (Sani et al. 2017).

4.5 Biosorbent Composites of Montmorillonite

Biosourced sorbents such as algae, bacteria, cellulose, or residue of cereals are focused in recent studies. Lignocellulose, which includes lignin, hemicellulose, and cellulose, is low cost and an efficient adsorbent for heavy metals (Ngah and Hanafiah 2008; Zhong et al. 2012; Mahmood-ul-Hassan et al. 2018). Bunhu and Tichagwa fabricated lignocellulose–montmorillonite composite by in situ intercalative polymerization using methacryloxypropyltrimethoxysilane and investigated competitive adsorption of methyl orange from aqueous solution in the presence of Cd(II) and Pb(II) ions. It was observed that methyl orange adsorption onto composite increased in the presence of those heavy metal ions. This situation was attributed to existence of new active sites sourced from heavy metals (Bunhu and Tichagwa 2012). In fact, the enhancement of methyl orange adsorption can be better explained by the possible formation of ternary surface–metal–methyl orange complexation via metal bridge on the composite sorbent.

Cr(VI) uptake using cellulose–montmorillonite composite as an adsorbent was studied by Kumar et al. High adsorption capacity of adsorbent was explained considering the pH dependency of Cr(VI) species and surface of adsorbent. Because the formation of Cr(VI) species depends on the pH of solution, in this study the favorable pH for the Cr(VI) adsorption was determined to be the pHs between 3.8 and 5.5. In this pH range, $HCrO_4^-$ species is dominant, and the author suggested that the ion pair formed between negatively charged Cr(VI) and the positively charged cellulose–montmorillonite composite. High determination coefficients were yielded for both linearized Langmuir and Freundlich models. The kinetics of Cr(VI) adsorption fitted second-order model, and the adsorbent were reused for tenfold cycles (Kumar et al. 2012).

Bacteria are considered as efficient biosorbents for heavy metals. Thus, bacteria can affect mobility and speciation of heavy metals in environmental systems. The characteristics and mechanisms of competitive adsorption of Pb(II) and Cd(II) on *Pseudomonas putida*–montmorillonite composite were inspected by Du et al. Du et al. observed that when the adsorption of Cd(II) and Pb(II) mixture was performed, the maximum adsorption capacity of composite for both ions decreased. This situation was explained by the authors by the fact that Cd and Pb were bound to same types of adsorption sites on the sorbent. Du et al. also declared that bacteria–clay composites showed different behavior in competitive adsorption with respect to competitive adsorption on individual clay and bacteria (Du et al. 2016a).

As known clays, bacteria and humic substances are soil components. In a continuing work, Du et al. tried Cd(II) adsorption on montmorillonite–humic acid–*Pseudomonas putida* composite in order to provide better understanding of the biogeochemical cycling and fate of heavy metals in natural soils and sediments. As a result, Du et al. observed that the Cd(II) adsorption on ternary composite decreased with respect to the adsorption on individual and/or binary components, and the decrease in Cd(II) adsorption was attributed to "blocking effect" between humic acid and bacterial cells (Du et al. 2016b).

In another study, Cu(II) adsorption on montmorillonite–alginate microcapsules at pH 5 and at different montmorillonite–alginate ratios was performed by Ely et al. and showed that the increase in montmorillonite–alginate ratio caused decrease in heavy metal adsorption. When montmorillonite amount is higher, the intercalation of alginate into clay layers disables the interaction of functional groups of alginate with heavy metal ion. The kinetics of the metal adsorption was explained by pseudo-second-order model (Ely et al. 2009).

Alginate–montmorillonite–polyaniline nanocomposite was fabricated by Olad and Azhar by performing chemical oxidative polymerization of aniline in alginate–montmorillonite nanocomposite dispersion. This nanocomposite was used to Cr(VI) uptake from aqueous solution. Cr(VI) adsorption was described by pseudo-second-order model, while adsorption isotherm fitted Freundlich model. It was implied that the Cr(VI) sorption was endothermic reaction. Additionally, it was observed that adsorbed amount of Cr(VI) on alginate–montmorillonite–polyaniline nanocomposite was higher than that on alginate–montmorillonite. On the other hand, the adsorption on alginate–montmorillonite composite was lower than the adsorption on alginate–polyaniline. This situation was explained by the intercalation of alginate into silicate layers of montmorillonite preventing Cr(VI) to penetrate into montmorillonite layers (Olad and Azhar 2014).

Ni(II) and Mn(II) adsorption onto montmorillonite–rice husk composite, fabricated by furnace at 300 ˚C, was done by comparing the result with obtained results for heavy metal adsorption on unmodified montmorillonite. It was expressed that the surface area and total pore volume of the composite were dramatically higher than those of unmodified montmorillonite, while the mean pore diameter was smaller. The improved microstructural properties resulted in the enhancement of cation exchange and adsorption properties. Mn(II) and Ni(II) adsorptions were expressed by the Freundlich isotherm model, but the maximum adsorption capacities were calculated using the linearized Langmuir model because the determination coefficient was high enough. The addition of rice husk to montmorillonite enabled to have more efficient and cheaper novel adsorbent for environmental remediation (Akpomie and Dawodu 2015).

Charcoal and active carbon are also considered as biosorbents (Wang and Chen 2009; Reddy and Reddy 2014; Kırbıyık et al. 2016). In a study, activated carbon–montmorillonite–thiolated graphene oxide composite was used to removal of Pb(II). The fast sorption occurred in 20 min with the pseudo-second-order kinetic. The maximum Pb(II) adsorption capacity of fabricated composite was approximately 1 mmol/g. The high adsorption of Pb(II) was explained by chemical and electrostatic interaction between Pb(Π) and composite surface having many donor groups such as carboxyl and hydroxyl groups. The authors suggested the activated carbon–montmorillonite–thiolated graphene oxide composite as a high-performance adsorbent for Pb(Π) removal from polluted water (Mojoudi et al. 2019).

Recently, clay–biochar composites became popular for various purposes. Biochar is obtained by pyrolysis of animal or plant residues. Biochar is a carbon and functional groups rich porous solid and is an environmentally friendly sorbent. Thus, it is an excellent adsorbent for different types of pollutants (Han et al. 2019). Montmorillonite–biochar composites were used by many researchers for organic dye, pharmaceuticals, or anion removals (Yao et al. 2014; Chen et al. 2017; Pereira et al. 2013). But, heavy metal adsorption onto montmorillonite–biochar composites has not been encountered yet.

Apart from all these composites, there are many types of montmorillonite composites used for the purpose of heavy metal removal. The graphene oxide, which is a single monomolecular layer graphite, has both hydrophilic and hydrophobic characteristics, enabling graphene oxide to adsorb heavy metals. Zhang et al. fabricated montmorillonite–graphene oxide in the presence of stearyltrimethylammonium chloride as cross-linking agent. The composite suspension had positive zeta potential. The kinetics of Pb(II) adsorption on fabricated composite fitted pseudo-second-order model. The adsorption character showed metal-like adsorption. Although the author expressed that the presence of stearyltrimethylammonium chloride did not reduce the adsorption capacity, and hydrophilic functional groups of graphene oxide gave more active sites, Pb(II) adsorption capacity on fabricated composite was lower than given Pb(II) adsorption capacity in literature (Zhang et al. 2019).

Table 4.1 shows the data about adsorption properties of various heavy metals on various types of montmorillonite composites. As seen from the table, however, the heavy metal adsorption onto different kinds of montmorillonite composite has been widely explored for approximately 10 years. More exploration should be performed to serve industrial purposes.

4.6 Conclusion

As seen from so far examined studies, various composites of montmorillonite have high affinity to heavy metal ions and have been widely used for heavy metal removal. In general, composites show higher adsorption capacity for particular heavy metal than parent sorbents/components of composite. Many montmorillonite composites including organic functional groups or natural components such as humic acid, alginate, or bacteria may simulate environmental conditions. Determining heavy metal adsorption parameters is decisive for the fortune of heavy metal in environment. Biochar composite of montmorillonite as an adsorbent for heavy metals needs more studies to achieve better understanding and to find convenient usage area. On the other hand, efficient, reusable, and low-cost montmorillonite composites should be used in industrial application.

Table 4.1 The adsorption properties of various heavy metals on various types of montmorillonite composites

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Kinetic model	Isotherm	Reference
ZrO–montmorillonite composite	Fe(III)	23.80 mg/g	Second-order kinetics	Langmuir model	Bhattacharyya and Gupta (2008)
	Co(II)	22.80 mg/g			
	Ni(II)	22.00 mg/g			
Carbon modified	Cd(II)	28 mg/g	Second-order kinetics	Langmuir model	Yu et al. (2008)
Aluminum-pillared montmorillonite					
Calcined tetrabutylammonium montmorillonite	Fe(II)	22.60 mg/g	Second-order kinetics	Langmuir model	Bhattacharyya and Gupta (2009)
	Co(II)	22.30 mg/g			
	Ni(II)	19.70 mg/g			
Intercalated Fe–montmorillonite	Cd(II)	25.70 mg/g	Pseudo-second order	Langmuir model	Wu et al. (2009)
Montmorillonite-supported magnetite nanoparticles	Cr(VI)	13.88 mg/g	Pseudo-second order	Langmuir model	Yuan et al. (2009)
Chitosan–clinoptilolite composite	Cu(II)	11.32 mg/g	Pseudo-second order	Langmuir model	Dinu and Dragan (2010)
	Co(II)	7.94 mg/g			
	Ni(II)	4.21 mmol/g			
Intercalated montmorillonite–hydroxyaluminum and montmorillonite–cetyltrimethylammonium bromide composites	Cr(VI)	9.09 mg/g	Pseudo-second order	Langmuir model	Hu and Luo (2010)
Sodium dodecyl sulfate-modified iron-pillared montmorillonite	Cu(II)	18.70 mg/g	–	Langmuir model	Li and Wua (2010)
	Co(II)	16.00 mg/g			
TiO_2– montmorillonite composite	Hg(II)	123.80 mg/g	Elovich equation	Langmuir model	Dou et al. (2011)
Alginate–montmorillonite composite	Pb(II)	244.60 mg/g	–	Langmuir model	Shawky (2011)

(continued)

Table 4.1 (continued)

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Kinetic model	Isotherm	Reference
Fe intercalated–montmorillonite complex	Cu(II)	173 mmol/kg	–	Langmuir model	Zhu et al. (2011)
Cellulose–montmorillonite nanocomposite	Cr(VI)	22.2 mg/g	Second-order kinetics	Langmuir model	Kumar et al. (2012)
Magnetite–polyethylenimine montmorillonite	Cr(VI)	8.77 mg/g	–	Langmuir model	Larraza et al. (2012)
Poly(methacrylamide-co-acrylic acid)–montmorillonite nanocomposites	Cu(II)	–	Poly(methacrylamide-co-acrylic acid)–montmorillonite nanocomposites	–	Barati et al. (2013)
Chitosan–montmorillonite magnetic microsphere-based geopolymer	Cr(VI)	58.82 mg/g	Pseudo-second order	Langmuir model	Chen et al. (2013)
Montmorillonite–polyacrylamide/montmorillonite–polyacrylate nanocomposites	Fe(III)	2.94 × 10^{-3} mol/g	–	Langmuir model	Natkański et al. (2013)
Chitosan–montmorillonite biocomposite	Cu(II)	1.23 mg/g	Pseudo-second order	Temkin model	Pereira et al. (2013)
Exfoliated polypyrrole–organically modified montmorillonite composite	Cr(VI)	119.34 mg/g	Pseudo-second order	Langmuir model	Setshedi et al. (2013)
Organically modified montmorillonite (OMMT) nanocomposites	Cu(II)	–	Pseudo-second order	–	Wu et al. (2013)
Lipopeptide–montmorillonite intercalated composite	Cu(II)	49.80 mg/g	Pseudo-second order	Langmuir model	Zhu et al. (2013)
	Zn(II)	48.25 mg/g			
	Cd(II)	52.19 mg/g			
	Pb(II)	62.90 mg/g			
	Hg(II)	38.22 mg/g			
Lignocellulose-g-acrylic acid–montmorillonite nanocomposite	Pb(II)	918.2 mg/g	Pseudo-second order	Langmuir model	Du et al. (2014)
	Cd(II)	482.5 mg/g			

Montmorillonite supported carbon nanosphere	Cr(VI)	156.25 mg/g	Pseudo-second order	Langmuir model	Li et al. (2014)
Chitosan–montmorillonite composite	Co(II)	150 mg/g	Pseudo-second order	Temkin model	Wang et al. (2014)
Organo-montmorillonite–sodium alginate graft poly(acrylic acid-co-2-acrylamido-2-methyl-1-propane sulfonic acid) superabsorbent composite	Pb(II)	1485 mg/g	–	Langmuir model	Zhu et al. (2014)
	Cu(II)	294 mg/g			
	Ni(II)	303 mg/g			
Montmorillonite–rice husk composite	Ni(II)	0.118 mmol/g	Pseudo-second order	Freundlich	Akpomie and Dawodu (2015)
	Mn(II)	0.056 mmol/g			
Montmorillonite–N-isopropylacrylamide–sodium 2-acrylamido-2-methylpropane sulfonate	Ni(II)	769.20 mg/g	–	Langmuir model	Atta et al. (2015)
	Co(II)				
Montmorillonite–TiO$_2$ composite	Pb(II)	71.10 mg/g	–	Langmuir model	Đukić et al. (2015)
	Cu(II)	42.90 mg/g			
	Zn(II)	15.40 mg/g			
	Cd(II)	13.80 mg/g			
Fe$_3$O$_4$ –montmorillonite nanocomposite	Pb(II)	263.15 mg/g	Pseudo-second order	Langmuir model	Kalantari et al. (2015)
	Cu(II)	70.92 mg/g			
	Ni(II)	65.78 mg/g			
L-Cystein-modified montmorillonite–immobilized alginate nanocomposite	Cu(II)	100 mg/g	Pseudo-second order	Langmuir model	Mittal et al. (2015)
	Pb(II)	111.11 mg/g			
	Ni(II)	125 mg/g			
Lignocellulose–montmorillonite nanocomposite	Ni(II)	94.86 mg/g	Pseudo-second order	Langmuir model	Zhang and Wang (2015)
Cross-linked chitosan–montmorillonite hydrogel composite	Cu(II)	240.68 mg/g	Pseudo-second order	Langmuir model	Ngwabebhoh et al. (2016)
Dextrin–oxalic acid/cetyltrimethylammonium Bromide–montmorillonite nanocomposite	Pb(II)	0.898 mg/L	Pseudo-second order	Freundlich model	Ahmad and Mirza (2017)
L-Methionine montmorillonite encapsulated guar gum-g-polyacrylonitrile copolymer hybrid nanocomposite	Pb(II)	125 mg/g	Pseudo-second order	Langmuir model	Ahmad and Hasan (2017)
	Cu(II)	90.91 mg/g			

(continued)

Table 4.1 (continued)

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Kinetic model	Isotherm	Reference
Porous lignin-based poly(acrylic acid)–organo-montmorillonite nanocomposites	Pb(II)	1.04 L/g	Pseudo-second order	Freundlich	Ma et al. (2017)
ZnO–montmorillonite nanocomposite	Pb(II)	88.50 mg/g	Pseudo-second order	Langmuir model	Sani et al. (2017)
	Cu(II)	54.06 mg/g			
Chitosan-reduced graphene oxide–montmorillonite composite hydrogels	Cr(VI)	87.03 mg/g	Pseudo-second order	Langmuir model	Yu et al. (2017)
Persulfate–zero-valent iron–magnetic biochar	Pb(II)	187.70 mg/g	Pseudo-second order	Langmuir model	Chen et al. (2018)
Xanthan gum–montmorillonite bionanocomposite	Pb(II)	17.17 mg/g	Pseudo-second order	Freundlich	Mirza and Ahmad (2018)
Chitosan–acid-activated montmorillonite composite hydrogel	Pb(II)	5.97 L/g	Nonlinear	Nonlinear Redlich–Peterson	Vieira et al. (2018)
	Ni(II)	0.04 L/g	Pseudo-second order		
Zinc oxide–montmorillonite composite	Pb(II)	864 mg/g	–	–	Egirani et al. (2019)
Porous hydrogel of chitosan–2D montmorillonite	Pb(II)	76.74 mg/g	Pseudo-first order	Langmuir model	Wang et al. (2019)
Lignin and montmorillonite-based superadsorbent hydrogel	Cu(II)	74.35 mg/g	Pseudo-second order	Freundlich	Sun et al. (2019)
Lysine–montmorillonite composite	Pb(II)	0.49 mmol/g	–	Langmuir model	Zhu et al. (2019)

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Chapter 5
Cellulose-Based Adsorbents for Heavy Metal Removal

Soma Nag and Swarup Biswas

Contents

Abstract Pollution of water bodies has become a worldwide problem since the last few decades due to the increased load of population and industrial activities. Excessive use of fertilizers and pesticides is also an important reason. Heavy metals are one of the key toxic elements of wastewater and remain for a long time in the system due to their nonbiodegradability. Adsorption technique using activated carbon is a convectional approach for heavy metal eradication but a costly method. Scientists are attempting various waste materials in modern days to avoid the expensive activated carbon. Cellulose is a widely available, cheap natural polymeric material and has metal binding properties. Researchers have attempted several natural cellulose-based materials and found promising results for heavy metal removal and further observed that the adsorption capacity enhances with its treatment. This chapter highlights a detailed review of works carried out by scientists using the cellulosic materials from different natural sources for heavy metal remediation. Modification of cellulosic materials either through physical and chemical processes

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or by grafting enhances their performance, strength, and reusability. The char and activated carbon prepared from cheap cellulosic sources may even replace the costly commercial activated carbon. The performances of modified cellulose, cellulose beads, grafted cellulose, cellulosic composites, nano-cellulose, and hydrogels on heavy metal eradication have been elaborated. A broad list of different cellulose-based adsorbents and their adsorption capacities has been compiled, which indicates their significant comparable metal removal capacities with the commercial adsorbents. Moreover, most of the modified adsorbents have strong regeneration ability and are reusable in many cycles efficiently with a feasibility of metal recovery.

Keywords Cellulose · Heavy metal ions · Adsorption · Isotherm · Langmuir · Freundlich · Microcrystalline cellulose · Nano-cellulose · Grafted cellulose composites · Hydrogel · Cellulose beads

5.1 Introduction

Water contamination is a severe problem to the mankind (Darabos et al. 2015; Li et al. 2013). Though human body needs some of the heavy metals in small concentrations, lead, arsenic, mercury, cadmium, chromium, copper, iron, zinc, and nickel are very toxic in nature. They affect the enzyme systems and the metabolism of our body at even small doses (Li et al. 2013; Paulino et al. 2006). Exposure to these elements may cause immediate as well delayed adverse health effects like skin disease, digestion and respiratory problems, cancer, etc. People follow various well-established techniques since long to eradicate these pollutants from the wastewater or to minimize their level. Research and development has revealed various new directions for exclusion of toxic pollutants, especially heavy metals from water and wastewater, and adsorption is considered as one of the most sustainable, clean, cheap, and eco-friendly processes for solving these problem. Compared to other methods, adsorption process produces minimum biological or chemical sludge and has the potential of metal recovery, and the spent adsorbent may be burnt as fuel (Volesky 1990). Activated carbon is a very effective adsorbent and widely used, but its high cost is compelling people to find out other suitable materials (Khan et al. 2004). Large amounts of wastes are available from forest, as agricultural residues. Agricultural and biowaste materials contain lignin, cellulose, and hemicellulose and have a wide variety of hydroxyl, alcoholic, phenolic, and other functional groups which make them suitable for metal binding (Demirbas 2008). Cellulose is one of the main constituents of the natural wastes, by-products, and residues from a number of food processing industries. Photosynthesis process generates nearly 1 lakh crore tons of cellulose yearly throughout the world (O'Connell et al. 2008). Due to the abundant availability without much cost, these materials can be applied for elimination of heavy metals with or without modifications. Cellulose is often extracted from agricultural materials and further modified to enhance the adsorption capacity (Kyzas and Kostoglou 2014). Several researchers (Hokkanen et al. 2016; O'Connell et al. 2008) reviewed the modification methods of the cellulose-based materials to increase its adsorption capacity. In the past years, people have tried to use various cellulosic agricultural waste materials, such as sugarcane bagasse (Gupta and Ali 2004; Mohan and Singh 2002), rice husk (Ajmal et al. 2003; Srinivasan 1998), sawdust (Kadirvelu et al. 2003; Selvi et al. 2001), coconut husk (Tan et al. 1993), rice mill wastes, neem leaves, coconut shell, hyacinth roots (Singha and Das 2012), rubber leaf (Nag et al. 2015), etc., for heavy metal removal and noted their adsorptive potential.

The above observations suggest cellulosic materials can be used for metal removal processes in raw form without any surface modifications. However, acid or alkali treatment and some more specific treatments enhance their adsorption potential, and the modified cellulose is formed. Some examples of modified cellulose are cellulose gels, beads, derivatives, composites, holocellulose, and so on. They are biodegradable and non-toxic and have huge adsorption capacity. A critical review was conducted to assess the potential of cellulosic materials in wastewater treatment.

5.2 Availability, Uses, Types, and Properties of Cellulosic Materials

Cellulose is widely available in nature. Plants are grown throughout the world and cellulose is present in the cell wall in high amount. The major sources are fibers of various plants, like cotton, jute, hemp, flax, and many more. The plant wood consists of 45–50% of cellulose (Holtzapple 2003) and is an important source of our dietary fiber. It has many other uses, like manufacturing of paper, plastic, film, some kinds of clothes, alternative source of energy, different chemicals, etc. The cellulose content of various plant sources is presented in Table 5.1.

The simplest form of sugar is known as glucose which is produced by plants through the process of photosynthesis and stored as long-chained polymeric form known as cellulose. It is a complex carbohydrate with carbon, oxygen, and hydrogen having common structure [$C_m(H_2O)_n$] and is made up of a number of D-anhydroglucose pyranose or simply glucose units. These glucose units jointly form a fundamental cellulose unit, known as β-(1–4)-glycosidic bonds (Gupta et al. 2016). Figure 5.1(a and b) depicts the common structure of glucose and cellulose, while Fig. 5.2 demonstrates the scanning electron microscopic image of rubber leaf, a common cellulosic material at a magnification of 15,000X. Natural sources of cellulosic materials and preparation of useful adsorbents from them are presented in Fig. 5.3.

Cellulose is hydrophilic and non-toxic and has good mechanical strength and returns to the carbon cycle by natural decay. Methyl and hydroxyl functional group is present in one repeating molecule of cellulose, and the functional groups contribute in metal binding. It is a semi-crystalline linear polymer and has both crystalline

Table 5.1 Cellulose content of various agriculture and forest materials

Material	Cellulose ranges (%)	Source
Vegetables	1–21	Holtzapple (2003)
Fruits	0.6–4.2	
Seeds	2–12	
Agricultural residues	31–59	
Wood	41–53	
Flax and hemp	70	
Cotton	95	
Dried coconut shell	33.61	Ahluwalia and Goyal (2007)
Bagasse	50	Khan et al. (2004)
Wood sawdust	45–50	Sciban et al. (2006b)
Jute	60–65	Hokkanen et al. (2016)
Leaf fiber	55–73	
Bamboo	40–55	
Barley	48	
Oat	44–53	
Wheat	49–54	
Rice husk	32.24	Chuah et al. (2005)

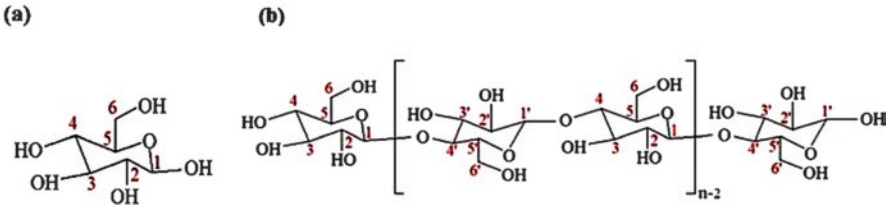

Fig. 5.1 (**a** and **b**). Structure of glucose and cellulose. (Modified after Chaplin 2010)

and amorphous phases. Cellulose gives strength to the plant and is commonly found in the cell walls of stems, roots, leaves, fruits, seeds, etc. They have porous structure and are insoluble in water. Commercial cellulose is synthesized mostly from wood and cotton.

Different forms of cellulosic materials, such as crystallites, nanocrystals, whiskers, nano-fibers, nano-fibrils, etc., are applied nowadays in various fields. They are synthesized after modifying chemically/physically or enzymatically to enhance the adsorption capacities. Organic and inorganic acids, bases, oxidizing agents, and other compounds are applied for modification of celluloses. Monomer grafting by irradiation to attach a number of specific functional groups is also tried by a number of researchers (Hokkanen et al. 2016). Cellulose beads are prepared by a series of chemical treatments followed by freeze-drying of fruit wastes and other cellulosic materials (Maaloul et al. 2019).

Microcrystalline cellulose is made from natural polymeric cellulose such as hard wood, soft wood, and other agricultural residues. It is partially depolymerized using

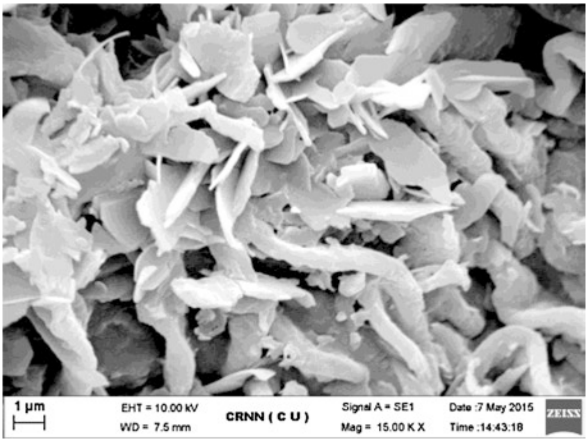

Fig. 5.2 Scanning electron microscopic image of powdered rubber leaf showing its surface morphology

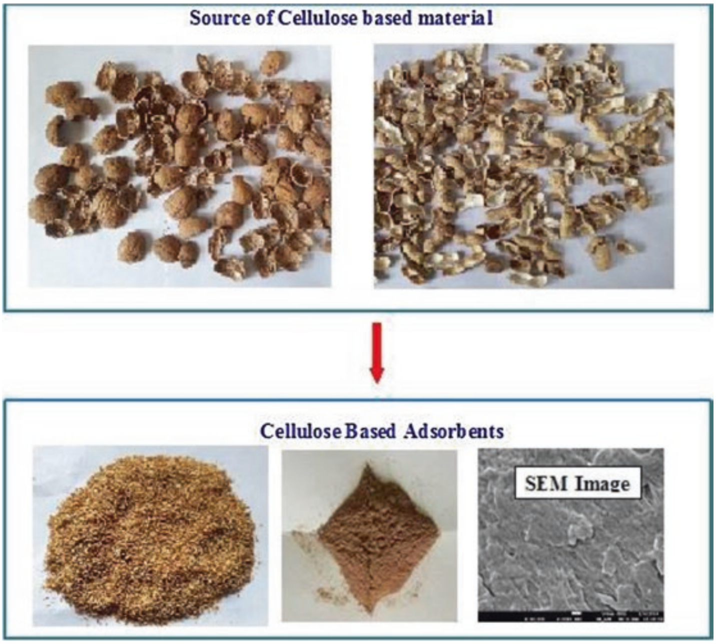

Fig. 5.3 Flow diagram for preparation of adsorbents from natural cellulosic sources and their structure

acids or enzymes to remove the amorphous region leaving the crystalline form. The process of depolymerization increases the surface area considerably making it more suitable for the heavy metal adsorption. It does not dissolve in water and water binds on its surface strongly (El-Naggar et al. 2017). Though three hydroxyl functional groups are present, microcrystalline cellulose has weak binding forces for heavy metals; however, it may be modified by alcohols for introduction of carboxylic groups for enhancing the adsorption capacities (Cao et al. 2017). Nano-cellulose is referred as crystallites, nano-fibers or nanocrystals, etc. Wood, sugar beet, potato, hemp, flax, cotton, algae, and certain bacteria are its typical sources of synthesis (Hokkanen et al. 2016).

5.3 Heavy Metal Sources and Their Impacts

Heavy metals commonly include metals with specific gravity 5 or higher and finally metals beyond calcium in the periodic table (Nieboer and Richardson 1980). Cadmium, cobalt, iron, lead, zinc, chromium, mercury, etc. are considered as toxic heavy metals (Wagenet et al. 1978). Anthropogenic reasons and increase in industrial activities have enhanced greatly their release in the environment, causing harms to the flora and fauna. Electroplating, mining, paints and pigments, leather tanning, textile dyeing, inorganic chemical manufacturing industries, wood treatment, etc. are the industrial sources of Cr(VI) (Udy 1956; Casarett and Doul 1980), and mining, metal plating, cadmium-nickel battery manufacturing units, smelting, sewage sludge, etc. are responsible of Cd(II) discharge (Alqudami et al. 2012). Petrochemical, fertilizer, oil refineries, and automobile industries (Abdel-Halim et al. 2003; Uzu et al. 2011) release lead, copper, and zinc. Nickel comes mainly from metal plating, tannery, brewery, boiler pipe, cooking utensil, fertilizer, paper, rubber vulcanization, ceramics, textile, fertilizer, pharmaceutical, and steel production units (Parker 1980, Kim et al. 2007). Chlor-alkali, oil refining, battery, rubber processing, pesticide, thermometer, cosmetics and pharmaceuticals, etc. industries are sources of mercury contamination (Krishnan and Anirudhan 2002; Namasivayam and Periasamy 1993).

Heavy metals are water-soluble, and their long persistence in the nature is causing serious health issues (Choi et al. 2009; Stratton 1987). Their toxicity increases with solubility (Milojkovic et al. 2016). Chromium exists as Cr(III) and Cr(VI) in aqueous medium with different chemical and biological properties (Ahmad et al. 2005). Cr(VI) is very toxic and is considered as group A human carcinogens by the Environmental Protection Agency (US-EPA 2006; Cieslak-Golonka 1996; Farhan et al. 2012; Raji and Anirudhan 1998). All cadmium compounds are potentially harmful and instigate hypertension, nephritis, and dysfunctions of the nervous system, renal system, birth defects, and itai-itai disease and act as a cumulative poison (Brower et al. 1997; Dror et al. 2012). Lead and its compounds even at trace level cause harm to the gastrointestinal track, nervous system, liver, kidney, and brain and even may cause death. Chronic exposure leads to abortion and neonatal death (Sittig 1981). Excess intake of Cu(II) damages the liver, kidney, and stomach and causes anemia. It is considered to be carcinogenic and source of neurotoxicity, commonly known as Wilson's disease (Baum 1982). Excess zinc intake sets off restlessness, muscular stiffness, loss of appetite, nausea, infertility, and pancreas problems (Pahlsson 1989). Nickel causes lung and bone cancer. Headache, dizziness, nausea, vomiting, and weakness are also related problems (Kadirvelu 1998; Meena et al.

Table 5.2 Discharge limits of different toxic heavy metals

	Discharge limits (mg L^{-1}) as per the Indian Standards	
Heavy Metal	into inland surface waters IS 2490 (1974)	Into public sewers IS 3306 (1974)
Arsenic	0.20	0.20
Mercury	0.01	0.01
Cadmium	2.00	1.00
Lead	0.10	1.00
Chromium	0.10	2.00
Nickel	3.0	3.0
Zinc	5.00	15.00
Copper	3.00	3.00

2005). Mercury damages nerve cells, kidney, and pulmonary functions (World Health Organization 2002) and originates Minamata disease. The maximum permissible discharge limits of heavy metals by the Indian Standards are presented in Table 5.2.

5.4 Theoretical Aspects of Heavy Metal Adsorption

Adsorption by using cellulosic materials is recognized as a gainful way for wastewater management over the conventional metal treatment methods. It is environmental-friendly and is a field of emerging research. Treatment may be conducted either in batch process or in column process. Figure 5.4 represents laboratory treatment techniques for heavy metal contaminated wastewater by adsorption method. The type of material (adsorbent) and its concentration, solution pH, adsorbate concentration, time, temperature, particle size, etc. are the affecting parameters for the adsorption process, and the metal ion removal efficiency is dependent upon them.

The metal uptake per gm of adsorbent at any time t, q_t (mg g^{-1}), and percentage removal is calculated by

$$q_t = \frac{(C_0 - C_t)V}{m_s} \tag{5.1}$$

$$\text{Percentage removal } (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{5.2}$$

where C_0 and C_t are the adsorbate concentration (mg L^{-1}) at $t = 0$ and at time t, V denotes the total volume of the experimental liquid (L), and m_s is the mass of the adsorbent taken (g).The reaction rate is normally represented by pseudo-first-order

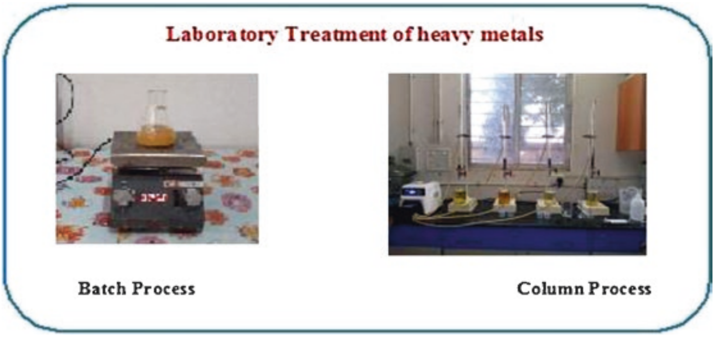

Fig. 5.4 Laboratory treatment of contaminated wastewater by adsorption technique in batch and column process

or pseudo-second-order model (Lagergren 1898; Ho et al. 2000), demonstrated by Eqs. 5.3 and 5.4.

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 t}{2.303} \tag{5.3}$$

$$\frac{t}{q_t} = \frac{1}{k_2} + \frac{1}{q_e} t \tag{5.4}$$

In the above equations, q_e indicates the equilibrium metal uptake and k_1 (min^{-1}) and k_2 ($\text{mg g}^{-1}\ \text{min}^{-1}$) are the pseudo-first- and pseudo-second-order rate constants. The equilibrium models predicted by Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) are commonly applied for representation of the equilibrium condition as given in Eqs. 5.5 and 5.6.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{5.5}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5.6}$$

C_e signifies the adsorbate concentration (mg L^{-1}) at equilibrium, q_{max} is the maximum adsorption capacity, and b denotes the Langmuir constant (L mg^{-1}). K_f is the Freundlich equilibrium constant ($\text{mg g}^{-1}\ (\text{mg L})^{-1/n}$) and n is the intensity of adsorption. Numerical values of $n > 1$ indicate favorable adsorption (Erdem et al. 2004).

5.5 Uses of Cellulose-Based Materials for Heavy Metal Removal

Agricultural materials and their wastes normally have high cellulose content, and these materials have been used by many scientists as adsorbents without any modifications. But some of them have considerable amounts of hemicelluloses, lignin, pectin, etc. along with cellulose; they are physically or chemically modified for use as adsorbents (Jamshaid et al. 2017). Pretreatment using various kinds of acid or base solutions or salts increases the metal ion adsorption efficiency. Dilute sulfuric acid improves hydrolysis of cellulose and achieves high reaction rates; however, concentrated acid was not recommended due to its toxicity (Esteghlalian et al. 1997).

5.5.1 Sugarcane Bagasse

Bagasse is a cellulose-rich material (50%) and contains hydroxyl and phenolic groups. It is used in both treated and untreated forms. Khan et al. worked on sugarcane bagasse for Cr^{+6} removal and obtained promising results (Khan et al. 2001). Rao et al. treated the waste bagasse from sugar industry with NaOH and is used for Cr(VI) and Ni(II) removal. They compared the results with commercial powdered activated carbon and observed that bagasse was effective and cost comparative over the activated carbon for both the metal ions. They suggested its use in wastewater treatment (Rao et al. 2002). Some other researchers treated Cd^{+2} and Zn^{+2} laden solution by using activated carbon made from sugarcane bagasse heated at 800–850 °C. The reaction was endothermic, and the adsorption capacity increased with temperature for both metal ions (Mohan and Singh 2002). Bagasse fly ash was treated with hydrogen peroxide and attempted (Gupta and Ali 2004) for exclusion of Pb(II) and Cr(VI). 96–98% elimination of metal ions was observed at low flow rates in column. The chemically modified sugarcane bagasse was attempted (Karnitz Jr. et al. 2007) for remotion of copper, cadmium, and lead ions. The treatment was done initially with succinic anhydride to synthesize the modified sugarcane bagasse containing carboxylate functions and further to introduce chelating functions of amide groups. The modified sugarcane showed better performance for all metal ions, and the removal efficiency was related directly to the amide functions introduced from outside. Another group of scientists used native sugarcane bagasse and modified it after anaerobic degradation and used it for adsorption of both Cd(II) and Zn(II). The improved sugarcane bagasse (after anaerobic degradation) had 2 times more adsorption capacity for Zn(II) and 2.3 times for Cd(II) compared to the native one; moreover, the anaerobic degradation process yielded biogas (Joseph et al. 2009). Cellulose and sugarcane bagasse were mercerized with NaOH and then treated with EDTA (Junior et al. 2009) and tried for copper, cadmium, and lead management. They observed that the mercerized form displayed better results compared to non-mercerized form for both the cellulose and sugarcane bagasse.

Sugarcane bagasse in its original and immobilized form was tried by researchers (Ullah et al. 2013) for remediation of tannery wastewater contaminated with Cr(III) and Cr(VI). Pseudo-second-order kinetics and Langmuir model represented the adsorption process. Immobilized sugarcane removed 80.6% Cr(VI) and 41.5% Cr(III). Sugarcane bagasse treated with NaOH and HCl was used by others (Khoramzadeh et al. 2013) for biosorption of Hg(II) from aqueous solutions. 97.58% mercury was removed at pH 4 and q_{max} value was 35.71 mg g^{-1}. Both Langmuir and Freundlich equilibrium models were found applicable. Adsorption capacities of pure and modified sugarcane bagasse are presented in Table 5.3.

5.5.2 *Wood Sawdust*

Wood sawdust is an abundant waste of wood industry and contains nearly 45–50% cellulose and polyphenolic groups which help in heavy metal adsorption (Ngah and Hanafiah 2008). Sharma and Forster tried sawdust for Cr(VI) eradication and found encouraging results. The adsorption capacity of sawdust was 39.7 mg g^{-1} (Sharma and Forster 1994). Researchers tried phosphate-treated sawdust for removal of Cr(VI), Ni(II), Cu(II), and Zn(II) and noted change in adsorption capacity of the raw and treated sawdust. The process was pH-dependent and favored at pH less than 2.

Table 5.3 Adsorption capacities for different toxic heavy metals by sugarcane bagasse-based adsorbents

	q_{max} (mg g^{-1})						
Adsorbent	Cr^{+6}	Zn^{+2}	Cu^{+2}	Cd^{+2}	Hg^{+2}	Pb^{+2}	Sources
Sugarcane bagasse	13.4						Sharma and Forster (1994)
Activated carbon from sugarcane bagasse		31.11		38.03			Mohan and Singh (2002)
Bagasse fly ash modified with hydrogen peroxide	4.35					2.50	Gupta and Ali (2004)
Modified sugarcane bagasse 2			114	196		189	Karnitz Jr. et al. (2007)
Modified sugarcane bagasse 5			139	164		189	
Modified sugarcane bagasse 6			133	313		313	
EDTA-treated cellulose			49.8				Junior et al. (2009)
EDTA-treated bagasse			66.7				
EDTA-treated mercerized cellulose			66.7	112.0		232.0	
EDTA-treated mercerized bagasse			76.9				
EDTA-treated twice-mercerized bagasse			92.6	149.0		333.0	
Immobilized sugarcane bagasse					35.71		Khoramzadeh et al. (2013)

The treated sawdust removed 100% Cr(VI), 83% Ni(II), 86% Cu(II), and Zn(II) each from water. 87% of the adsorbed Cr(VI) was recovered by 0.01 M NaOH solution (Ajmal et al. 1996). Some other scientists investigated sawdust as potential adsorbent for wastewater treatment (Shukla et al. 2002). Sciban and Klasnja used poplar sawdust for Cu(II) remotion, and the maximum Langmuir value was 3.24 mg g^{-1} (Sciban and Klasnja 2003). They also (Sciban et al. 2006a) attempted poplar and fir tree sawdust treated with NaOH and Na_2CO_3 for Cu(II) and Zn(II) removal and compared the results with the untreated one. They observed that the modified sawdust from both origins had higher removal capacity than the unmodified one. However, the removal capacity of Cu(II) was less than Zn(II). In another work, they (Sciban et al. 2006b) further observed that 1% conc. NaOH solution was sufficient for surface modification of sawdust, and thereafter, concentration increase was not effective, and temperature was not an important factor. Acar and Eren used sulfuric acid-treated poplar sawdust, and 92.4% Cu(II) was removed, while the untreated poplar sawdust could remove only 47% at pH 5. The kinetics of the adsorption was fast, and 70–80% copper was removed in 10 min (Acar and Eren 2006). Coconut tree sawdust modified with sulfuric acid was tried by researchers (Kadirvelu et al. 2003) for Hg(II) and Ni(II) remotion. 100% Hg(II) and 81% Ni(II) were removed in 1 h. Others attempted sawdust for Cr(VI) and obtained better removal at pH 1. More than 95% desorption efficiency was achieved by acid and base treatment of the used adsorbent (Gupta and Babu 2009). Others tried Romanian fir tree sawdust (Nagy et al. 2013) and coconut tree sawdust (Putra et al. 2014) for the treatment of different heavy metal-laden wastewater. The Langmuir adsorption capacity of various sawdust-based materials is presented in Table 5.4.

Table 5.4 Adsorption capacities of sawdust

Adsorbent	q_{max} (mg g^{-1})						Sources
	Cr^{+6}	Zn^{+2}	Cu^{+2}	Cd^{+2}	Hg^{+2}	Pb^{+2}	
Sawdust	39.7						Sharma and Forster (1994)
Sawdust	15.82						Dakiky et al. (2002)
Poplar sawdust			3.24				Sciban and Klasnja (2003)
Poplar sawdust modified with NaOH and Na_2CO_3		15.83	6.29				Sciban et al. (2006a)
Fir sawdust modified with NaOH and Na_2CO_3		13.41	12.7				
Sulfuric acid-treated poplar sawdust			13.94				Acar and Eren (2006)
Untreated poplar sawdust			5.43				
Sawdust	41.5						Gupta and Babu (2009)
Sawdust from fir tree		23.81	3.89			25.0	Putra et al. (2014)

5.5.3 Rice Wastes

Rice husk has 32.24% cellulose (Rahman et al., 1997) and is known for its metal removal capacity. Chuah et al. observed that arsenic, gold, cadmium, mercury, copper, zinc, cobalt, nickel, and lead, i.e., most of the heavy metals, were remediated by rice husk successfully (Chuah et al. 2005). Some others applied treated rice husk in column mode for Cd(II) removal, and the regeneration efficiency was 97–95.4% in the first two cycles, indicating the reversibility of sorption process without loss of binding efficiency (Kumar and Bandyopadhyay 2006). Mohan and Sreelakshmi conducted column study with raw and treated rice husk. The adsorption rate and capacity were double in case of the treated rice husk compared to raw one (Mohan and Sreelakshmi 2008). Another group of scientists (Bansal et al. 2009) attempted treated rice husk. The boiled rice husk removed 71% Cr(VI), whereas formaldehyde-treated rice husk could remove 76.5%. Different rice and other wastes were tried (Singha and Das 2011, 2013) for Cr(VI) and Cu(II) removal. The spontaneity and reusability suggested the use of these wastes as effective adsorbents. Other researchers found rice husk was successful for iron, lead, copper, and nickel treatment within the experimental limits (20–60 mg L^{-1}) for real wastewater (Hegazi 2013, Vieira et al. 2014). Research findings also indicated that other wastes, like rice hull and rice bran, were effective for treatment of Ni^{+2}, Cr^{+3}, Cu^{+2}, Zn^{+2}, and Co^{+2} ions from wastewater (Marshall et al. 1993). Mercury was eliminated successfully by rice husk and straw activated with NaOH (Song et al. 2013). Table 5.5 provides the performances of the rice wastes.

Table 5.5 Rice wastes

	Maximum adsorption capacity, q_{max} (mg g^{-1})						
Adsorbent	Cr^{+6}	Zn^{+2}	Cu^{+2}	Cd^{+2}	Hg^{+2}	Pb^{+2}	Sources
Tartaric acid-treated rice husk (TARH)			29.0			108	Wong et al. (2003)
Rice hull and bran		0.75	1.21	0.23			Marshall et al. (1993)
Rice husk ash					66.66		Tiwari et al. (1995)
Rice husk ash			5.17			22.38	Vieira et al. (2014)
Rice bran	12.34		20.98				Singha and Das (2011, 2013)
Rice straw	12.17		18.35				
Rice husk	11.39		17.87				
Rice husk – pure					62.89		Song et al. (2013)
RH-NaOH					82.64		
Rice straw – pure					75.19		
RS-NaOH					58.14		

5.5.4 *Coconut Wastes*

Coconut coir, pith, and its shell have average 21–26% cellulose, and its pretreatment further increases the cellulose content. Coconut shell-based activated carbon was attempted by researchers (Alaerts et al. 1989) for Cr(VI) removal, and the results were compared with other activated carbons. Coconut husk fiber was used by Tan et al. for Cr(VI) remotion in both batch and column processes. It was prepared by boiling the grounded fiber with distilled water in steps: 1.5 M NaOH solution, distilled water, 2 M HNO_3, and distilled water in order. Coconut husk fiber displayed better removal at pH 2 (Tan et al. 1993). Another group of people used natural coconut husk for Cu(II) remediation and modified it with three different reactive dyes, such as reactive yellow 2, acid blue 29, and acid blue 25, respectively. The dye-coated forms had more adsorption capacity, and the yellow two dye-coated coconut husk yielded the maximum value. The process followed Langmuir equilibrium model (Low et al. 1995). Baes et al. treated the coconut coir with sulfuric acid first and then by 5% formaldehyde solution followed by HNO_3 and water and finally dried at 100 °C and named as modified coconut coir. The modified coconut coir could eliminate lead, copper, and nickel successfully, and they observed that the adsorption capacity was highest at pH 6 and the sequential order was Pb(II) > Cu(II) > Ni(II) (Baes et al. 1996). Manju and Anirudhan studied the performance of coconut pith fiber for Cr(VI) removal from aqueous solution. They observed 99.2% Cr(VI) was removed at 2 pH for 50 ppm solution. Cr(VI) adsorption was not obstructed by the co-ions present. The spent adsorbent was reusable by washing with alkali solution (Manju and Anirudhan 1997). Others observed that coconut shell had high uptake (285.7 mg g^{-1}) efficiency for Cd(II) at pH 7 over a broad choices of concentrations (20–1000 mg L^{-1}) and ion-exchange mechanism followed (Pino et al. 2006). Table 5.6 depicts the q_{max} values obtained by researchers.

5.5.5 *Other Agricultural Wastes*

Different parts of plants are rich in cellulose, and they have been used by scientists for remediation of heavy metals since long. Dakiky et al. detoxicated Cr(VI) with various wastes from agricultural origin and found their satisfactory removal efficiencies (Dakiky et al. 2002). Researchers (Dupont and Guillon 2003) used a lingo cellulosic substrate prepared from wheat bran for Cr(VI) removal. They observed large number of protons helped in reducing chromium from six oxidation state to three, and concurrently lignin moieties were oxidized to form several hydroxyl and carboxyl functional groups which contributed for ion exchange and displayed commendable performance. Others (Ozer et al. 2004; Ozer and Ozer 2004) used sulfuric acid-treated wheat bran for Cu(II) and Cr(VI) removal and noted that the acid treatment increased the active surface area. A novel bioadsorbent was developed from matured neem leaves by others for Cr(VI) and Cd(II) adsorption in batch process, and around 87% metal was removed. They suggested high removal potentiality of

Table 5.6 Coconut waste-based materials

	q_{max} (mg g^{-1})							
Adsorbent	Cr^{+6}	Zn^{+2}	Cu^{+2}	Cd^{+2}	Hg^{+2}	Pb^{+2}	Ni^{+2}	Sources
Coconut shell-based activated carbon	20.0							Alaerts et al. (1989)
Coconut husk fiber	29							Tan et al. (1993)
Natural coconut husk			3.07					Low et al. (1995)
Coconut husk coated with reactive yellow 2			12.27					
Coconut husk coated with reactive acid blue 29			8.13					
Coconut husk coated with reactive acid blue 25			7.75					
Modified coconut coir			227.5			957.3	109.1	Baes et al. (1996)
Green coconut shell powder				285.7				Pino et al. (2006)

the adsorbent (Sharma and Bhattacharyya 2005). Sarin and Pant attempted activated eucalyptus bark in column for chromium removal (Sarin and Pant 2006). Scientists (Ozer and Pirincci 2006) were able to eliminate 82.8% lead by using sulfuric acid-treated wheat bran. Chen et al. observed a very good bed performance for removal of Cr(VI) using modified corn slack (Chen et al. 2012). Other researchers (Martins et al. 2013) used dried minced castor leaves for detoxification of Cd(II)- and Pb(II)-laden water of Paraná River. The high nitrogen and sulfur content of the leaf favored the adsorption process. Lopez et al. attempted plum (*P. domestica* L.) tree bark for eradication of hexavalent and total chromium (Lopez-Nunez et al. 2014). Netzahuatl-Munoz et al. attempted *Cupressus lusitanica* bark for Cr(VI) removal. It was endothermic reaction with metal uptake of 305.4 mg g^{-1} (Netzahuatl-Munoz et al. 2015). Another group of researchers (Martin-Lara et al. 2014) suggested a new treatment method for real electroplating wastewater containing Cr(VI), Cu(II), and Ni(II) by using olive stone, a biomaterial. Others (Nag et al. 2017, 2018a) effectively used different leaves for Cr(VI) and Cd(II) removal. These green adsorbents were useful for Cr(VI) and Cd(II) remotion in column also (Nag et al. 2015, 2018b). Das et al. tried nut shells for Cr(VI) adsorption (Das et al. 2019). The performances of these adsorbents are presented in Table 5.7.

5.5.6 Modified Cellulose

Cellulose was modified by several researchers, and the modified cellulose exhibited better and promising performances in many cases as compared to the unmodified one. It has high recycling ability and biodegradability. Navarro et al. modified

Table 5.7 Other agricultural waste materials

Adsorbent	Maximum adsorption capacity, q_{max} (mg g^{-1})						Sources
	Cr(VI)	Zn(II)	Cu(II)	Cd(II)	Hg(II)	Pb(II)	
Olive cake	33.44						Dakiky et al. (2002)
Pine needles	21.50						
Wool	41.15						
Modified wheat bran	35.6						Dupont and Guillon (2003)
Sulfuric acid-treated wheat bran			51.5	101.5			Ozer and Ozer (2004) and Ozer et al. (2004)
Sulfuric acid-treated wheat bran						55.56	Ozer and Pirincci (2006)
Cupressus lusitanica bark	305.4						Netzahuatl-Munoz et al. (2015)
Acid-treated rubber leaf	29.79						Nag et al. (2017, 2018a, 2018b)
Rubber leaf	22.97			15.53			
Mango leaf	35.7			16.35			
Jackfruit leaf	32.29			20.37			
Onion peel	19.88						
Garlic skin	9.22						

porous cellulose with polyethyleneimine, and modified material showed appreciable results for Hg (II) removal in acidic condition. The adsorption capacity was 288 mg g^{-1} (Navarro et al. 1996). Others (Pyrzynska and Trojanowicz 1999) observed that the substituted carboxyl groups in modified cellulose improve the ion-exchange capacity compared to the unsubstituted one. They also suggested that the metal ion sorption on cellulose was rapid compared the inorganic collectors, such as Al_2O_3 or SiO_2. Castro et al. modified cellulose with p-aminobenzoic acid and tried this modified cellulose for treatment of Cu(II), Cd(II), Pb(II), Ni(II), and Zn(II) ions from an aqueous medium in column mode. p-aminobenzoic groups helped the cellulose to remove almost 100% metal ions. The adsorptive capacities for Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) were 1.72 ± 0.02, 1.96 ± 0.02, 1.88 ± 0.04, 2.01 ± 0.03, and 1.93 ± 0.03 mmol g^{-1}, respectively (Castro et al. 2004). Amidoximated wood sawdust and amidoximated wood flour were used for remediation of cadmium, copper, chromium, and nickel ions, and the results were compared with the untreated one (Saliba et al. 2005). Treated adsorbent showed better performance as expected. Shukla and Pai attempted some cheap cellulose-containing groundnut shells and sawdust for Cu^{+2}, Ni^{+2}, and Zn^{+2} ions adsorption and recorded their worthiness. Further, application of C.I. Reactive Orange 13 dye onto these materials enhanced the adsorption capacity (Shukla and Pai 2005). O'Connell et al. modified the wood pulp industry wastes by glycidyl methacrylate, imidazole, and other chemicals and used the modified materials for elimination of nickel and lead. The reaction for lead was completed within 30–40 min, but it took 350–400 min for nickel. Langmuir capacity was 71.9 and 45.2 mg g^{-1} for Pb(II) and Ni(II) adsorption, respectively (O'Connell et al. 2006). Some others (Wu et al. 2012) modified the adsorbent cotton, sawdust, and wheat hull with thioglycolic acid, acetic anhydride, acetic acid, and concentrated sulfuric acid to form thiol-functionalized adsorbents and tried these modified stuffs for trimming down Pb(II) from glucose solution. The thiol-modified adsorbents had nearly two to three times better performance compared to the unmodified one. Another cellulose-based adsorbent was synthesized and used (Zhou et al. 2014) for eradication of Pb(II), and excellent adsorption capacity (584.80 mg g^{-1}) was recorded. The sorption obeyed Langmuir model and second-order rate equation. They also found that the adsorbent was eco-friendly, had good regeneration ability, and can be reused for at least six times. Others (He et al. 2014) synthesized polyethyleneimine-modified porous cellulosic material and got excellent result for Cr(III) and Fe(III) removal. The new adsorbent had six times reusability. Table 5.8 depicts the performances of the different modified adsorbents.

Cellulose Beads

Environment-friendly beads were prepared by many researchers and were applied successfully for heavy metal eradication. A new adsorbent in the form of spherical cellulose beads was prepared after chemical modification of cotton and named as spherical cellulose adsorbent for metal ions, and both adsorption and desorption studies were conducted for Cu(II). The bead had enhanced area of 189.12 m^2 g^{-1} and Langmuir uptake of 83.56 mg g^{-1} at 40 °C. They had good regeneration capacity, and only 7.2% of its initial adsorption power was lost after three cycles (Liu et al. 2002). A biodegradable chitin/cellulose bead was prepared by others (Zhou et al. 2004) and that could effectively treat lead, cadmium, and copper. 98% performance was regained using 1 M HCl solution. Chitosan–cellulose hydrogel beads were synthesized (Li and Bai 2005) by blending chitosan with cellulose and cross-linking with ethylene glycol diglycidyl ether. Both the beads were applied for copper remediation, and high adsorption capacity was achieved by both the chitosan cellulose and cross-linked chitosan-cellulose hydrogel beads. However, cross-linked chitosan beads had little less adsorption capacity. Scientists (Luo et al. 2016) fabricated magnetic cellulose beads by using nitric acid-modified activated carbon from cotton linter pulp and surrounded with carboxyl-decorated magnetic nanoparticles. They tried this chemically modified beads for Cu(II), Pb(II), and Zn(II) eradication. The micro- and nano-porous structure of the beads contributed in high metal ion adsorption. The process was spontaneous and endothermic in nature. Almond shell was bleached with 1-butyl-3-methylimidazolium chloride and coagulated and freeze-dried to synthesize a novel adsorbent, named as cellulose bead-based biosorbents. The surface was modified to 3D macroporous structure with interconnected pores and the beads efficiently removed Cu(II) (Maaloul et al. 2019).

Table 5.8 Adsorption capacities of modified cellulose-based adsorbents

	q_{max} in mg g^{-1}								
Adsorbent	Cr(VI)	Zn(II)	Cu(II)	Cd(II)	Hg(II)	Pb(II)	Ni(II)	Fe(III)	Sources
Cellulose-g-polyacrylic acid						23.9			Okieimen and Ebhoaye (1986)
Polyethyleneimine-modified cellulose					288.0				Navarro et al. (1996)
Modified cellulose beads						61.74			He et al. (1999)
Spherical cellulose Adsorbent for metal ions			83.56						Liu et al. (2002)
Modified lignocellulosic material							187.8		Saliba et al. (2005)
Cellulose-modified with p-aminobenzoic		126.18	124.54	193.3		414.5	110.4		Castro et al. (2004)
Chitin/cellulose beads			19.06	35.97		68.0			Zhou et al. (2004)
Cellulose-containing groundnut shell		7.62	4.46				3.83		Shukla and Pai (2005)
Dye-coated groundnut shell		9.57	7.6				7.49		
Cellulose-containing sawdust		10.96	4.94				8.05		
Dye-coated sawdust		17.09	8.71				9.87		
Polymer grafted banana stalk				65.88		185.3			Shibi and Anirudhan (2006)
Cellulose-g-GMA-imidazole						75.8	48.5		O'Connell et al. (2006)
CM-cellulose/chitosan hydrogel			169.49						Zhao and Mitomo (2008)
Unsubstituted chitosan			80.7						Ngah et al. (2002)
Chemically cross-linked chitosan			59.7						
Native sugarcane bagasse		1.76		2.58					Joseph et al. (2009)
Improved sugarcane bagasse		3.33		5.96					
Chitosan/cellulose beads	13.02	19.81	9.34			26.3	13.2		Sun et al. (2009)
Cellulose composite with sodium montmorillonite	22.2								Kumar et al. (2011)
Nano-hydroxyapatite-chitin composite			21.45						Gandhi et al. (2011)
Nano-hydroxyapatite-chitosan composite			26.11						

(continued)

Table 5.8 (continued)

	q_{max} in mg g^{-1}								
Adsorbent	Cr(VI)	Zn(II)	Cu(II)	Cd(II)	Hg(II)	Pb(II)	Ni(II)	Fe(III)	Sources
Thiol-modified adsorbent Cotton						28.67			Wu et al. (2012)
unmodified						10.78			
Thiol-modified wood sawdust						43.14			
Unmodified						17.03			
Thiol-modified buckwheat hull						44.84			
Unmodified						34.06			
Succinylated nano-cellulose		105.26	120.74	227.76			43.66		Hokkanen et al. (2013)
Cellulose-based adsorbent						584.80			Zhou et al. (2014)
Magnetic cellulose nanocomposite	171.5								Sun et al. (2014)
Porous cellulose modified with polyethyleneimine	83.98 Cr(III)							377.19	He et al. (2014)
Cellulose–TiO_2 nanocomposites						222.0			Li et al. (2015)
Chemically modified magnetic cellulose-based beads		20.8	47.57			37.99			Luo et al. (2016)
Cross-linked oxidized microcrystalline cellulose, S1			17.94	14.84		20.46			Cao et al. (2017)
S2			16.78	14.00		18.02			
S3			12.71	11.11		13.45			
Cellulose bead-based biosorbents			128.24						Maaloul et al. (2019)
Magnetic chitosan nanocomposites	142.32								Subedi et al. (2019)
Graphene-modified magnetic chitosan nanocomposites	101.31								

Grafted Cellulose

Chemical modifications followed by grafting enhance the cation exchange capacity of cellulose (Anirudhan and Senan 2011). Grafting of polyacrylonitrile and polyacrylic acid on holocellulosic materials was done at various levels, and the modified cellulose was attempted for Cu(II), Cd(II), and Pb(II) eradication by researchers (Okieimen and Ebhoaye 1986). The metal binding efficiency of the adsorbent was increased with the level of graft polymers. Others (He et al. 1999) treated alkaloid and aged cotton with CS_2 and $CaCO_3$, and then gradually, potassium oleate and chlorobenzene was added in sequence and heated to synthesis the cellulose xanthate viscose beads. The beads were filtered and washed to attain macroporous spherical-shaped cellulose, and it was further activated with epichlorohydrin and Tween-20. White macroporous spherical-shaped cellulose activated by epichlorohydrin was collected by extraction with acetone. The beads were then modified by 1,5-diamino ethyl-3-hydroxy-1,5-diazacycloheptane, and finally the modified cellulose bead-based biosorbents were obtained. The modified beads spontaneously removed copper and lead with excellent performance. Guclu et al. studied the influence of graft chains on four different types of cellulosic copolymers; synthesized with a variety of percentages of polyacrylic acid in the presence of other chemicals. The grafted cellulose treated Pb(II), Cu(II), and Cd(II) ions successfully. The reaction rate decreased with increase in grafting percentages of polyacrylic acid, but the overall metal adsorption enhanced (Guclu et al. 2003). Radioactive isotopes were used by others to graft polymers to the cellulose by irradiation technique (Nasef and Hegazy 2004). By grafting acrylamide on banana stalk, a new adsorbent was prepared by Shibi and Anirudhan and was applied for cadmium and lead treatment (Shibi and Anirudhan 2006). The modified adsorbent showed creditable adsorption capacity and the equilibrium reached in 3 h. The reaction obeyed pseudo-second-order rate.

Cellulose Composites

Cellulose composites are prepared by combining cellulose with other materials. Composite materials have better adsorption capacity compared to its constituting materials and have diverse applications and provide a solution for many engineering applications in wastewater treatment. Researchers (Sun et al. 2009) prepared a biocomposite by blending chitosan with cellulose, and the composite material was effective in removal of most of the heavy metals, such as Cu(II), Zn(II), Cr(VI), Ni(II), and Pb(II), in freeze-drying condition. Kumar et al. synthesized cellulose–montmorillonite composite material by reacting cellulose with sodium montmorillonite and applied the composite for Cr(VI) remediation (Kumar et al. 2011). The reaction followed second-order kinetics and the composite material had ten times regeneration capacity. The Langmuir adsorption capacity was 22.2 mg g^{-1}.Another group of scientists (Gandhi et al. 2011) prepared nano-hydroxyapatite compound by reaction with $Ca(NO_3)_2$ and ammonium dihydrogen phosphate at pH more than 10. The precipitate was washed and dried. This nano-hydroxyapatite was then combined with chitin and chitosan to form nano-hydroxyapatite-chitin and nano-hydroxyapatite-chitosan composites, respectively. These materials were useful for treatment of Cu(II). Sun et al. synthesized magnetic cellulose nanocomposites and obtained high removal efficiency for Cr(VI) with maximum adsorption capacity of 171.5 mg g^{-1} at 25 °C. The reaction was exothermic and very fast, reaching the equilibrium within 10 mins. The adsorbents showed good reusability (Sun et al. 2014). Researchers (Li et al. 2015) tried by immobilizing TiO_2 nanocrystals on cellulose fibers, and the new composite material had excellent capacity in Pb(II) removal. The adsorption capacity was 371.0 mg g^{-1} which was 18 times more than the sole material TiO_2 nanocrystal. Novel adsorbents were synthesized (Cao et al. 2017) by cross-linking oxidized microcrystalline cellulose for exclusion of heavy metals. Oxidized microcrystalline cellulose was combined with tetrafluoroterephthalonitrile at different ratios, and the new materials were named as S_1, S_2, and S_3. The materials were porous, and the surface area increased to 88.32 m^2 g^{-1} from 25.74 m^2 g^{-1} for the sample cross-linked with only epichlorohydrin. The adsorbents had reusability using dilute HCl. Others (Subedi et al. 2019) prepared magnetic chitosan nanocomposites and modified it with graphene oxide. They tried both the materials for Cr(VI) eradication and obtained encouraging results with four times reusability. The q_{max} value of magnetic chitosan nanocomposites and graphene-modified nanocomposite was 142.32 and 100.51 mg g^{-1}, respectively. The grapheme-modified composite surface had more negative charge, and thus adsorption of Cr(VI) complex anion was restricted compared to the magnetic chitosan. The reaction was endothermic and spontaneous and followed pseudo-second-order kinetics. The composites were successful in fixed bed column operation also.

Cellulose Chars and Activated Carbon

Due to high carbon content of cellulosic materials (40–44%), all wood parts are considered as a cheap source for preparation of char and activated carbon. Carbonization enhances the carbon content to nearly 80% in char and 95% in activated carbon (Gupta et al. 2016, Khezami et al. 2005). Powdered cellulose was burnt in nitrogen atmosphere at 200–1000 °C to prepare chars and further treated with steam or in acidic/basic conditions to activate it. The thermal treatment and activation helped in the improvement of surface characteristics. The pore size was related with the rate of heating and the temperature (Babel 2004, Shen et al. 2013). Carbonizing at a slower rate yields four times better surface area and pore volume compared to rapid heating. Brunner and Roberts suggested controlling the temperature and heating rate to yield better results (Brunner and Roberts 1980). The surface area of activated carbon prepared from cellulose may be as high as 1317 m^2 g^{-1} (Lorenc-Grabowska and Rutkowski 2014).

Cellulose Hydrogels

Hydrogels may be prepared from the natural cellulose in many ways, such as directly from native celluloses or from cellulose derivatives. Chitosan was blended with concentrated carboxymethylated cellulose to synthesize carboxymethylated cellulose/chitosan hydrogels which was then cross-linked by irradiation. This newly prepared hydrogel was employed for adsorption of Cu(II) in batch technique. Cu(II) formed complex ions with the amino and carboxyl groups present on the gel, and the metal uptake was as high as 169.49 mg g^{-1} (Zhao and Mitomo 2008). When compared the performance with the results obtained by previous researchers (Ngah et al. 2002), they observed that the unsubstituted chitosan and chemically cross-linked chitosan had much less q_{max} values. Zhao and Mitomo suggested adsorption capacity, and the degree of cross-linking was enhanced by the addition of chitosan. Cellulose-polymer composite, cellulose-inorganic hybrid hydrogels, etc. are considered as super adsorbents with variety of other applications. The hydrogels are transparent, non-toxic, and biodegradable. Being a low-cost, environmental-friendly material, it has the potential to replace the petroleum-based materials in the near future as a substitute (Chang and Zhang 2011). Liu et al. (2013) worked on magnetic hydrogels. These materials are biocompatible and renewable, indicating good scope for adsorption applications (Liu et al. 2013).

Nano-cellulose

Succinylated cellulose was synthesized by a series of modifications of microfibrillated cellulose (Hokkanen et al. 2013). Initially, commercially purchased microfibrillated cellulose was mercerized by NaOH solution and then treated with succinic anhydride and thereafter centrifuged and washed with a number of chemicals to yield the desired product. These steps helped to convert carboxylic groups to carboxylate which promoted chelating functions. The new material displayed high adsorption potential for a number of heavy metals, such as zinc, copper, cadmium, nickel, and cobalt in batch mode with 96 to 100% regeneration efficiency.

5.6 Conclusions

Heavy metal remediation from water and wastewater in a user-friendly way is a challenging job. The high cost of removal and the operational difficulties often prompt the small and medium sector industries to bypass the effluent treatment, thus leading toward a serious environmental degradation. The above study reveals the potential of cellulosic materials for elimination of toxic heavy metals form wastewater. Cellulose is rich in carbon, economical, and abundantly available from multiple natural sources. They have a natural binding capacity toward heavy metals and show good adsorption capacity even in untreated condition. Physical and chemical modifications of cellulose further enhance the binding capacity and reusability. Chemical modifications of natural cellulosic materials yield cellulose beads, gels, derivatives, and composites and these new materials are cheap, non-toxic, biodegradable, biocompatible, rigid, and reusable in many cycles with metal recovery capacity. Some of the modified cellulose may even have adsorption capacities like commercial adsorbents. The modified cellulose demonstrates 90–95% regeneration ability. Biochars and activated carbon may also be prepared from diverse sources by thermal reaction and have potential as replacement for commercial activated carbon. All these properties make them attractive for wastewater treatment. Finally, it may be concluded that the cellulose and its products have immense potential for use as cost-effective adsorbent and can play a major role in water and wastewater treatment.

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Chapter 6
Recovery of Heavy Metals by Membrane Adsorbers

Yilmaz Yurekli

Contents

Abstract Heavy metal contents in the effluents of various industrial activities have reached to an emergency level in recent decades due to the tremendous increase in volumetric production rate and insufficiency of the treatment methods. Recent developments on membrane technologies have indicated that they offer reliable and efficient methods of promising sustainable applications for supplying clean water of a quality that satisfies human and environmental needs. The incorporation of inorganic nanoparticles in polymeric membranes, which allows the filtration and adsorption processes to be combined in one unit, has brought a new insight to membrane materials in terms of recovery of valuable metals, high flux, and antifouling capabilities. In this chapter, manufacturing of adsorptive membranes using phase inversion by immersion precipitation method is introduced. Selection of nanoparticle type, size, and amount on the morphological properties of the membranes is also addressed in this chapter. Development of a mathematical model that can predict the long-term performances of any flat sheet or hollow fiber-based membrane adsorbers in terms of their throughput and rejection characteristics is discussed. Finally, suggestions are also given for further development of the membrane performances in the removal of heavy metals.

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Keywords Heavy metals · Fouling resistance · Membrane adsorbers · Modelling · Phase inversion

6.1 Introduction

Water is the source of life. Although it has been constantly supplied by the Earth since ancient times, a substantial decrease in water quality is faced across the globe nowadays. Around 780 million people worldwide suffer from accessing drinking water resources (WHO 2014). This water shortage problem has been caused by rapid population growth and intense industrial activity that result in the contamination of wastewater with organic pollutants and a large numbers of heavy metals. Heavy metals are toxic and carcinogenic and mostly found in poorly treated processed water of various industries including mining, plating, metal finishing, battery, paint, textile, leather, pesticide, and chemical (Jaishankar et al. 2014; Singh et al. 2011). Their nonbiodegradability and strong affinities to anionic species cause to continuously accumulate in the aquatic environment, hence, impairing the ecosystem health. Heavy metals intact for a long time in the environment ultimately reach to animals and people via the food chain, drinking water, and air and accumulate in the body by air and water or directly through the skin (Jan et al. 2015; Tchounwou et al. 2012; Mohammed et al. 2011). Due to severe health effects upon this accumulation, health authorities worldwide have adopted regulations on permissible limits to heavy metal effluent. Effects of heavy metals on human health and maximum exposure limits are listed in Table 6.1.

In order to prevent or minimize effects of heavy metals, wastewater treatment processes should be utilized which are enforced by stringent governmental

Table 6.1 Health consequences of some heavy metals with their maximum permissible level in water (Babel and Kurniawa 2003)

Heavy metals	Health effects	Maximum permissible level (μg/L)
Arsenic	Skin manifestations, gastrointestinal problems, visceral cancers, vascular problems	50
Cadmium	Renal failure, human carcinogen	10
Chromium	Headache, vomiting, diarrhea, nausea	50
Copper	Liver damage, Wilson's disease, insomnia	250
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	200
Zinc	Neurological signs, depression, increased thirst and lethargy	800
Lead	Diseases of the fetal brain, kidneys, nervous and circulatory systems	6
Mercury	Arthritic disease and kidney, circulatory, and nervous system damages	0.03

regulations. For this reason, thousands of wastewater treatment plants are established annually around the world, and physical, chemical, or biological processes including solvent extraction, chemical precipitation, coagulation/flocculation, electrochemical treatment, ion exchange, membrane filtration, and adsorption (Azimi et al. 2017; Duruibe et al. 2007; Carolin et al. 2017; Gunatilake 2015; Barakat 2011; Hashim et al. 2011; Hegazi 2013) are applied to remove these pollutants. However, since each heavy metal has its unique nature, usually a sequence of several removal processes should be performed for effective treatment (Fu and Wang 2011). Furthermore, conventional techniques such as electrochemical treatments require capital investments and power input that make them less desired. On the other side, chemical processes such as precipitation, coagulation, and ion exchange include usage of large amount of chemicals that can cause pollution in the processed water (Azimi et al. 2017). Furthermore, biological processes still require further research and are time-consuming (Carolin et al. 2017). Table 6.2 summarizes the advantages and disadvantages of different methods used for the recovery of heavy metals from contaminated waters.

Recent methods of heavy metal removal have shifted into adsorption-based processes as they satisfy flexibility in design and operation (Qdais and Moussa 2004). These processes are known as reversible processes, in which the adsorbents can be efficiently used multiple times, as they can be regenerated by suitable desorption processes (Hua et al. 2012). Adsorption-based studies mainly focus on the economy, environment, and efficiency of the processes; therefore, developing low-cost adsorbent with high affinity and regeneration capability under mild conditions is a challenge since it can meet alone all the requirements above. Recently, technical feasibilities of several low-cost adsorbents obtained from natural materials, agricultural and biological wastes, industrial by-products, biopolymers, and hydrogels have been explored for the treatment of heavy metal-containing wastewater and extensively reviewed in the literature (Khulbe and Matsuura 2018). On the other hand, among the existing ones, metal oxide nanoparticles, such as titanium oxides,

Table 6.2 Advantages/disadvantages of several processes available for the treatment of heavy metal-containing wastewater (Carolin et al. 2017)

Methods	Advantages	Disadvantages
Coagulation	Simple and cost-effective	Toxic sludge
Adsorption	Easy to operate, reusable, and low-cost adsorbent	Desorption
Membrane filtration	High rejection, lower space requirement, no chemical usage	High investment and operational cost, membrane fouling
Electrodialysis	High segregation of metals	Clogging, energy loss
Ion exchange	High transformation of components	Affinity to limited metal ions
Photocatalysis	Eliminates both metal ions and organic contaminants simultaneously	Requires prolonged time
Biological treatment	Beneficial	Stability problem under variable conditions
Oxidation	Does not need electricity	Rusting

aluminum oxides, ferric oxides, magnesium oxides, cerium oxides, and graphene oxides, and zeolites are classified as promising adsorbents for the removal of heavy metals from aqueous media (Vanbenschoten et al. 1994; Coston et al. 1995; Agrawal and Sahu 2006). This is partly due to the high surface-to-volume ratio, which significantly reduces the diffusion path and thus leads to high uptakes (Henglein 1989). However, as the size lowers to nanoscale, the increased surface energy leads to nanoparticles prone to agglomerate through physical interactions (e.g., van der Waals forces) (Pradeep and Anshup 2009), and hence high uptake and selectivity of metal oxide nanoparticles would pronouncedly reduce or even lost. Besides, metal oxide nanoparticles are not useful in fixed bed or any other dynamic systems due to the extremely high-pressure drop. In the case of simple batch adsorption processes, their separations from aqueous phase are another challenge. It is proposed that the applicability of metal oxide nanoparticles in real wastewater treatments can be effectively improved by impregnation into porous supports of large size as composite adsorbents (Pan et al. 2009).

Nowadays, membrane technologies have been successfully used in the applications of wastewater. For example, rejection of 98% of initial cadmium cations using asymmetric polysulfone membrane has been reported (Saljoughi and Mousavi 2012). However, in real wastewater treatment, the concentrated metals cannot be recovered by these treatments. Further processing is needed to be separated from other contaminating species (organics and/or inorganics) available in the feed solution. Therefore, a new engineered high-performance membrane architecture is required for the next-generation reusable and portable water treatments. For this, polymeric materials combined with inorganic nanoparticles have recently been designed for specific water treatments (Yin and Deng 2015). Desired outputs by the so-called membrane adsorbers could be achieved by simply adjusting their hydrophilicity, charge density, pore size, porosity, and mechanical stability. For example, dispersion of zeolite 4A to the selective layer of the polysulfone membrane helps both water flux and rejection values were simultaneously improved (Liu et al. 2014). Moreover, unique properties of nanoparticles such as photocatalytic, antibacterial, or adsorptive capabilities create a multifunctional membrane (Fathizadeh et al. 2011; Huang et al. 2012; Oh et al. 2009; Arthanareeswaran et al. 2008; Han et al. 2009).

In this chapter, membrane adsorbers (they represent inorganic nanoparticles mixed with polymeric membranes), which combine filtration and adsorption processes in one unit, are introduced in terms of their efficiencies on permeability, antifouling, and heavy metal recovery. Selection of nanoparticle type, size, and amount on the morphological properties of the membranes is also addressed in this chapter. Development of a mathematical model that can predict the long-term performances of any flat sheet and hollow fiber-based membrane adsorbers in terms of their throughput and rejection characteristics is discussed. A model for the prediction of time-derived permeate concentrations through a flat sheet membrane in dead-end mode is developed to better understand the effect of membrane morphologies and operating conditions on the process effectiveness. Finally, suggestions are also given for further development of the membrane performances in the removal of heavy metals.

6.2 Membrane Fabrication

Membrane technology provides a reliable and efficient separation through a range of membrane materials (polymeric, e.g., polysulfone, polyethersulfone, polyamide, polyvinylidene difluoride; ceramic, e.g., alumina, silica, titania; and metallic, e.g., silver, palladium) and pore sizes (reverse osmosis, nanofiltration, ultrafiltration, and microfiltration) (Yasuda and Tsai 1974; Meng et al. 2009; Pendergast and Hoek 2011; Hofs et al. 2011). Polymeric membranes have been mostly preferred due to their relatively low costs, wide ranges of pore sizes, flexibilities in configuration, and easy scalability. Functional nanomaterial inclusion into membranes is believed to overcome the natural limitations between permeability and selectivities of the membrane, reduce the membrane fouling, and provide adsorptivity. However, during material development, care must be taken to balance between the potential defect formation in the membrane and improved properties ensured by the embedded nanomaterial in order to derive positive benefits without compromising the integrity of these composites.

Synthesis of membrane adsorbers is similar to regular polymer membrane fabrication. Two procedures are more appropriate for dispersing inorganic nanoparticles in the suspension: first, dispersion of nanoparticles in the solvent followed by the addition of polymer, and, second, preparation of polymer solution and nanoparticle suspension separately followed by the addition of latter into the former (Lin et al. 2018; Cong et al. 2007). Those two techniques form low viscosity of the initial filler/solvent suspension; hence, particle agglomerations can be precluded by high shear rate during mixing. The synthesizing of a membrane and its application is schematically illustrated in Fig. 6.1. Phase inversion (Guillen et al. 2011), stretching (Tabatabaei et al. 2009), track-etching (Lalia et al. 2013), and electrospinning (Teo and Ramakrishna 2009) are the commonly preferred techniques used to prepare

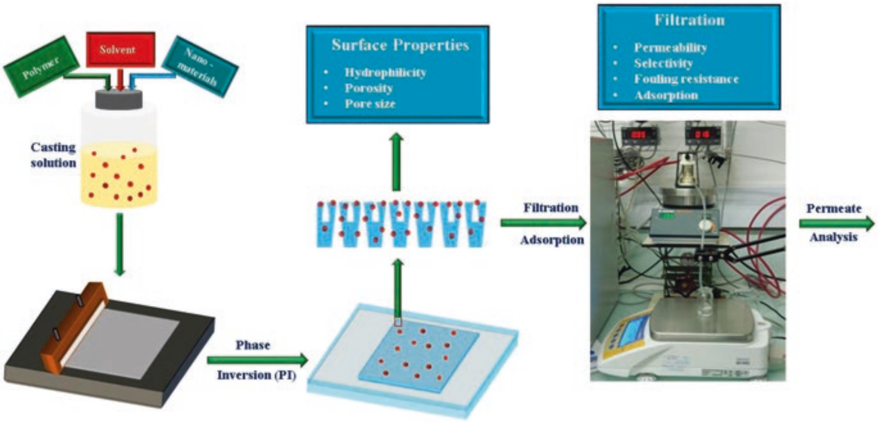

Fig. 6.1 A typical fabrication procedure of membrane adsorbers and their testings under dynamic conditions

membranes from a given material. Among them, phase inversion is the most extensively applied method due to its simplicity and flexibility (Han and Bhattacharyya 1994).

6.2.1 Phase Inversion

Phase inversion by immersion and precipitation method, a generic name of nonsolvent-induced phase separation relies on the variation in the stability of the casting solution during mass exchange of solvent and nonsolvent, occurred at the polymer water interface (Luccio et al. 2002). Depending on the mass exchange rate, an asymmetric structure consisting of a dense and a thin top layer, a porous sublayer with finger-like structure, and a sponge-like bottom layer can be accomplished at the end of the nonsolvent-induced phase separation. Obtaining an asymmetric structure is important since it provides less resistance to flow and hence high water flux. The important aspects in this process include solvent–nonsolvent system selection, polymer and coagulation bath composition, and casting conditions. Early history of the method relies on ternary phase diagrams that can be used to analyze thermodynamic aspects of the three components in the system and demixing which affects the structure of the resulting membrane (Fig. 6.2) (Guillen et al. 2011). The three components in the system (polymer, solvent, and nonsolvent) are represented in the corners of the triangle and indicate a different composition made of a mixture of the components at any point on the diagram. In the diagram, the system is composed of a single-phase and a two-phase region. The former contains miscibility of three components, while the solution is segregated to two phases, i.e., polymer-rich and polymer-poor phases in the two-phase region. Tie lines represent equilibrium compositions and the binodal line represents liquid–liquid phase boundary. The solution within the binodal curve segregates to two phases with different composition but in equilibrium with each other whose compositions are represented by a tie line. After submerging the casting solution into a nonsolvent bath (t < 1 s), the composition

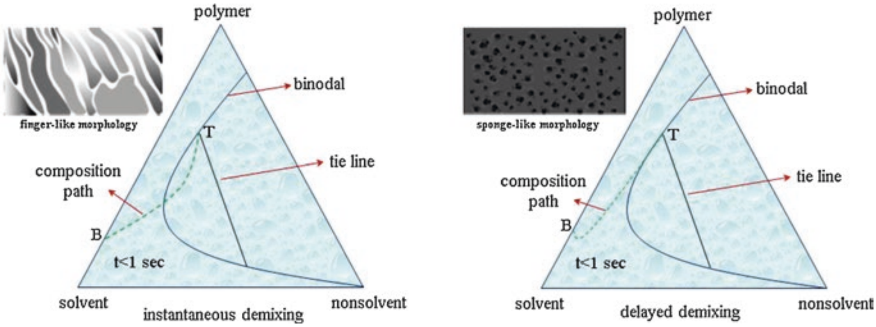

Fig. 6.2 Illustration of the mechanisms of the membrane formation immediately after immersion (t < 1 s): (**a**) fast and (**b**) slow demixing; T and B refer to top and bottom of the film, respectively

path crosses the binodal line, in which demixing occurs instantaneously (Fig. 6.2a). On the other hand, the compositions just below the top layer shown in Fig. 6.2b stay in the region of one phase and are still miscible reflecting no demixing occurred immediately after immersion. Demixing, in this case, will start after a long time period when the compositions beneath the top layer will cross the binodal line. Those two distinct demixing processes will give membranes with completely different morphologies (Strathmann et al. 1975). Demixing rate measured as the time difference between immersion of the casted solution into coagulation bath and that solution turns to opaque determines the ultimate structure of the membrane. Strathmann reported that slow demixing rates form sponge-like membrane morphologies, while instantaneous precipitation rates produce large finger-like voids extended across the membrane thickness as illustrated insets in Fig. 6.2. Low water fluxes and high salt rejections when tested as reverse osmosis membranes are the characteristics of the former case and vice-versa for the latter case. Consequently, the structure of a membrane can be tailored through variation of polymer types and additives (i.e., pore former, inorganic nanoparticles), their concentrations, and temperature and content (nonsolvents or their mixtures with different miscibilities) of the coagulation bath.

Recently, a few new works on the development of membrane adsorbers have been reported in literature. For example, Yurekli has prepared polysulfone ultrafiltration membranes impregnated with different amount of NaX nanoparticles (Yurekli 2016). The author calculated the change in membrane pore radius as a function of NaX loading by filtration velocity method using scanning electron microscopy analysis, porosity, and filtration results. Pore radius of the membrane was reported to increase from 10 to 18 nm when the NaX loading was 10% w/w of the casting solution. The large increment in the pore size was explained by the instantaneous precipitation and agglomerations of nanoparticles occurred during phase separation. However, rejection of bovine serum albumin was not significantly affected when compared to the neat polysulfone membrane reported in that study. In the study of Rahimpour et al. (2012), functionalized multi-walled carbon nanotube-incorporated polyethersulfone membranes have been prepared via nonsolvent-induced phase separation method. Raising the content of functionalized multi-walled carbon nanotubes to 1 wt.% has been reported to improve the membranes' pore size, porosity, and surface roughness.. Besides, incorporation of functionalized multi-walled carbon nanotubes into the casting solution enhanced the bovine serum albumin rejection of the polyethersulfone membrane. Several studies consisting of polymers such as polyvinylidene difluoride, polyamide, polyethersulfone, and polysulfone blended with nanoparticles, including ZnO, Al_2O_3, TiO_2, graphene oxide, silica, zeolite, multi-walled carbon nanotubes, SiO_2–graphene oxide nanohybrid, and TiO_2-coated multi-walled carbon nanotubes, have been summarized by Esfahania et al. (2019) in terms of their functions on morphologies, hydrophilicities, and water permeabilities of the composite membranes.

6.3 Effect of Nanoparticles on Water Permeability

The inherent properties of the added nanoparticles could be utilized to overcome the limitations of polymeric membrane trade-off between selectivity and permeability. The opposite behavior of the permeability and selectivity is a well-known phenomenon of polymeric membranes. Incorporation of hydrophilic nanoparticles into a membrane or depositing them on a membrane surface as a separate thin layer (thin film nanocomposite) has brought a new perspective to the transport properties of membranes. Nanoparticles show a considerable effect on the flux improvement. Because it is well agreed that accumulation of hydrophilic nanoparticles occurs preferentially at the membrane water interface due to the nonsolvent-induced phase separation process that involves a large gradient in water concentration. For example, membranes prepared by the incorporations of finely dispersed metal oxide nanoparticles for a wide range of applications including ultrafiltration (Bottino et al. 2001), nanofiltration, desalination, and water and wastewater treatment (Ng et al. 2013) enhanced the membrane properties in terms of water flux.

Generally, membrane water permeability depends on the porosity, surface pore size, pore interconnection, hydrophilicity, and skin thickness of the membrane. Incorporation of nanoparticles characterized by their unique properties such as small size, large surface area, high reactivity, hydrophilicity, and a large number of active sites greatly alters the resultant membrane properties with regard to their morphology and surface properties. Nanoparticles randomly distributed in a polymer matrix restricts the mobility and spreading of the polymer chains and eventually increases the average distance between the polymer chains, thereby causing an enhancement in membrane permeability. It is well known that during immersion precipitation, the presence of nanoparticles decreases the thermodynamic stability of the polymer solution, which results in a rapid liquid–liquid demixing with more porous structures across the membrane thickness. Furthermore, they act as nucleating agents giving rise to nucleation growth rate during the phase inversion process. The composition of the system crosses from one phase to two, upon addition of these nanoparticles. Microvoids formed by the interfacial stresses and defects between the two phases increase the pore connectivity in the bottom and sublayer (Zhang et al. 2013a, b). These fingerlike microvoids elongate across the sublayer by the addition of nanoparticles and gradually turn into spherical macrovoids, which could be suppressed at the maximum concentration of nanoparticles. At this point, viscosity is increased drastically causing to migrate nanoparticles difficult, and they settle in the bottom layer. This is the reverse of the polymer shrinkage during the demixing process (Rahimpour et al. 2012). In the case of a slow precipitation process, the polymer-rich phase occurs at the polymer-water interface, and the resultant membrane is denser at the top layer and less porous and has less finger-like macrovoids in the sublayer.

In the study of Ganpat et al. (2012), the effect of nanoparticles on the ultrafiltration membrane pore characteristics has been discussed by dispersing zeolite nanoparticles from 0.01 to 1 wt% in N-methyl pyrrolidone with additive D-α-tocopheryl polyethylene glycol succinate to prepare a nanocomposite of polysulfone/zeolite hollow fiber membrane. They found an increase in water permeability from 15.92 to 21.31 mL/m^2.h.mmHg when the amount of zeolite nanoparticles was increased from 0.01 to 0.05 wt%. Further increase of zeolite loading decreased the water permeability. However, the molecular weight cutoff of the composite membrane showed a steady increase from 9500 to 54,000 Da. with the increase in loading concentration. Those behaviors have been explained by the authors based on the variations of the number of pores and pore sizes, which are directly related to the zeolite nanoparticle loadings. The mechanism of the membrane formation during the phase inversion process has been discussed in detail and schematically illustrated in Fig. 6.3. Accordingly, polysulfone chains cluster around zeolite nanoparticles to reduce the unfavorable interactions created by an immediate precipitation

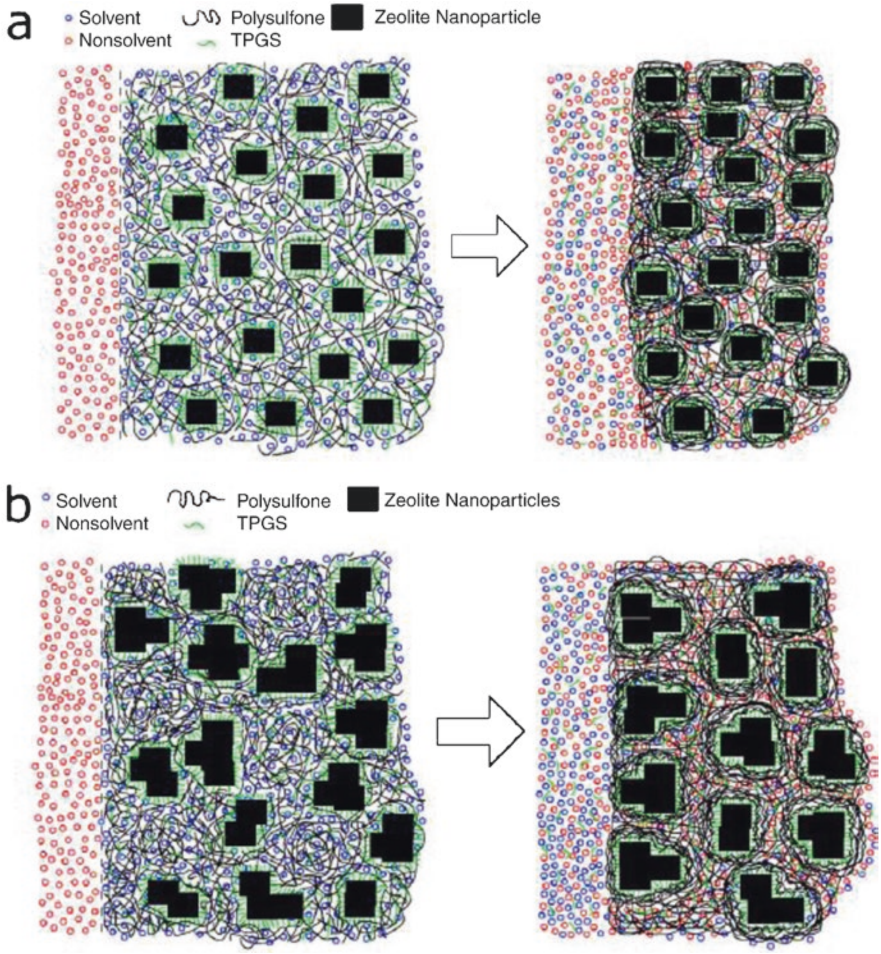

Fig. 6.3 Microstructural view of the proposed mechanism: (**a**) uniform suspension of zeolite nanoparticles ensures formation of small-sized nodules and pores, and (**b**) zeolite aggregates lead to large-sized nodules and pores with a low pore density. (Reprinted with permission of [Elsevier] from Ganpat et al. 2012)

through the thickness of the casting solution. These clusters also called as nodules are then interconnected together by entanglement because of the shared polysulfone chains. The pore sizes given for the composite membrane correspond to the apertures between nodules. A membrane skin consisting of a packed nodular morphology and a large number of pores at 0.05 wt% loading is responsible for the high flux, while upon further addition of zeolite, the membrane permeability reduces, because of the decrease in the number of pores which occurs due to the agglomeration of particles, causing to enlarge nodule size. Nucleating and growth increases with the amounts of zeolite leading to pore size significantly enlarged. The pore dimension and the number of pores which are directly related to the permeability and molecular weight cutoff of a membrane can be precisely tuned by the nature of zeolite suspension. Suspension with a well-dispersed zeolite nanoparticle produces a large number of small nodules and pores, while zeolite aggregates form a less pore density as a consequence of large-sized nodules.

In general, water permeability is predominantly dependent on surface hydrophilicity of the membrane. Thus, hydrophilic nanoparticles located on the membrane surface are mostly desired. On the other hand, recent observations have shown that the hydrophilic nanoparticles with high surface free energy preferably migrate to the polymer water interface during immersion precipitation process. Then, they hydrolyze forming surface hydroxides. The resultant membrane contributes to the passage of water and hence improves water flux. Deposition of TiO_2 nanoparticles onto a membrane surface, in this case, can be given as an example providing the binding of surface hydroxyl groups that are polar when initiated with UV light. The final surface structure demonstrated strong interaction with water molecule through hydrogen bonding and van der Waals forces (Qiu et al. 2009). This useful property of surface-adsorbed water layer enables the membrane with substantially high permeability. In another study, Lakhotia et al. (2019) prepared a thin film nanocomposite membrane by dispersing FeO nanoparticles on the surface of the composite. With the increase in surface density, the hydrophilicity (contact angle 85–50°), surface charge (−6.3 to −14.2 mC/m^2), flux (28–37 $L/m^2.h$), and salt rejection (>90%) of the nanocomposite membranes were significantly improved. A membrane without FeO nanoparticle, on the other hand, rejected salt lower than 65%.

Basically, nanoparticles are preferred to be located on membrane surface by coating or beneath the selective layer by impregnation. However, the former leads to pore narrowing or plugging on the membrane surface and release of nanoparticles from the matrix due to superficial binding (Gholami et al. 2017; Bottino et al. 2002). Particle aggregation and hence the formation of larger pore sizes in the selective layer due to changes in both kinetics and thermodynamics of the phase inversion process especially for the excessive loadings are the challenging issues for the latter case. Those property changes adversely affect the membrane permeability and selectivity. In addition, release of nanoparticles under operation is still valid if the interactions between nanoparticles and matrix are weak. In literature, the use of various sizes, concentrations, and types of nanoparticles and different surface modification strategies has been employed by the researchers for the reduction of agglomeration and improvement of homogenous dispersivity, stability, and nanoparticle–polymer interactions (Méricq et al. 2015; Yang et al. 2007; Vatanpour et al. 2012; Fu et al. 2008). In the study of Ayyaru and Ahn (2018), polyethersulfone nanocomposite membranes blended with surface-modified TiO_2 nanoparticles (anatase, 20–25 nm in size) have been fabricated via phase inversion method for the improvement of the hydrophilicity and surface charge and reduction of agglomeration at the same time. The TiO_2 nanoparticles were sulfonated by replacing the surface hydroxyl groups with $–SO_3H$ group, and the loading effect was investigated. The modified membranes were reported as exhibiting notable enhancement in surface roughness, porosity, and pore size compared to the polyethersulfone membrane. The addition of 1 wt% sulfonated or nonsulfonated TiO_2 nanoparticles into polyethersulfone membrane showed remarkable increase in water flux (102% and 63%, respectively). The same group has also investigated sulfonated graphene oxide nanoparticles blended with polyvinylidene difluoride membranes (Ayyaru and Ahn 2017). Nanocomposite membranes via nonsolvent-induced phase separation process have been prepared by distributing sulfonated graphene oxide nanoparticles in different concentrations (0.4–1.2 wt%). It was reported that improvement of polyvinylidene difluoride membrane properties including pore dimensions, surface roughnesses, and porosities was attributed to the addition of sulfonated graphene oxide. Maximum water permeability attained at 0.8 wt% of sulfonated graphene oxide addition was reported as 146% higher than the neat polyvinylidene difluoride. The enhancement of the water flux has been explained by the improved charge density due to the availability of extra sulfonic groups on sulfonated graphene oxide supports that can attract more water layer. In addition, the attached $–SO_3H$ group in sulfonated graphene oxide provides stronger hydrogen bonding with respect to –OH/-COOH groups available in native graphene oxide.

6.4 Effect of Nanoparticles on Antifouling

Membrane fouling caused by pore blocking, physical adsorption, and cake formation decreases flux greatly, affects the quality and quantity of products, and shortens the membrane lifetime. Concentration polarization explained by the formation of a relatively high concentration layer at the membrane interface due to retention of solutes is also another phenomenon. All the resistances in series reduce driving force ($\Delta P–\Delta\pi$) at the membrane interface by exerting an osmotic pressure difference, $\Delta\pi$, which increases progressively. Further, foulant concentration on the membrane surface increases as time proceeds and eventually turns into gel. Fouling can be categorized as reversible (directly occurring phenomena) or irreversible (long-term phenomena), and they can be analyzed by flux recovery tests. Accordingly, pure water flux of the virgin membrane (J_{wv}) under constant pressure for a certain time is measured. Then, the foulant solution (e.g., 0.5 g/L and pH 7) is filtered at the same condition. Next, the fouled membrane is washed several times with water, and the water flux of the cleaned membrane is remeasured (J_{wc}). This cycle is repeated many times to observe the operational stability of the membrane. Generally, bovine serum albumin or humic acid is used as a model foulant. Figure 6.4 schematically illustrates the aforementioned scenario. From the filtration results,

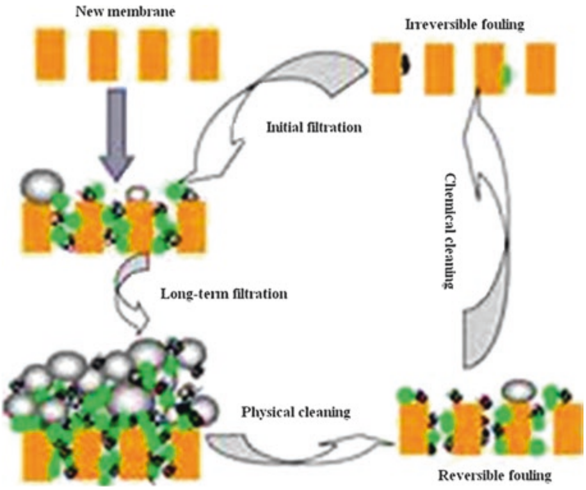

Fig. 6.4 A schematic illustration of fouling scenario and flux recovery protocol

flux recovery ratio (FRR(%)), reversible (R_r(%)), irreversible (R_{ir}(%)), and total (R_t(%)), fouling ratio can be calculated by the following equations to determine antifouling capacity of the membrane (Xu et al. 2018):

$$\text{FRR}(\%) = \frac{J_{wc}}{J_{wv}} \times 100\% \tag{6.1}$$

$$R_r(\%) = \left(\frac{J_{wc} - J_F}{J_{wv}} \right) \times 100\% \tag{6.2}$$

$$R_{ir}(\%) = \left(1 - \frac{J_{wc}}{J_{wv}} \right) \times 100\% \tag{6.3}$$

$$R_t(\%) = \left(\frac{J_{wv} - J_F}{J_{wv}} \right) \times 100\% \tag{6.4}$$

where J_F is the flux of foulant.

One of the main reasons underlying membrane fouling is known as surface roughness. The total local area present for the binding of a foulant species largely increases with a high surface roughness that results in a consequent clogging of the ridge and valley surface structure (Boussu et al. 2006). In addition, high surface roughness protects the foulants from high shear and keeps them near the membrane surface (Basri et al. 2011). Therefore, the membrane with antifouling capability should exhibit a smooth surface. On the other hand, development of a hydrophilic membrane has been commonly acknowledged as a more feasible and appropriate way to address the fouling issue. Hydrophilic surfaces have high affinities to water which might form a thicker layer impeding hydrophobic attractions between the foulant and the membrane surface (Zhou et al. 2014). This means hydrophobic foulants need more energy to approach the membrane surface.

Among diverse surface modification methods, nanoparticle-incorporated membrane offers an effective solution with their inherent properties. In literature, various types of nanoparticles have been developed, characterized, and utilized in membrane materials. Besides hydrophilicity enhancement, TiO_2, ZnO and Ag NPs (Luo et al. 2005; Li et al. 2015; Zhu et al. 2010) provide antibacterial, SiO_2 NPs (Yin et al. 2012) electrical conductivity, carbon nanotubes such as single-walled carbon nanotubes and multi-walled carbon nanotubes (Mendez et al. 2017) and graphene oxide (Hassan et al. 2014) new pathways, Fe and FeO NPs, respectively, (Homayoonfal et al. 2015) catalytic and magnetic properties to membranes. Several studies have shown that antibacterial properties of the membrane could appreciably assist to improved antifouling capacity (Damodar et al. 2009; Sui et al. 2012; Yao et al. 2009). These antibacterial agents present on the membrane surface may prevent the reproduction of bacteria and, in some conditions, destruct the bacteria cell wall (Sawada et al. 2012). Another noteworthy of the inorganic nanoparticles is their photocatalytic properties, which play important roles in degrading the foulants when they are irradiated. This feature has been considered to be a reliable way to minimize membrane fouling (Zhang et al. 2013a, b). Deposition of inorganic nanoparticles on the membrane skin layer has been known to increase surface roughness. In contrast to what is known for surface roughness, it is stated that increase surface roughness could significantly enhance hydrophilicity and hence lower the attractions at the membrane foulant interface (Lu et al. 2006). In addition, removal of contaminants from the membrane surface has been reported to have achieved easily in some studies, which can be attributed to the impacts of shear force and self-cleaning properties provided by the nanoparticles. Based on the observation of Ayyaru and Ahn (2018), even if the surface roughness increased, the addition of surface-modified TiO_2 nanoparticles into polyethersulfone membrane resulted in a higher resistance to fouling as compared to the unmodified TiO_2-incorporated and the original polyethersulfone membranes. This is because of the density of the surface functional groups, in which $sTiO_2$ has much more negative groups than TiO_2 (Ayyaru and Ahn 2018). Schematic diagram of this fouling behavior is indicated in Fig. 6.5.

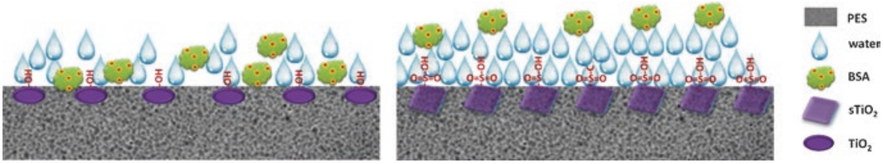

Fig. 6.5 Illustration of the antifouling mechanisms for the TiO_2–PES membrane (left) and $sTiO_2$–PES membrane (right). (Modified after Ayyaru and Ahn 2018)

6.5 Effect of Nanoparticles on Heavy Metal Recovery

Membrane technologies provide superior advantages such as zero sludge production, environmentally friendly, high separation efficiency, and easy scalability. Nanofiltration and reverse osmosis membranes for the removal of heavy metal cations have been attracted more attention. Size repellent and Donnan charge repulsion are the main mechanisms responsible for the separation. Successful treatments of these membranes in wastewater have been reported. For example, 98% rejection of cadmium cations has been accomplished with an asymmetric polyethersulfone membrane (Saljoughi and Mousavi 2012). However, concentrated retentate solutions in these systems include complex chemicals depending on the source of the wastewater; hence, further treatments are generally required. In addition, they need high working pressures but yet have low permeate volume. On the other hand, adsorption provides a simple, easy, and efficient separation process especially when the size of the adsorbent is at nanoscale. However, instability of nano-sized particles, excessive pressure drop in flow-through systems, and tedious posttreatment for recovery of nanoparticles reduce their wide range of applications. Combination of superior adsorption properties of nanoparticles with polymeric membranes that offer dual functionality of adsorbing and filtrating toxic metals simultaneously has opened a new era in the removal of heavy metals. This type of membrane configuration has been practically used in the gas phase operations since 1970 by utilizing the sorption characteristics of the adsorbent which alters the selectivity of the gas mixtures (Zornoza et al. 2011). Their performances in wastewater applications, however, started to be explored after the pioneered work of Ladhe et al. (2009). In their study, polysulfone or cellulose acetate polymer matrix, to the aim of capturing silver ion (Ag^+) from aqueous solution, was incorporated with the functionalized silica particles using 3-mercaptopropyltrimethoxy silane to introduce free thiol groups. The performance of the composite membrane against silver ion capacity was studied as a function of particle size, specific surface area, and porous/nonporous morphology of the silica particles. The authors demonstrated the composite membrane has a high capacity at low operational pressures to capture aqueous phase Ag^+ selectively and also remarked that the concept of composite membrane is a promising platform in the process of heavy metal capture. Current advances in the development of membrane adsorbers for removal of heavy metals in the aqueous environment have been extensively studied by Nasir et al. (2019a, b).

Zeolite nanoparticles are an important class of adsorbent with their well-defined porous structures and cation exchange property that comes from the charge deficiency between $Si^{4+}$and Al^{3+}in the framework. Nano-sized zeolite provides more active sites, high specific surface area, and rapid response, hence increasing the efficiency of the sorption processes. In addition, zeolite nanoparticles offer high selectivity and stability at harsh conditions (wide pH and temperature range), easy regeneration, and multiple reuses preserving almost all initial sorption capacity Yurekli (2019). Yurekli (2016) studied the effect of zeolite nanoparticle loading on the Pb^{2+} and Ni^{2+} removal capability of the polysulfone membrane adsorbers under different initial metal concentrations using dead-end stirred cell. Accordingly, polysulfone membrane had no contribution alone to adsorption, and the sorption almost linearly increased with the addition of zeolite nanoparticles. High sorption capacity reported as 682 and 122 mg/g for Pb^{2+} and Ni^{2+} cations, respectively, was attained for the membrane adsorber at the end of 60 min of filtration, under 1 bar of transmembrane pressure. In another study of Yurekli et al. (2017), the same membrane architecture was used in a cross-flow mode of filtration for the optimization of the working conditions including transmembrane pressure, system temperature, and filtration time. Reusability of the membrane adsorber was first determined in static conditions by one-step desorption approach using NaCl solution. The membrane was exposed to $(\text{adsorption/desorption})_5$ cycles and was reported as preserving of its initial uptake of 77% for Pb^{2+} and 92% for Ni^{2+} as illustrated in Fig. 6.6. The adsorption and desorption percentages for both metals measured through each cycle were added in Fig. 6.6. A significant decline in desorption amounts compared to the initial metal adsorption value has been attributed to the stability of the nanoparticles, such that they could be more stable in the forms of metal (PbX or NiX). According to the nonlinear rational regression model analysis, low values of feed concentrations and pressures in a short time are recommended to work at acceptable permeate concentrations.

In literature, metal oxide nanoparticles such as TiO_2, CeO_2, Al_2O_3, MnO_2, and Fe_2O_3 have been pronouncedly prefer for the removal of heavy metals because of their vast surface area and higher capacity and selectivity (Hua et al. 2012; Ghaemi 2016). Abdullah et al. prepared membrane adsorbers by blending hydrous ferric oxide nanoparticles with polyethersulfone to remove Cr(VI) cations. The effect of hydrous ferric oxide nanoparticle addition (0–1.5 wt%) into polyethersulfone membrane on the physicochemical properties of the resultant hydrous ferric oxide/polyethersulfone membrane adsorbers was studied. Based on the findings in batch adsorption tests, the highest Cr(VI) removal capacity (13.5 mg/g) was obtained when the weight ratio of hydrous ferric oxide/polyethersulfone was 1.0. In the

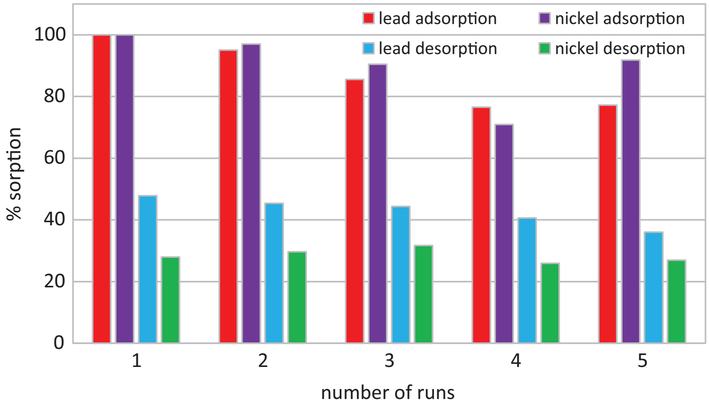

Fig. 6.6 Regeneration capacities of the polysulfone/NaX against Pb^{2+} and Ni^{2+} cations observed in static condition. (Reprinted with permission of [Elsevier] from Yurekli et al. 2017)

dynamic case, hydrous ferric oxide addition enhanced both water flux (629.3 L/m^2.h) and removal efficiency of Cr(VI) cations (75%). More importantly, the authors remarked that the Cr(VI) concentration in permeate maintained below the maximum permissible limit up to 9 h of filtration. In another study, zirconia (ZrO_2) nanoparticles at different contents were used by He et al. for the fabrication of polysulfone hollow fiber nanocomposite membranes (He et al. 2014). The batch adsorption experiments revealed a maximum uptake of As(V) as high as 132 mg/g. The oxygen atoms present in Zr nanoparticles in the form of Zr–O and O–H was reported to be responsible for the As(V) adsorption. The equilibrium sorption capacities of polysulfone/zirconia membranes with different loadings were demonstrated in Fig. 6.7a. Freundlich isotherm model described the data well, and their fits were also included in the same figure. Results in Fig. 6.7b observed during the continuous filtration mode revealed that the first 106 L of permeate content met the requirements for drinking water standards (10 mg/L) proposed by United States Environmental Protection Agency and World Health Organization. The authors reported that during long-term filtration release of zirconia was below the detection limit.

Delavar et al. (2017) introduced titania nanotubes into polycarbonate in order to remove Cd^{2+} cations from synthetic solutions. High rejection of Cd^{2+} (70%) was reported to be attained during the filtration of 120 ppm feed solution with a water flux of 497 L/m^2.h. Zhang et al. (2018) synthesized polyethersulfone membranes incorporated with iron oxide microspheres to investigate their adsorptive capacities against As(V). The maximum uptake has been reported as 278 mg/g with a satisfactorily high water permeability (251 L/m^2.h). It was further confirmed that the adsorptive membrane was capable of treating 2.5 tons of polluted water while still in accordance with the World Health Organization standards for at least three cycles. This could be explained by the tight connection between microspheres and the As(V) ions by the internal spherical complexation.

Graphene oxide, a carbon-based material, has recently been attracted considerable attention in the modification of ultrafiltration membranes due to its oxygen-containing functional groups, extremely high aspect ratio, low density, high strength,

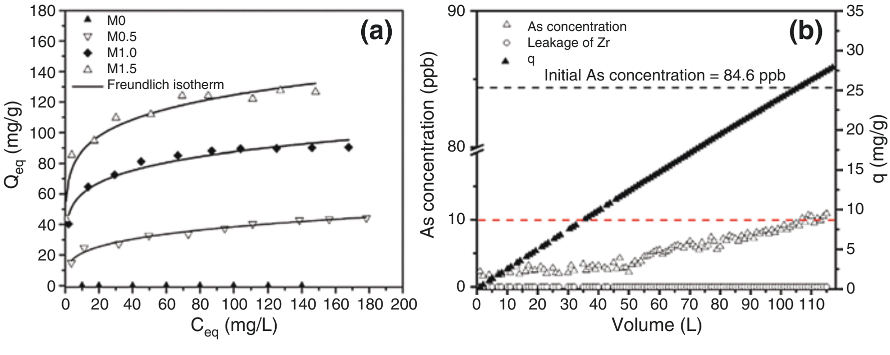

Fig. 6.7 (**a**) Batch isotherm studies and (**b**) continuous filtration of M1.5 PSF/zirconia membrane adsorber. (Reprinted with permission of [Elsevier] from He et al. 2014)

unique graphitized planar structure, and easy surface functionalization (Sangil et al. 2007). These unique properties of graphene oxide were introduced with the polysulfone for the development of highly permeable and adsorptive ultrafiltration membranes (Mukherjee et al. 2016). Different amounts of graphene oxide nanoparticles (dp190 nm.) were mixed with polysulfone, and the ultrafiltration membranes were prepared based on the nonsolvent-induced phase separation process. According to the simple batch adsorption results, the prepared membrane configuration was reported that it had a high sorption capacity as 79, 75, 68, and 154 mg/g for the Pb, Cu, Cd, and Cr cations, respectively, at natural pH. The increase in permeability and adsorptivity by the addition of graphene oxide was attributed to the alteration of properties of the polysulfone membranes such as hydrophilicity, negative charge density, roughness, and pore size. Dynamic studies revealed that 90 and 96% of rejection values with breakthrough times around 10 h were observed for different operating conditions and metal ions. An acidic solution at pH 5.5 was found to be sufficient to regenerate the membrane in situ.

In spite of inorganic nanomaterials alone meeting the desired requirements for adsorption processes, it is believed the use of two or more metal oxides in a composite form exhibits a synergistic effect using the benefits of the distinguished properties of the individuals. For example, adsorption and oxidation properties originated from the individuals in the metal oxide composite would signify synergistic effect during recovery of heavy metals. This approach is especially valuable for the metallic pollutants which are neutral in the wide range of pH. As an example, arsenite (As(III)) available in wastewater in the neutral form in the pH range of 1.0 and 9.22 has higher toxicity and is more dangerous compared to arsenate (As(V)). Nasir et al. (2019a, b) prepared new hydrous iron–nickel–manganese trimetal oxide-embedded PSF hollow fiber membranes for the recovery of As(III). In fact, iron-based composite metal oxides for arsenic removal have already been used because of their superior properties such as environmentally friendly, regenerability, and strong affinity to arsenic. In the case of composite metal oxide architecture, manganese dioxide has a function of oxidation (oxidation agent for arsenite), and positively charged Ni on the surface of hydrous iron–nickel–manganese trimetal oxides could form electrostatic interaction with the negatively charged of the oxidized arsenite. The as-synthesized particle size of the nanocomposite metal oxide was determined by scanning tunneling electron microscopy image and reported in between 34 and 68 nm. The elemental compositions determined as 45.4%, 39.4%, and 15.2% for lead, nickel, and manganese, respectively, from energy dispersive X-ray analysis were similar to the compositions in the synthesis conditions of hydrous iron–nickel–manganese trimetal oxides (3:2:1). Based on 12 h. of batch adsorption studies, the highest arsenite adsorption was achieved (62 mg/g) when the loading of hydrous iron–nickel–manganese trimetal oxides was 1.5 wt% in the PSF. The highest adsorption was explained by the uniform distribution of hydrous iron–nickel–manganese trimetal oxides throughout the cross-section, which was evidenced from energy dispersive X-ray mapping. The uniformity of nanoparticles ensured more active sites which enhanced the rate of adsorption of arsenite. However, the addition of 2.0 wt% hydrous iron–nickel–manganese trimetal oxides caused agglomeration that might block the sorption sites for arsenite. Leaching of the nanoparticles is another important issue as they might be unhealthy for the water body and alter the membrane stability. In the same study, it was reported that the as-synthesized membrane had no leaching of hydrous iron–nickel–manganese trimetal oxide nanoparticles within a wide range of pH (2–14) at the end of 12 h of batch adsorption experiments. Dynamic filtration study revealed that the polysulfone hollow fiber composite membrane could maintain the arsenite level below the maximum allowable concentration of 0.01 mg/L for approximately 3665 mL of filtrated volume, and this membrane configuration could be efficiently used for the treatment of wastewater containing arsenic that has lower concentration of 1.0 mg/L under 0.5 bar.

6.6 Modelling the Performance of the Membrane Adsorber

The primary reason for considerable interest in the application of membrane adsorbers comes from the fact that membrane tailor is made to accomplish high selectivity in a specified separation process. Introducing inorganic nanoparticles with a polymeric matrix increases the membrane selectivity while preserving its high throughput. In the conventional membrane filtration concept, mechanism of the flux decline and rejection are mainly ascribed to the concentration polarization phenomena caused by a reduction in driving force, formation of gel layer, electrokinetic effects, and pore blocking. Conversely, solute adsorption coupled with diffusion and convection in the membrane separation process displays a great significance on the mechanisms of both rejection and the flux profile in the membrane adsorber. Therefore, understanding the details in the mechanisms of the transport processes is important for membrane adsorbers. In addition, membrane adsorber similar to any adsorption-based processes has a definite lifetime, beyond which the concentration of foulant in the filtrate exceeds the allowable limit, known as breakthrough time. Prior to the breakthrough time, the filtrated volume is known as the breakthrough volume. Generally, dead-end modes of filtration with flat sheet membranes are selected in lab-scale applications for forecasting their short-term behaviors. During the transport of solute molecules, model equations were developed for the two limiting cases of adsorption or diffusion dominating at steady-state conditions (Doshi 2011). However, filtration is a dynamic process, in which adsorptive and diffusive processes might be in transient region that covers both of the terms in the model equation. In the case of cross-flow filtration that uses either flat sheet or hollow fiber types of membranes, modelling is required to achieve the proper scaling up in long-term sustainable filtration. This can be accomplished by comprehensive modelling which enables concrete and a reliable forecasting of the long-term characteristics of the filtration unit including fluid flow in lumen side, coupling of velocity and concentration field, transmembrane and osmotic pressures, channel length, and time-dependent permeate flow. Below, a comprehensive unsteady-state two-dimensional model for solute filtration though hollow fiber membrane adsorber, which was developed by Mukherjee et al., by considering the equations of continuity, momentum, and convective+diffusive+adsorptive-based species transport through cylindrical membrane adsorber, is given (Mukherjee et al. 2019).

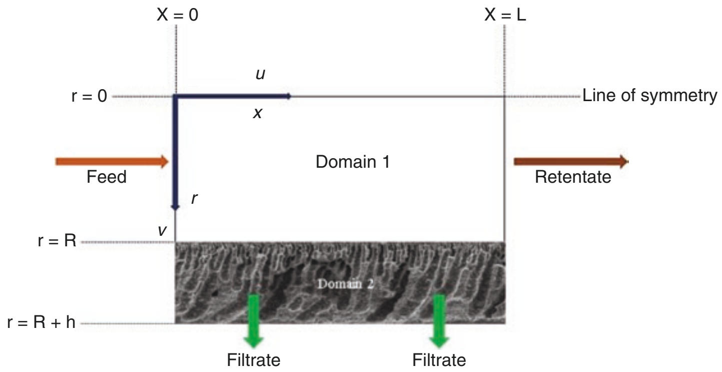

Fig. 6.8 A schematic illustration of the symmetric and cylindrical membrane filtration unit. (Modified after Mukherjee et al. 2019)

In their model, transport equations in flow channel (Domain 1) and in porous media (Domain 2) are related to each other at the membrane solution interface as represented in Fig. 6.8. In Domain 1, velocity and concentration profiles with respect to radial and length dimensions of the fiber are solved in unsteady-state condition ($0 \leq r \leq R;\ 0 \leq x \leq L$), while only the convective+diffusive+adsorptive species continuity equation is solved in Domain 2 ($R \leq r \leq R + h$) considering the Darcy velocity which is a function of only z through the membrane. Symmetry axis through cylindrical coordinate is selected. Mathematical model equations developed for Domain 1 are given below. The continuity equation is

$$\frac{1}{r}\frac{\partial(rv)}{\partial r}+\frac{\partial u}{\partial x}=0 \tag{6.5}$$

r-component of Navier–Stokes equation for an incompressible fluid ignoring the $\frac{\partial^2 v}{\partial z^2}$ term as the radial dimension is too small with respect to fiber length,

$$\rho\left(\frac{\partial v}{\partial t}+v\frac{\partial v}{\partial r}+u\frac{\partial v}{\partial x}\right)=-\frac{\partial p}{\partial r}+\mu\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial v}{\partial r}\right)\right]-\frac{v}{r^2} \tag{6.6}$$

Similarly, the z-component is

$$\rho\left(\frac{\partial u}{\partial t}+v\frac{\partial u}{\partial r}+u\frac{\partial u}{\partial x}\right)=-\frac{\partial p}{\partial x}+\mu\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u}{\partial r}\right)\right] \tag{6.7}$$

As shown in Eqs. 6.5–6.7, u, v, and p are the functions of r, z, and t. The appropriate boundary and initial conditions for those three equations are as follows:

(i) at $r = 0$, for all z: from symmetry, $\frac{\partial u}{\partial r}=\frac{\partial v}{\partial r}=\frac{\partial p}{\partial r}=0$

(ii) at $r = R$, for all z: $u = 0$ and $v = v_w(x)$ (coupling with Darcy velocity in Domain 2)
(iii) $x = 0$ for all r (at the entrance of the channel): $v = 0$ and $u = u_0$
(iv) at $z = L$: $p = p_{atm}$ – it is necessary to solve $p(r,x)$
(v) initially, $t = 0$: $u = v = 0$

Mean velocity, u_0, can be calculated by dividing volumetric flow rate, V, to the cross-sectional area ($A = n_f \pi R^2$), where n_f is fiber numbers in the module.

The species continuity equation eliminating the second-order term in z can be simplified as

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial r} + u\frac{\partial c}{\partial x} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right)\right] \tag{6.8}$$

The initial and boundary conditions required for the solution of Eq. 6.8 are as follows:

(i) at $t = 0$: $c = c_0$
(ii) at $r = 0$: $\dfrac{\partial c}{\partial r} = 0$
(iii) at r = R: $v_w c\big|_{r=R^+} = v_w c\big|_{r=R^-} - D\dfrac{\partial c}{\partial r}$
(iv) at $z = 0$: $c = c_0$ for all r

The model equations for Domain 2 (in the porous media, $R \le r \le R + h$) are proposed as follows: Darcy velocity with the assumptions that the fiber thickness, h, is too small with respect to inner radius and flow is only a function of r can be written as follows:

$$v_w = \frac{1}{\mu\left(R_m + R_{ad}\right)}\left[\Delta P - \Delta\pi\right] \tag{6.9}$$

where transmembrane pressure $\Delta P = P_{r=R} - P_{atm}$, osmotic pressure $\Delta\pi = \gamma(c_{r=R} - c_{r=R+h})$, and adsorption resistance $R_{ad} = \alpha_1 q_{avg}^{\alpha_2}$. The average adsorption capacity $q_{avg} = \frac{1}{h}\int_{R+h}^{R} q dr$. Finally, the species convective+diffusive+adsorptive continuity equation can be written as follows:

$$\varphi\frac{\partial c}{\partial t} + v_w\frac{\partial c}{\partial r} = \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) - \rho_m\frac{\partial q}{\partial t} \tag{6.10}$$

where φ, q, and D are the membrane porosity, the adsorbed amount by the solid phase, and the diffusion coefficient of the contaminating species through the membrane adsorber, respectively. q can be obtained from adsorption kinetics with the expression below:

$$\frac{\partial q}{\partial t} = k_{ads} c\left(q_{\max} - q\right) - k_{des} q \tag{6.11}$$

where k_{ads}, k_{des}, and q_{max} are the adsorption and desorption rate constants and maximum uptake, respectively. At equilibrium, Eq. 6.11 simplifies Langmuir isotherm model, expressed as

$$q_e = \frac{k_0 q_{\max} c_e}{1 + k_0 c_e} \tag{6.12}$$

where $k_0 = k_{ads}/k_{des}$.

Diffusion coefficient of solute in the composite membrane can be calculated by the following expression:

$$D = \varphi \varnothing_i K_{i,D} D_{i,\infty} \tag{6.13}$$

where membrane porosity $\varphi = (w_w - w_p)/(A \bullet l \bullet \rho_w)$, partition coefficient $\varnothing_i = (1 - \lambda_i)$, and the solute diffusive hindrance $K_{i,D}$ factor is dependent on the ratio of the particle diameter of the solute to the pore size of the membrane ($\lambda_i = d_{i,s}/d_p$). Based on the assumption of parabolic fully developed species flow through the membrane pores, $K_{i,D}$ can be identified as $K_{i,D} = 1.0 - 2.30\lambda_i + 1.154\lambda_i^2 + 0.224\lambda_i^3$. Membrane pore diameter is obtained from filtration velocity method, $d_p = \sqrt{\frac{\left(2.9 - 1.75\varphi\right) \cdot 32 \mu l V}{\varphi \cdot A \cdot \Delta P}}$, and finally the solute free diffusion in aqueous solution can be predicted by Wilke–Chang equation: $D_{i,\infty} = \frac{117.3 \cdot 10^{-18} \left(\varepsilon M_w\right)^{1/2} T}{\mu \vartheta_A^{0.6}}$.

Equation 6.10 can be solved by the following initial and boundary conditions:

(i) at $t = 0$: $c = q = 0$

(ii) at $r = R$: $v_w c\big|_{r=R^+} = v_w c\big|_{r=R^-} - D\frac{\partial c}{\partial r}$

(iii) at $r = R + h$: $\frac{\partial c}{\partial r} = 0$

In summary, the model equations consist of five functions (u, v, p, c, and q), each of which depends on r, x, and t. After nondimensionalized, finite element method can be utilized by solving the set of governing equations. Mukherjee et al. first correlated the model equations with the long-term experimental data from the filtration of aqueous chromium (VI) solution; then, the predictive capability of the model was tested in terms of flux and rejection characteristics of Cr(VI) with the filtration data obtained by real-life chrome tanning effluent (Mukherjee et al. 2019). Finally, the validated model was further extended to simulate a large-scale filter with high-throughput volume interrelating number and length of fibers with the operating conditions. The mathematical model equations above can be used for design and scale up of any hollow fiber membrane adsorber-based filtration systems.

Model equations in the case of dead-end mode of filtration through a flat sheet membrane with a constant volume of feed side (diafiltration mode) can be developed by the differential mass balance of the contaminating species as follows:

$$\varphi \frac{\partial c}{\partial t} + \varphi v_w \frac{\partial c}{\partial x} = \varphi D \frac{\partial^2 c}{\partial x^2} - \left(1-\varphi\right)\frac{\partial c_s}{\partial t} \tag{6.14}$$

where c_s, kmol/m^3 is the concentration of solute adsorbed on the solid phase. Equation 6.14 is the expression of Eq. 6.10 in rectangular coordinate system. The first term on the left side is the time derivation of the solute concentration in bulk phase, and the second one defines the axial convective flux. The solute diffusive component and the solute adsorption/desorption onto porous surface of the solid phase with respect to time are corresponded to the first and the second terms of the right-hand side of the expression. The initial and boundary conditions can be expressed as

$$\text{at}\, t = 0\, \text{and}\, x \geq 0, c = 0$$

$$\text{at}\, t = 0\, \text{and}\, x \geq 0, c_s = 0$$

$$\text{at}\, t > 0\, \text{and}\, x = 0, \left(K_{i,C} v_w c - \varphi K_{i,D} D \frac{\partial c}{\partial x} \right)\Bigg|_{x=0} = k_f A \left(c - c_{f,i} \right)\Big|_{x=0}$$

$$\text{at}\, t > 0\, \text{and}\, x = L, \left(K_{i,C} v_w c - \varphi K_{i,D} D \frac{\partial c}{\partial x} \right)\Bigg|_{x=L} = k_p A \left(c_{p,i} - c \right)\Big|_{x=L}$$

where $K_{i,c}$, k_f, and k_p are solute convective hindrance factor, feed side, and permeate side mass transfer coefficients, respectively, and they can be estimated by the following equations:

$$K_{i,C} = \left(2 - \varnothing_i\right)\left(1 + 0.054\lambda_i - 0.988\lambda_i^2 + 0.441\lambda_i^3\right)$$

$$\frac{k_f \cdot d_p}{2 \cdot D_{i,\infty}} = \alpha Re^{0.567} Sc^{0.33}$$

$$k_p = \frac{D_{i,\infty}}{\delta_p}$$

where Reynolds number $Re = \dfrac{D_p^2 N \rho_w}{\mu_w}$, Scmidt number $Sc = \dfrac{\mu_w}{\rho_w - D_{i,\infty}}$, and water 2.6 is appropriate for the value of α. In those expressions, D_p, N, and δ_p reflect the impeller diameter, mixing rate as rpm, and boundary layer thickness of the permeate side, respectively (Yurekli and Altinkaya 2011). The model equations include equilibrium and dynamic parameters that can be estimated from experimental run. With those estimated parameters, the model can further be expanded to describe the process with different membrane materials and under different operating conditions.

6.7 Concluding Remarks and Perspectives

Introduction of the membrane adsorbers in the removal of heavy metals in water provides an advanced treatment when compared to the conventional suspension adsorption process. Membrane adsorber is a new class of membrane used in water treatment applications and has been improved in terms of their throughput and rejection characteristics. Single-step contaminant removal, exceptional high flux, and fouling resistance due to hydrophilic properties of nanoparticles are among the advantages of the membrane adsorbers. Size, type, and functionality of the nanoparticles, as well as strong bonding to polymeric matrix, are known as important issues nowadays. Nanocomposite nanoparticles, which bring more than one metal oxide together to utilize their individual characteristics, should be introduced into membrane matrix. Researches have been previously focused on the fabrication of membrane adsorbers in the form of flat sheet membrane. The relatively lower surface area has led the researchers to hollow fiber configuration as it offers a larger surface area for the optimum adsorption process. Much more data should be generated for the evaluation of the model parameters that would then be used safely for predictive purposes.

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Chapter 7

Metal Hexacyanoferrate Absorbents for Heavy Metal Removal

Mario Berrettoni, Angelo Mullaliu, and Marco Giorgetti

Contents

Abstract Alternative energy sources are currently worldwide under development to contribute to the increasing energy demand. Along with the introduction of new technologies, heavy metals, such as radionuclides from nuclear power plant leaks, might be released into the environment and contaminate waters, air, and soil. Among the investigated methods, the use of adsorbents has been proven the most suitable one, able to extensively remove heavy metals, e.g., radioactive $^{137}Cs^+$. Prussian blue analogs (PBAs) have been demonstrated to be effective adsorbents toward the sequestration of a variety of heavy metals, including the recovery and valorization of rare earth elements. Here, we point out the structure-property link of PBAs: the

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large channels and cavities are able to accommodate a variety of ions, ranging from monovalent to multivalent ones, while the ion exchange may be either diffusion-controlled or electrochemically driven. While distribution coefficients are shown to be key parameters in the diffusion driven process, resulting in high affinities of PBAs toward metals such as Cs^+, Tl^+, Cu^{2+}, and Zn^{2+}, electrochemical ion exchange is considered to be promising due to the effectiveness in the removal of metals and the possibility to reversibly restore the adsorbent to its initial state. Related examples concerning the capture of Cs^+ from wastewaters and the recovery of rare earth elements are herein presented and commented.

Keywords Prussian blue analogs · Cesium · Thallium · Ion exchange · Insertion and release · Electrochemically driven ion exchange · Metal removal · Metal sequestration · Metal uptake · Rare earth

7.1 Introduction

During the last decades, the increased request of energy worldwide and concerns over global warming made the nuclear power as a carbon-free energy source contributing to the moderation of global warming. However, the occurrence of nuclear accidents has warned us of the extent of radioactive waste. Several metals and radionuclides such as ^{134}Cs, ^{137}Cs, ^{90}Sr, and ^{131}I have been contaminated the environment due to nuclear energy activities, causing irreversible damage not only to the environment but also to human health (Park et al. 2010; Abdi et al. 2008; Shi and Fernandez-Jimenez 2006). Cesium, with its high solubility and mobility, can easily combine with aquatic and terrestrial organisms. It can be therefore accumulated, through the nutrition, into the human body and eventually placed into tissues (Yasunari et al. 2011). Even nonradioactive cesium can be considered toxic since its chemistry similar to the potassium one favors competition between the two ions in biological interactions, possibly causing hyperirritability and spasms.

Among the methods nowadays used for the removal of radioactive ^{137}Cs from liquid waste, precipitation, coagulation, membrane usage, and electrodialysis occupied a leading position (Iwanade et al. 2012). However, the process of choice for the remediation of ^{137}Cs in contaminated water can be considered the adsorption: it is simple and efficient as is capable of processing large volumes of radioactive liquid. This requires a selection of the potential adsorbent. Silicotitanates (Liu et al. 2015a, b), aluminum molybdophosphate and zeolites (Borai et al. 2009) have been extensively studied so far but their they poor Cs selectivity limits the application.

In this chapter, we highlight the efficacy of materials based on Prussian blue for the large-scale remediation of wastewater due to pollution not only by cesium but also by other metals, including the rare earth recovery and valorization.

7.1.1 Prussian Blue

Prussian blue, named iron hexacyanoferrate, or ferric ferrocyanide and Milori blue, is a mixed valence (Fe^{II} and Fe^{III}) polynuclear blue compound of Fe that was accidentally synthesized in 1704 by a Berlin artist (Ware 2008). The painter, named Diesbach, was preparing a red pigment. Unfortunately, one of the precursor salt was not available in his atelier, and he borrowed some of the alchemist Dippel, and this was found to be the source of the cyanides as the chemicals were contaminated. Its discovery made the pigment suddenly used in painting, flags, stamps, wallpaper, and tea colorant and can be considered the first synthetic coordination compound. Today, Prussian Blue is still used as a pigment, but it also has other applications.

7.1.2 Structure of Prussian Blue

The determination of the Prussian blue crystalline structure was made in the 1936 by Keggin and Miles through X-ray diffraction (Keggin et al 1936). The analysis of the X-ray pattern revealed that Prussian blue consists of a 3D cubic network, where alternating iron species (Fe^{II} and Fe^{III}) are octahedrally coordinated by carbon and nitrogen, respectively, with the cyanide ligand forming bridges. Overall, a three-dimensional network of repeating -Fe^{II}-C-N-Fe^{III}- units was seen. Keggin and Miles also found that each crystallographic unit (unit cell) composes of four cubes with a lattice parameter of about 10 Å. Compared to similar salts, Buser et al. (1977) observed experimentally an unusual low density, a scenario related to the peculiar crystallographic network where the presence of cavities and vacancies favor interesting physico-chemical characteristics.

A precipitate of Prussian blue can be obtained by mixing an hexacyanoferrate (II) salt and a Fe(III) salt, such as ferric chloride $FeCl_3$. Surprisingly, the same product is formed while a solution of a hexacyanoferrate(III) salt is mixed to a solution of a Fe(II) salt, as evidenced by ^{57}Fe Mossbauer (Ito et al. 1968) and neutron diffraction experiments (Herren et al. 1980). The mixed valence nature of Prussian blue was reported to be the cause of those experimental findings, where a metal-metal electron transfer is occurring. Being the electronic transition from Fe^{II} to Fe^{III} (t_{2g} to e_g) in the range of an electronvolt, a strong absorption in the visible spectrum (680–730 nm) is observed (Robin 1962), therefore explaining the intense blue color which in turn is used as pigment.

As reported in Fig. 7.1, Prussian blue structurally exists in two forms, namely, *insoluble* and *soluble*, reported, respectively, as $Fe_4[Fe(CN)_6]_3$ and $KFeFe(CN)_6$. Both are insoluble in water and only partially in moderated alkali solution, and both form colloids but with a different size, thus the name above reported. In the *soluble* Prussian blue structure, alkali metals are accommodated into the channels available in the 3D network, forming very regular cubes. Unlike, the *insoluble* Prussian blue is characterized by $[Fe(CN)_6]^{4-}$ vacancies, which are replaced by water molecules

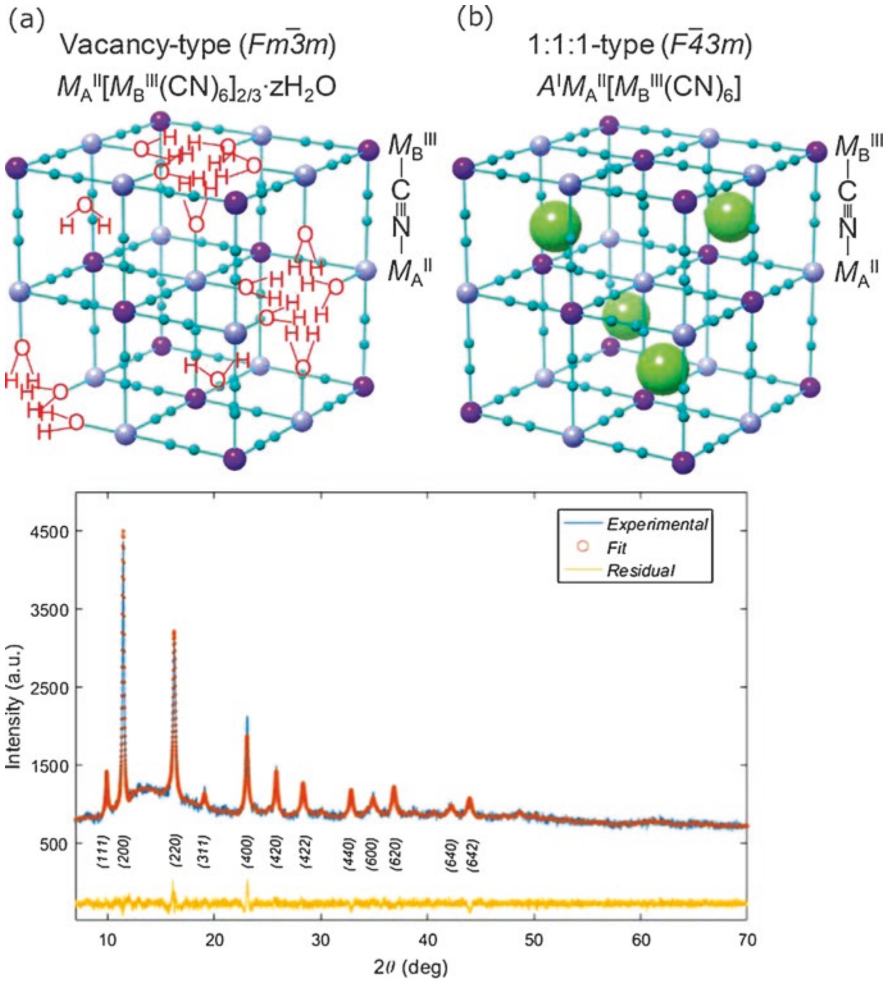

Fig. 7.1 Schematic crystal structures of Prussian blue analogs. (**a**) $M_A^{II}[M_B^{III}(CN)_6]_{2/3}\cdot zH_2O$ and (**b**) $A^IM_A^{II}[M_B^{III}(CN)_6]$. Reprinted with permission of Royal Society of Chemistry Publishing from Tokoro and Ohkoshi (2011). Example of Powder X-Ray Diffraction pattern of a copper hexacyanoferrate material. (Reprinted with permission of American Chemical Society from Mullaliu et al. (2018a, b))

in large extent. In this last structure of Prussian blue, the vacant sites (see Fig. 7.1) can be either randomly (forming a crystal in the 225 space group *Fm-3m*) or systematically distributed (Space group 221 *Pm-3m*) (Buser et al. 1977; Wills 2005). Nevertheless, as evidenced by a synchrotron radiation powder X-ray diffraction study (Bueno et al. 2008), soluble species also display a certain degree of vacancies and therefore the usage of the *soluble* and *insoluble* terminology may perhaps be reconsidered.

7.1.3 Metal Hexacyanoferrates or Prussian Blue Analogs

An extensive research was conducted based on Prussian blue, and therefore a wide variety of Prussian blue analog compounds, fabricated by simply substitution of one of the transition metals, were reported. Due to the strong Fe-C ligation, the easiest structural modification concerns the N-coordinated site of the CN group; therefore its replacement leads to the general class of metal hexacyanoferrate materials. More generally, including the possibility of substituting also the C-end site, the class of materials called Prussian blue analogs or metal hexacyanometallates would be obtained, with general formula $Z_xM_y[B(CN)_6]{\bullet}mH_2O$. In the formula here reported, M and B are transition metals, while x and y stoichiometric coefficients, and Z is an alkali ion. The atom B is iron for metal hexacyanoferrates. Structurally speaking the metal hexacyanometallates feature the same extended and periodic structure of the Prussian blue, i.e., the metal ions are placed in the corners of the cube structure, alternatingly, and cyanide anions act as links between the metals (forming a -B-C-N-M- linear fragment) along the three directions of space. Generally, structures with different concentration of $M(CN)_6^{n-}$ ion vacancies are possible, and thus both images of the Fig. 7.1 still apply for the Prussian blue analogs. The space available as large empty cavities (sometimes called zeolitic cavities) can be occupied by alkali ions, and this is the motivation of their use as sorbents for metals in environmental pollution remediations.

Not all the Prussian blue analogs adopt the cubic structure, but even in the hexagonal lattice (Rodríguez-Hernández et al. 2007), the presence of open channels and cavities ensures the ion-exchange characteristics. Eventually, the -B–CN–M–NC–B– structural moiety can be tuned to define the size and the structure of metal hexacyanoferrates, therefore modulating a series of physicochemical properties described below.

7.1.4 Application of Prussian Blue Analogs, Uses, and Characteristics

The peculiar structure of Prussian blue and Prussian blue analogs coupled with the easy and scalable synthesis procedure has foster an intense research toward multiple applications. The synthesis of the Prussian blue analogs is generally performed in aqueous media by coprecipitation, and controlled temperature (Mullaliu et al. 2018a, b). The obtained precipitate can be easily recovered by filtration. Alternatively, the material can be fabricated by electrochemical routes, in which a conductive substrate of large surface area can be enriched by several suitable functional groups (Mortimer and Rosseinsky 1983; Guadagnini et al. 2010). This device is well usable as electrochemical sensor for a wide variety of analytes.

Neff (1978) first deposited thin films of Prussian blue by electrochemical means, observing an electrochromic behavior of the material: a color change when the material is placed in an electric field, due to a redox reaction occurring at the electrodeposited Prussian blue film. A $K_2FeFe(CN)_6$ phase called Everitt's salt is formed during reduction, while the formation of Berlin green, $K_xFe(Fe^{III\text{-}x}(CN)_6$; $x < 1$, was observed through the cathodic polarization. The alkali ion occupying the cube center site (crystallographic 8c position of the *Fm3m* cubic structure) also played a key role as they are shuffling into and out of the structure. Because they used a potassium salt in their experiment, they provided evidence for a potassium insertion during the positive scan, and subsequent release during the negative step. This example sheds light into two general characteristics of the Prussian blue analogs, (i) the electrochemical activity of the metals; (ii) the flux of alkali metal inside the tridimensional structure. Therefore, Prussian blue and its analogs exploit their analytical features by either performing electrochemical reactions driven by the metal sites (amperometric sensors) or intercalating the suitable analytes (potentiometric sensors). Amperometric sensors were developed for ascorbic acid (Shankaran and Narayanan 1999) dopamine (Zhou et al. 1996) and cysteine (Chen and Chan 2003). Prussian blue films and metal hexacyanoferrates were found suitable for the hydrogen peroxide detection at both reduction and oxidation with activity and selectivity close to those of electrodes based on peroxidases (De Lara González et al. 2007; Karyakin 2001; Guadagnini et al. 2010. Ricci and Palleschi (2005) highlighted the use of Prussian blue analogs as electrochemical sensors, recently. The characteristic of the materials to accommodate several ions in the structure will be exploited in Sect. 7.2.

In addition to the previous applications, Prussian blue analogs have proven to exhibit a photoinduced magnetization. This behavior is closely correlated to the fact that Prussian blue analogs can be considered mixed-valence compounds (Martinez-Garcia 2007) because of the charge transfer involving the two metals. Berrettoni et al. (2010) extended this concept by adopting the $(FeCo)^{\text{ox number}}$ notation and proposing a generalized oxidation state of the metal hexacyanoferrate. A photoinduced magnetization phenomenon was first reported by Sato et al. (1996), by using the cobalt analogs. Basically, by irradiating through red light, a change in spin states of cobalt is experienced. The photoinduced magnetization was therefore studied in the following years becoming common feature in Prussian blue analogs (Champion et al. 2001; Escax et al. 2001), giving novel magnetic functionalities to this class of compounds (Tokoro and Ohkoshi 2011; Bordage et al. 2018). Giorgetti et al. (2015) reported that, besides photo-irradiation, a Co spin transition can be induced by anatase (polymorph of TiO_2) doping as well.

7.1.5 Batteries Based on Prussian Blue

Because of its peculiar structure characterized by a well-defined 3D atomic linear arrangement with open spaces and channels for the alkali metal diffusion, there was an increasing interest in the past few years in developing cathode and anode materials for batteries based on Prussian blue and, in general, on Prussian blue analogs

(Qian et al. 2018). A significant result using a Prussian blue analog as an electrode material for battery was suggested by Wessells et al. (2011), who showed interesting performance of the copper analog in aqueous media, able to perform as many as 40,000 cycles. Furthermore, You et al. (2014) demonstrated the role of structural defects on the electrode performance. Not only the most common ions such as lithium (Wessells et al. 2012; Mullaliu et al. 2019) and sodium (Moritomo et al. 2016; Song et al. 2015) can be used for ion battery technology but also potassium (Eftekhari 2004), the divalent calcium (Shiga et al. 2015), and magnesium (Chae et al. 2017), as well as the trivalent aluminum (Liu et al. 2014). From a structural perspective on the inserted cation occupancy, Ling et al. (2013) observed that large cations prefer the body-centered site, whereas for small cations the face-centered site are favored. Table 7.1 lists the electrochemical performances of some electrode materials based on Prussian blue analogs, specifically for Na^+-hosting positive materials, as an example.

Figure 7.2 shows details of a cathode material by using Prussian blue for Na-ion battery applications (Wu et al. 2013). An interesting delivered capacity of 120 mAh g^{-1} was reported at 20C rate. They also observed a noteworthy cyclability which extends over 500 cycles, reported to be due to its phase purity and lattice perfection.

There might be a couple of shortcomings in the application of Prussian blue analogs based electrodes for batteries: (1) the presence of significant amounts of

Table 7.1 List of the performance characteristics of representative Prussian blue analogs for sodium-ion batteries

Material	Potential vs. Na^+/Na	Reversible capacity (mAh g^{-1})	Cycling stability	References
$Na_{0.84}Ni[Fe(CN)_6]_{0.71}$ $6H_2O$	3.1 V	66 at 20 mAg^{-1}	99% after 200 cycles	You et al. (2013)
$Na_2Zn_3[Fe(CN)_6]_2$ xH_2O	3.3 V	56 at 10 mAg^{-1}	85% after 50 cycles	Lee et al. (2012)
$Cu_3[Fe(CN)_6]_2$	3.3 V	44 at 20 mAg^{-1}	57% after 50 cycles	Jiao et al. (2017)
$Fe[Fe(CN)_6$	3.4 V/2.8 V	120 at 60 mAg^{-1}	87% after 500 cycles	Wu et al. (2013)
$Na_{1.56}FeFe(CN)_6$ 3.1 H_2O	3.4 V/2.9 V	103 at 20 mAg^{-1}	97% after 400 cycles	Li et al. (2015)
$Na_{1.70}FeFe(CN)_6$	3.45 V/2.7 V	129 at 200 mAg^{-1}	71% after 100 cycles	Liu et al. (2015a, b)
Dehydrated $Na_{1.70}FeFe(CN)_6$	3.3 V/3.0 V	160 at 10 mAg^{-1}	80% after 750 cycles	Wang et al. (2015)
$Na_{1.32}Mn[Fe(CN)_6]_{0.83}$ $3.5H_2O$	3.2 V/3.6 V	109 at 50 mAg^{-1}	90% after 100 cycles	Matsuda et al. (2013)
R-$Na_{1.89}Mn[Fe(CN)_6]_{0.97}$	3.5 V	150 at 15 mAg^{-1}	75% after 500 cycles	Song et al. (2015)
$Na_{1.96}Mn[Mn(CN)_6]_{0.99}$	2.8 V/3.6 V	209 at 40 mAg^{-1}	75% after 100 cycles	Lee et al. (2014)

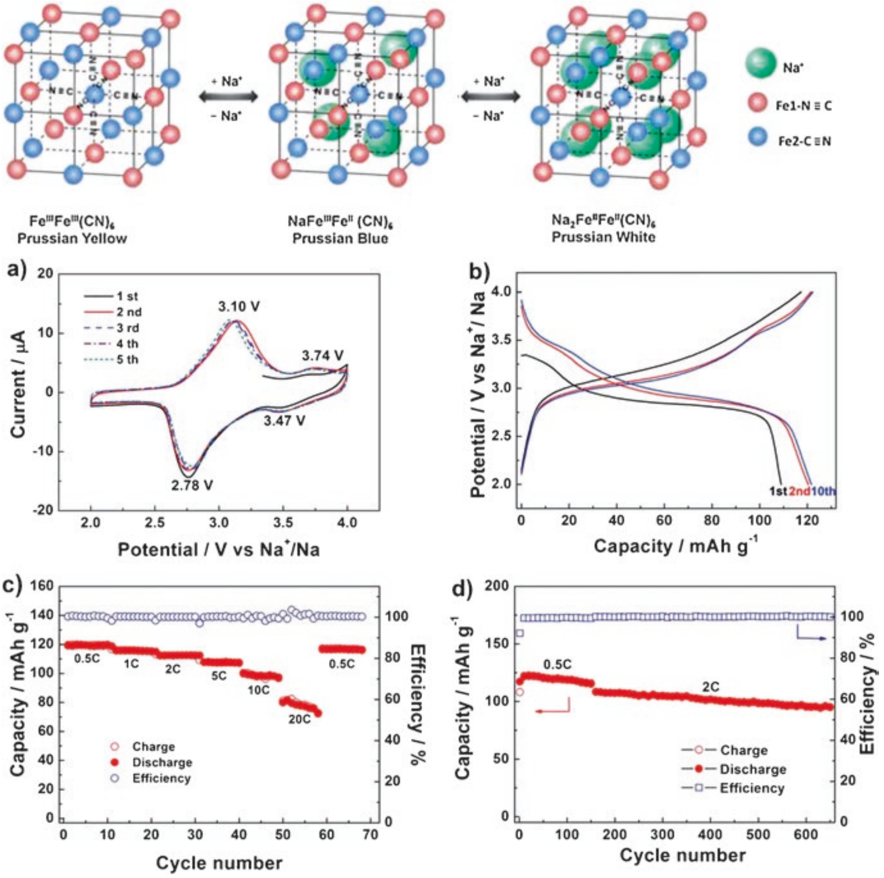

Fig. 7.2 Redox mechanism of single crystal Prussian blue nanoparticles. Both Fe are in the +3 oxidation state at the pristine state (Prussian yellow). By applying a negative potential, the material intercalates sodium and the structure becomes first Prussian blue and then Prussian white, at a potential visible in panel (**a**). Panel (**b**) displays the charge and discharge profiles. Panels (**c**) and (**d**) report the cyclability at different current rates. (Reprinted with permission of Royal Society of Chemistry Publishing from Wu et al. (2013))

interstitial water that can hinder the cycle life of the electrode by saturating some active sites (Itaya et al. 1984); (2) only the C-coordinated site of the CN ligand was considered electroactive, making half of the vacant lattice spaces typically unused (Yue et al. 2014). However, recent studies (Mullaliu et al. 2018a, b, 2019) made by using the atomic sensitivity of X-ray absorption spectroscopy (XAS) demonstrated that the copper or cobalt is electrochemically active in either copper or cobalt hexacyanoferrate electrode.

7.2 Heavy Metal Sequestration and Remediation by Prussian Blue Analogs

The peculiar structure of Prussian blue analogs combined with the presence of metallic sites (at least two) makes them useful in a wide range of applications. In this section, however, the utilization of Prussian blue analogs as adsorbent for the heavy metal removal is highlighted. We address first the basis of the ion exchange characteristics of the Prussian blue analogs, which is closely linked to the development of potentiometric sensors. Then, we introduce the notion of electrochemically switched ion exchange as a friendly method for ion separation on the next subsection. The second subsection includes the cesium removal from wastewaters, the remediation of the thallium intoxication followed eventually by an original application where metal hexacyanoferrates was utilized for rare-earth elements recovery.

7.2.1 Ion Exchange, Potentiometry, and Voltammetric Response

Among the structural characteristics of the Prussian Blue analogs reported in the Fig. 7.1, the presence of cavities and free space inside the cube offers the possibility of accommodating several ions and molecules. Metal ions, for instance, can be shuttled inside and outside the structure, and thus their recovery is a strong potential application. A key factor is represented by the metal dimension compared to the available size of the cavities that may affect the selectivity and the activity of the Prussian blue analogs toward different ions. A relevant study was performed by Tani et al. (1998) who suggested that the effective dimension of the hydrated cation plays a key role. Cations with small hydrated radius are reported to be allocated easily into the Prussian blue like structure but the opposite holds true for large cations. In other words, there is a selectivity order for the metal ions. The observed selectivity coefficients for alkali metal ions of a copper hexacyanoferrate electrode were in the order cesium ion > rubidium ion > potassium ion > sodium ion > lithium ion. This order follows their dehydration energies, as the ion must be partially dehydrated for the insertion into the given structural site. Interestingly, the highest selectivity coefficient was observed for cesium, highlighting the perspective of metal hexacyanoferrate-based technology for its sequestration. Giorgetti et al. (2001) observed the same selectivity order in the nickel derivatives.

Following these ion-exchange possibilities offered by the Prussian blue analogs, the different abilities of the Prussian blue analogs were tested in real and complex matrices, such as seawater. The figure of merit in this case is quantitatively represented by the *Nernst partition law* that describes the partition coefficient. A metal ion (generally an analyte) is partitioned in two media according to its relative concentration in both phases:

$$K_d = \frac{a_{\text{phase1}}}{a_{\text{phase2}}}$$

The formula states that a stronger affinity of a given metal ion with the phase 1 is observed for high K_d value. Generally speaking, a value of 5000 is good, and a K_d value greater than 50,000 can be considered excellent. According to the work of Sangvanich et al. (2010), the copper analogs displays high selectivity (the partition coefficient can be as high 140,000) with respect to Cs^+ and Tl^+ (see Table 7.2). They also reported similar selectivity for Cu^{2+} and Zn^{2+} but at neutral conditions.

A representative electrochemical response of a Prussian blue analog in aqueous solution of several metal alkali ion is displayed in Fig. 7.3. A single electrochemical reaction characterizes all the curves. The following electrochemical reaction holds

Table 7.2 Distribution coefficients (K_d, mL/g) for adsorption of various cations on copper hexacyanoferrate on mesoporous silica (SAMMS) and Prussian blue (PB) in seawater as a function of pH

Competing metal	Concentration (ppm)	Sorbent	pH 0.1	pH 2.1	pH 3.4	pH 6.3	pH 7.3
Cs(I)	0,5	SAMMS	26,000	46,050	75,000	110,000	140,000
		PB	680	770	950	17,000	53,000
Tl(I)	0,5	SAMMS	8300	12,000	14,000	14,000	14,000
		PB	450	280	550	4500	8600
Na(I)	4500	SAMMS	0	19	0	14	0
		PB	0	1			
Mg(II)	1000	SAMMS	0	15	0	10	5
		PB	0	0	13	11	5
Ca(II)	200	SAMMS	0	13	2	10	0
		PB	0	0	26	0	0
K(I)	100	SAMMS	0	0	0	8	0
		PB	0	0			
Se(IV)	1	SAMMS	8	0	120	110	140
		PB	0	29	230	450	490
Mn(II)	0,5	SAMMS	0	0	16	68	270
		PB	0	1	19	910	4100
Fe(III)	0,5	SAMMS	26	26	3300	1400	520
		PB	0	0	0	1700	0
Cu(II)	0,5	SAMMS	0	0	4200	14,000	6500
		PB	6800	14,000	20,000	610,000	560,000
Zn(II)	0,5	SAMMS	0	0	4200	19,000	79,000
		PB	0	29	110	260,000	81,000
Mo(IV)	0,5	SAMMS	61	130	220	41	17
		PB	170	110	660	170	95

Reprinted from Sangvanich et al. (2010)
Measurements done in pH adjusted filtered seawater, S/L of 1.0 g/L

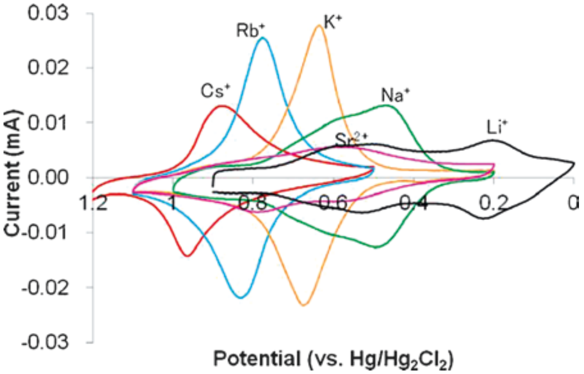

Fig. 7.3 Cyclic voltammetry of copper(II) hexacyanoferrate(III) film (working electrode) in various 0.1 M aqueous solutions of alkali metal nitrates. Reference electrode: $Hg/Hg_2Cl_2/KCl$ saturated. Counter: Pt. Scan rate 5 mV/s. The electrochemical response strongly depends on the electrolyte composition. (Reprinted with permission of Elsevier Publishing from Chen et al. (2013a, b))

in this case, where an oxidation of the iron from 2+ to 3+ is observed during the anodic scan and the presence of the reversible peak also suggests that the electrochemical reaction can be reversed, i.e., a reduction of the iron takes place in the cathodic scan.

$$\mathrm{ZCuFe^{III}\left(CN\right)_6 + Z^+ + e^-} \underset{\text{release}}{\overset{\text{insertion}}{\rightleftarrows}} \mathrm{Z_2CuFe^{II}\left(CN\right)_6} \tag{7.1}$$

and by applying the Nernst equation:

$$E = E^0 + \left(\frac{RT}{F}\right)\ln\frac{a_{\mathrm{Fe^{III}}}.a_{\mathrm{Z^+}}}{a_{\mathrm{Fe^{II}}}} \tag{7.2}$$

where Z^+ denotes the metal alkali ion.

By considering constant the ratio $a_{\mathrm{Fe^{III}}} / a_{\mathrm{Fe^{II}}}$, a Nernstian response is predicted for the metal ion Z^+ concentration. The metal cations participation in Prussian blue analogs electrochemistry have challenged potentiometric sensors capabilities in the last 20 years. Table 7.3 lists a series (not exhaustive) of potentiometric sensors developed and based on Prussian blue analogs. As seen from the table, not only monovalent but also divalent ions can be determined.

Table 7.3 Examples of potentiometric sensors based on metal hexacyanoferrates(MHCF)

Analyte	Metal in MHCF	References
K^+	Cu, Fe, Co, Ni	Engel and Grabner (1985) Cox and Das (1985) Krishnan et al. (1990) Ho and Lin (2001) Zhiqiang et al. (1991)
Cs^+	Cu	Huang et al. (1994)
K^+, NH^{4+}	Cu	Thomsen and Baldwin (1989)
K^+, Rb^+, Cs^+, NH^{4+}	Cu, Ni, Fe	Thomsen and Baldwin (1990) Hartmann et al. (1991)
Mono and divalent cations	Cu, Ni	Tani et al. (1998)
Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+	Tl	Chen et al. (2005)
Cs^+, Na^+, K^+, Na^+	Ni	Giorgetti et al. (2001)
As^{3+}	Fe	Zen et al. (2003)
NH^{4+}	Cu	Liu et al. (1996)
K^+, Cs^+	Fe, Cu, Ag, Ni, Cd	Düssel et al. (1996)

7.2.2 Electrochemically Switched Ion Exchange

The participation of metal cations in the redox reaction (7.1) suggests that the necessary electron flow for the reaction can be mediated by an electrochemical technique. At the same time, ions are inserted, and released, into the peculiar structure of the metal hexacyanoferrate. This simple concept has been called electrochemically switched ion exchange. It was introduced at the beginning of 2000 (Lilga et al. 2001), allowing ion separations in a reversible and selective manner. It is also an environmentally friendly method. Basically, after deposition of a suitable Prussian blue analog on a conductive substrate, the potential can be varied to a negative/positive direction forcing the reduction/oxidation of the active material as indicated by Eq. (7.3) in the case of nickel hexacyanoferrate $KNi^{II}Fe^{III}(CN)_6$ and Cs^+. Also, Eq. (7.3) not only suggests that a cesium ion uptake takes place simultaneously but also that the reverse process is possible, by inverting the electrode polarization. This, in turn, triggers the release of Cs^+ which causes the regeneration of the pristine nickel hexacyanoferrate.

$$KNi^{II}Fe^{III}\left(CN\right)_6 + Cs^+ + e^- \underset{\text{release}}{\overset{\text{uptake}}{\rightleftarrows}} KCsNi^{II}Fe^{II}\left(CN\right)_6 \tag{7.3}$$

This concept is presented in Fig. 7.4 that reports the cyclic voltammetries of electrosynthesized copper hexacyanoferrate material (i) in aqueous K^+-solution, (ii) successively immersed and cycled in a solution containing Cs^+, and finally (iii) immersed again into a solution containing potassium-ion. During step (ii) the traces changed accordingly to the uptake of Cs^+ by observing a shift at higher potential of

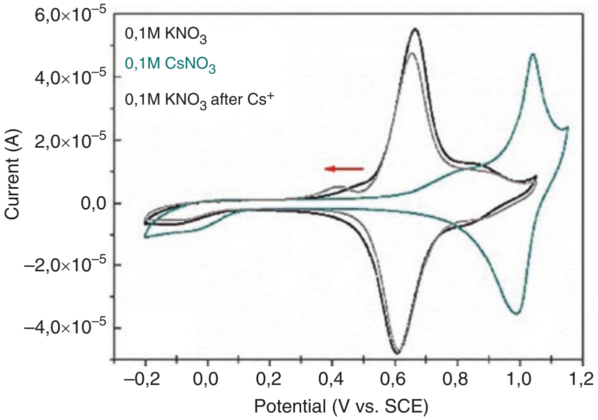

Fig. 7.4 Cyclic voltammetry of electrosynthesized copper hexacyanoferrate in the $-0.2 < E < 1.05$ V vs. SCE (Standard Calomel Electrode) range at 20 mV/s scan rate. Counter: Pt wire. The electrode was immersed in potassium, cesium, and potassium again 0.1 M aqueous solution. (Reprinted with permission of Elsevier Publishing from Ventura et al. (2018))

the main peak. The system is reversible, as seen from step (iii), where the electrochemical response is completely set back to the initial position.

Eventually, electrochemically switched ion exchange is an electrochemically (potentiostatic or potentiodynamic) driven method, which alternative to conventional diffusion-driven processes based on both inorganic and organic ion exchangers. It also allows overcoming typical problem of the latter, e.g., the generation of secondary wastes, such as the solution used for elution, the load, and the single use of the exchanger, which discourages the use of the sorbent in continuous systems. An example will be discussed in the next section.

7.2.3 Recovery of Cesium from Wastewaters

Following the rapid development of the nuclear power for the energy demand in the last century, there has been a wide concern on the associated environmental issue, most likely on the water contamination by radioactive nuclides. The wastewater recovery represents a required step prior to the release in the environment. On the other hand, several accidents such the one in Brazil in 1987, or more recently the Chernobyl and Fukushima calamities, contributed suddenly in a tremendous release of radioactive material. Specifically, in Goiania, Brazil, a cesium-137 teletherapy unit break took place, causing the contamination of several persons (International Atomic Energy Agency 1988). Cesium-137 can be considered one of the most dangerous pollutant for both the environment and the humans, however, it is not present in the nature as such but comes from nuclear reactions. Its danger comes from its radioactive decay that produces very high energetic gamma rays. Following the exposure to gamma rays, the human body can suffer from several diseases and eventually death (Altagracia-Martinez et al. 2012).

The recovery of radioactive cesium can be performed with two main processes, precipitation and extraction. Among several compounds, Prussian blue analogs occupy a principal place (Vincent et al. 2015) because of one key property toward cesium and other heavy metals sequestration: the selectivity. For instance, due to its versatility in a wide pH range, copper hexacyanoferrate was used for Cs removal from wastewaters (Chen et al. 2013a, b; Arisaka et al. 2015; Sangvanich et al. 2010; Parajuli et al. 2016). However, the challenge for the utilization of Prussian blue analog materials in large-scale applications is still open: the relatively small size of the particles, regularly in the nano- or submicro-domain, may represent a serious drawback especially due to the required filtration step. This engineering problem can be solved by using, for instance, water-ink based metal hexacyanoferrate nanoparticles (Chen et al. 2012, 2013a, b) or by using an immobilization technique for the potassium copper hexacyanoferrate based on three-dimensional porous hydrogel structure (Kim et al. 2017). Zheng et al. (2017) proposed a dendritic copper hexacyanoferrate/carbon nanotube approach, while a functionalized magnetic nanocluster of sodium copper hexacyanoferrate was employed by Yang et al. (2017). More recently, El-bahy et al. (2018) proposed a carbomer encapsulated potassium copper hexacyanoferrate for batch techniques, where several variable were measured, evaluated, and probed. Zong et al. (2017) fabricated a composite based on potassium copper ferrocyanide particle demonstrating the suitability of this adsorbent in a moderate acid condition. As Fig. 7.5 reports, the adsorbent selectivity for the cesium are very interesting at pH of about 5.

To evaluate the Prussian blue analogs capabilities as exchanger materials in nuclear wastewater and, more generally, in industrial wastewaters, the work of Sangvanich et al. (2010) is relevant as different sorbents and matrices are considered. His study reveals not only a high affinity toward cesium but also for thallium. Table 7.2 summarizes his study, by reporting the measured distribution coefficient for several cations on copper hexacyanoferrate immobilized in silica and of the Prussian Blue in seawater. Although the selectivity of both agents based on Prussian blue are similar for a given cation, some differences are clearly evident, especially while different pH condition are considered.

As indicated in the Sect. 7.2.2, a device based on the sorption characteristic of a Prussian blue-based material can be used as a superior sorbent for the Cs^+ uptake if an external force, i.e., the electricity, is used. This strategy is called electrochemically switched ion exchange, and the Fig. 7.6 displays its potentiality, while a conventional versus the electrochemically switched ion exchange method is used, as reported by Chen et al. (2013a, b). The plot at the left indicated that both methods can be used, but the electrochemically switched ion exchange not only turned out to be more efficient but also reversible.

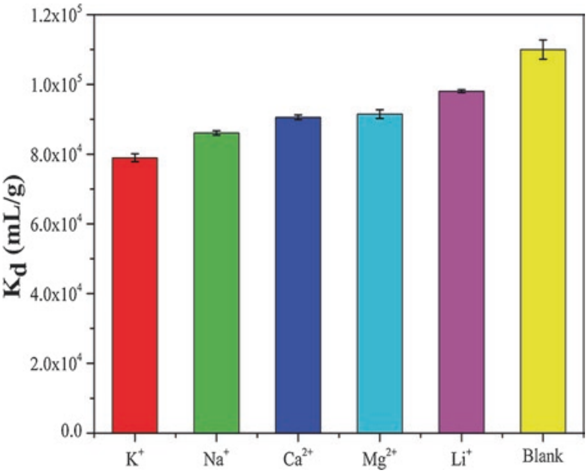

Fig. 7.5 Effect of competing ions on K_d value of cesium for a composite based on potassium copper ferrocyanide particle (pH: 5, initial cesium concentration: 20 mg L^{-1}, adsorbent dose: 0.02 g, temperature: 298.15 K). The selectivity coefficient K_d of cesium was substantially increased in the following sequence: $K^+ < Na^+ < Ca^{2+} < Mg^{2+} < Li^+$. (Reprinted with permission of Royal Society of Chemistry under the Creative Commons Attribution 3.0 Unported Licence from Zong et al. (2017))

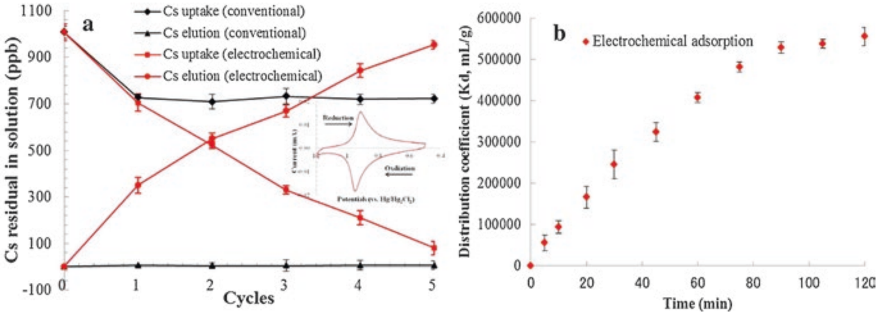

Fig. 7.6 (**a**) Comparison of the cesium uptake/elution using copper hexacyanoferrate film in conventional and electrochemical system. The recovering procedure was repeated up to five times and the residual Cs concentration measured by ICP-MS. The insert displays the cyclic voltammograms response, scan rate = 20 mV/s; A three-electrode cell was employed for the experiment, by using SCE (Standard Calomel Electrode) as the reference electrode, platinum as counter, and the copper hexacyanoferrate film as working electrode (2.5 × 2.0 cm^2). (**b**) Dependence of the Cs uptake in terms of distribution coefficient to the contact time up to 120 min; Cs concentration 1 ppm; pH 0.3; measured at room temperature. (Reprinted with permission of American Chemical Society from Chen et al. (2013a, b))

7.2.4 *Prussian Blue as Medical Treatment for Cesium and Thallium Poisoning*

Because of the high affinity for cesium and thallium cations (Zadronecki et al. 2001), Prussian blue has found therapeutical applications as a medical treatment of people poisoned by radioactive cesium or thallium. The health and environmental hazard of Cs-137 concerns the radioactive decays which produce γ photons and β particles. Capsules of Prussian blue have been approved by the US Food and Drug Administration as the active chemical in Radiogardase® (Heyltex Corporation, Katy, TX) and a study performed by Faustino et al. (2008) pointed out the basic physicochemical phenomenon at the basis of the cesium and Prussian blue binding.

Thallium intoxication is considered mainly accidental and the second most frequent cause of human poisoning. The main chemical form of thallium is thallium sulfate (Tl_2SO_4) which is colorless, tasteless, and odorless. Thallium sulfate might still be used nowadays as rodenticide, so accidental human poisoning is possible. In analogy with the cesium, thallium also is retained from and dispersed throughout the body, mimicking the potassium uptake, but blocking its enzymatic action. Kravzov et al. (1993) studied the effect of the crystalline size and the morphology of several different Prussian blue analogs on their medical efficacy, exploiting in vivo experiments, verifying that the smaller the size the better the capacity.

7.2.5 *Rare Earth Element Recovery and Valorization by Metal Hexacyanoferrates*

The use of rare earth elements in the electronic industry is growing. For instance, digital displays are fabricated by using rare earth oxides. The limited availability of rare earth elements also plays a decisive role in the current geopolitics. In this perspective, their recovery from waste of the electronic industry can be valuable from both the environmental and the social perspectives. In the earth's crust rare earth elements are not available as free metals but as minerals, containing various rare earth metals combined to other transition metals. Therefore, there is a strong motivation in searching for technologies for the recovery and valorization of rare earth elements from waste of the electronic industry.

A recent paper reports the ability of the nickel hexacyanoferrate to host in reversible way cations with nominal charge up to 3^+, namely, Al^{3+}, Cr^{3+}, In^{3+}, Gd^{3+}, and Er^{3+} (Ciabocco et al. 2018). This feature makes the nickel hexacyanoferrate a suitable material for all electrochemical processes based on the host/guest mechanism also involving trivalent cations. The procedure here proposed allows a separation erbium (III) by means of a two-step electrochemical process.

The proof of concept is visualized in the Fig. 7.7 which displays the polarization profile of a nickel hexacyanoferrate film cycled in 1.0 M KNO_3. The observed electrochemical response is due to the $K_2Ni^{II}[Fe^{II}(CN)_6]$ and $KNi^{II}_{1.5}[Fe^{II}(CN)_6]$ phases

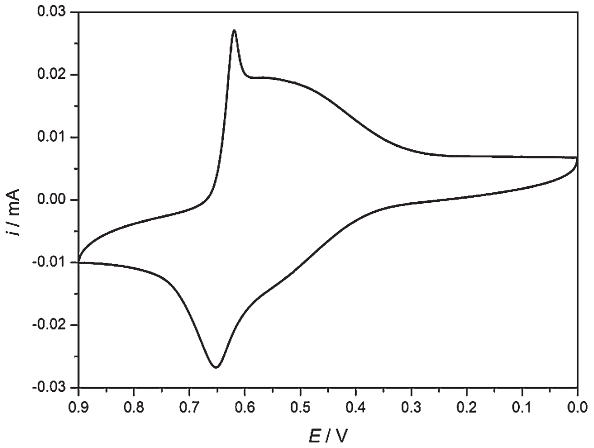

Fig. 7.7 Typical cyclic voltammogram of a nickel hexacyanoferrate film recorded at 0.1 V s^{-1} in a 1.0 M KNO_3 solution. Reference electrode: Standard Calomel Electrode (SCE)

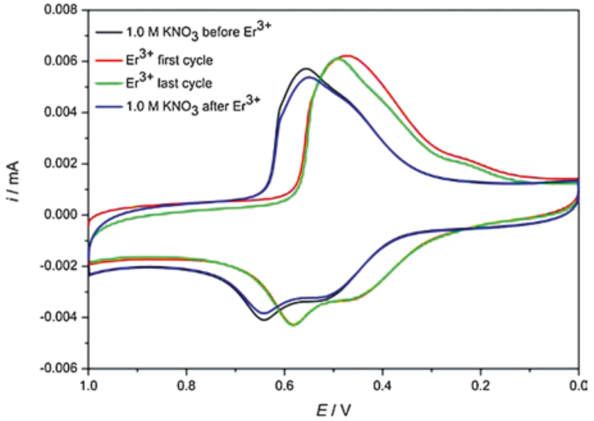

Fig. 7.8 Cyclic voltammograms recorded at 0.1 V s^{-1} of a nickel hexacyanoferrate film in 1.0 M KNO_3 and $Er(NO_3)_3$ solutions at spontaneous pH. Reference electrode: Standard Calomel Electrode (SCE)

(Zamponi et al. 2003). Figure 7.8 indicates voltammetric response of an electrodeposited nickel hexacyanoferrate in potassium or erbium solutions at spontaneous pH, demonstrating the fast switching capabilities of the electrodeposited Prussian blue analog material. The first cycle, registered in potassium salt electrolyte (black line) is significant different to the one obtained after one single cycle containing Er^{3+} (red curve). The same figure also displays that by keeping cycling the Er^{3+} solution up to 100 cycles, the first and the last curve match with each other, underlying a perfect reversibility and stability of the electrodeposited films. A reversibility test, made by cycling the Prussian blue analog film on potassium salt after the erbium, reveals an almost perfect match of the two signals, thus highlighting the potentiality of NiHCF for rare earth metal valorization. In addition, similar tests made by using other rare earth elements, such as La^{3+}, Gd^{3+}, and Dy^{3+}, indicate the same potentiality.

The electrochemical equation involving the Er^{3+} insertion/release in the nickel hexacyanoferrate can be written as:

$$\mathrm{Ni_{1.5}}\left[\mathrm{Fe^{III}}\left(\mathrm{CN}\right)_6\right]+1/3\mathrm{Er^{3+}}+\mathrm{e^-}\rightleftarrows \mathrm{Er_{1/3}}\left[\mathrm{Ni_{1.5}Fe^{II}}\left(\mathrm{CN}\right)_6\right] \tag{7.4}$$

Therefore, the erbium is inserted during reduction, and the opposite holds true by inverting the electrode polarization. By applying the Nernst equation to the equilibrium (7.4), we obtain:

$$E = k + \left(\frac{0.059}{3}\log\left[\mathrm{Er^{3+}}\right]\right) \tag{7.5}$$

The Eq. (7.5) suggests a theoretical slope of about 19 mV per decade of concentration of the erbium salt. Additional experiments made by varying the erbium concentration confirm experimentally the quotation of this Nernstian slope.

7.3 Conclusion

Prussian blue analogs, derivatives of Prussian blue, are characterized by a peculiar porous structure and the presence of tunnels, cavities, as well vacancies. The structure coupled to the electroactive capability of the metals define a series of physicochemical properties, being this class of materials adopted in several applications, for instance, electrochromic and battery devices. In particular, the ability to reversibly exchange different ions, ranging from monovalent to divalent, has been used as cheap and effective adsorbent for heavy metals, in particular for the extraction of cesium from wastewaters, the remediation of the thallium intoxication, and the recuperation of the rare earth elements. Ion affinity is crucial in diffusion driven processes, being Cs^+ and Tl^+ selectively captured also in complex matrices, such as seawater. In particular, the high affinity displayed toward these two metals and the biocompatibility promote the use of Prussian blue and its analogs as medicinal agents for internal contamination from radioactive cesium or thallium. Electrochemically driven ion exchange (either potentiostatic or potentiodynamic) shows promising results due to the effectiveness in the removal of metals and the possibility to reversibly restore the adsorbent to its initial state, avoiding the production of secondary wastes. The presented example about the recovery of Cs^+ from wastewaters reached by means of a potentiostatic method evidences excellent performance in terms of quantitative recovery and reversibility. Moreover, Prussian blue analogs manifest ion exchange properties for other several ions, such as Li^+, NH_4^+, Rb^+, Cu^{2+}, Sr^{2+}, As^{3+}, and so on. Finally, the removal of heavy metals based on a simple electrochemical method is combined to their valorization, as presented in the case of rare earth elements, whose importance is significant in current technologies, yet traditional recovery is excessively complex and expensive.

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Chapter 8
Agricultural Waste Absorbents for Heavy Metal Removal

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Abstract Large numbers of toxic and poisonous chemicals are released in our surroundings from different industries resulting in contamination of aqueous medium, atmosphere, and geosphere at an alarming level. Aqueous medium pollution that results from heavy metal has come into being as a severe environmental issue. Some poisonous metals include zinc, mercury, lead, chromium, cadmium, nickel, and copper, which are of particular concern in curing industrial wastewater. They are non-biodegradable in nature, make aggregate in living bodies and most of them are cancer-causing agents. A number of extensive industrial researches have been conducted for the safe removal of pollutants and metallic elements from industrial effluents and wastewater. There are many different ordinary treatment strategies that have been utilized to treat these aqueous phase toxins, such as flotation, ion-exchange, coagulation, reverse osmosis, electrolysis, and complexation.

The adsorption is more widely accepted, and more promising techniques can be utilized to eliminate certain types of pollutants by selecting appropriate adsorbent. It offers many advantages over other conventional methods and is accepted as one of the productive, effective, labor-saving, valuable, and reasonable methods. There are large number of adsorbents that have been used to adsorb heavy metals from aqueous media such as activated carbon, activated alumina, clays, zeolites, polymer clay-based nanoadsorbents, metal oxide-based nanoadsorbents, graphene, and carbon nanotubes; some other absorbents including chitosan, lignin, cellulose, starch, and fungi have also been used for safe removal of heavy metals. Agricultural wastes come from the growing and initially processed agricultural stuff, including organic products, vegetables, fruits meat, and dairy items, which nowadays have been used as economic and environment-friendly adsorbents. Agricultural wastes especially those that contain cellulose have a high biosorption capacity. Adsorbents from plant wastes can be used with or without modification for the reduction of a pollutant from aqueous media. Generally, chemical modification of plant wastes enhances their adsorption capacities as compared to unmodified. Rice husk in pristine form and in activated rice form is utilized for chromium (VI) removal. Different kinds of agricultural waste materials including peanut shells, soybean hulls, rice straw, bagasse, sugarcane, and walnut shells have been applied for lead adsorption. In some studies, rice and wheat bran were analyzed for cadmium adsorption, and excellent results were reported. Other studies showed the application of rice husk and rice polish in both pristine and composite forms for effective cadmium adsorption. The bark of some plants including *Picea glehnii* and *Abies sachalinensis* and biomass of dried plants (*Parthenium*) were checked for cadmium removal. Adsorption experiments performed using hazelnut shells, green shell, walnut shells, and peanut hulls exhibited good results toward cadmium adsorption. Some other adsorption studies conducted using activated carbon prepared coir pith, bagasse pith, and dates and peanut shells. Their cadmium adsorption capacity was found to be up to 98%. One study showed that tea-based adsorbent reduced almost 70% of the hexavalent chromium into Cr(III). In short, agricultural waste can be used as low-cost and most beneficial adsorbent for removal of heavy metals from aqueous media.

Keywords Environmental issues · Industrial effluents · Heavy metals · Adsorbent · Nanocomposites · Agricultural waste · Chitosanyremediation

8.1 Introduction

Environmental contamination related to the substantial release of heavy metal in wastewater coming from quick industrial development and urbanization is a worldwide concern. Therefore, different conventional treatment strategies have been utilized to limit the issues related to these aqueous phase toxins. Industrial effluents and heavy metal pollution are a noteworthy biological issues due to their harmful nature and inclination to aggregate in the food chain. They are nonbiodegradable in nature and make aggregate in living bodies, a lot of them are cancer-causing agents. Some poisonous metals include zinc, mercury, lead, chromium, cadmium, nickel, and copper, which are of particular concern in curing industrial wastewaters (Patel et al. 2018).

The industrial sources of frequently encountered heavy metals are hydroelectric mining municipal wastewater, coal-fired power plants, pulp, and paper and refineries for mercury (Streets et al. 2018; Urgun-Demirtas et al. 2012); tanneries, electronic metal finishing mining operations, and plastics and etching for copper (Al-Saydeh et al. 2017; Kazemipour et al. 2008); cadmium-containing folders, pigments, cadmium–nickel batteries, manufacturing of other metal, zinc ores, phosphate fertilizers, and nonferrous metal smelting for cadmium (Mortaheb et al. 2009); leaded gasoline, effluents from plastic, metal smelters, lead-based paint, used batteries, microelectronics, and wood preservative-producing industries for lead (Davis et al. 2001; Zhang et al. 2012); and coal mining and manufacturing, sewage sludge, pharmaceutical products, steel production, waste combustion, insecticides, cosmetics, paints, and electroplating for zinc (Vongdala et al. 2019) (Fig. 8.1).

Among all toxic metals, cadmium, arsenic, and mercury are viewed as more lethal big three classification of overwhelming metals posing highest potential risk to human being and environments (Gautam et al. 2014). Consequently, these substantial metals can make irreversible damage to human health and natural environment; furthermore, these lethal effluents cause serious damage to nearby ecosystem if remain untreated (Jain and Jayaram 2010). There are different methods including coagulation, adsorption, membrane separation, precipitation, filtration, electrolysis,

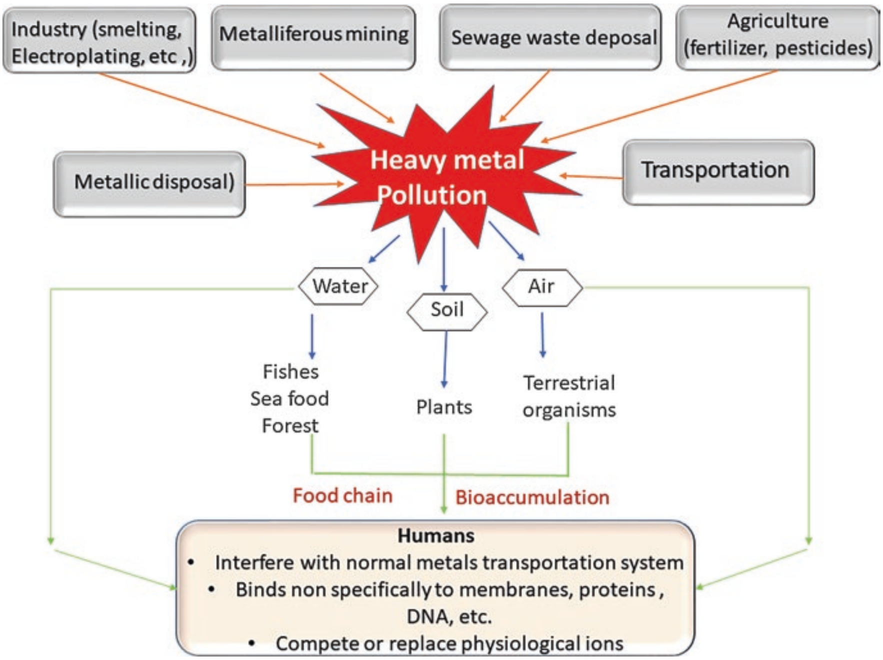


Fig. 8.1 Sources of heavy metals in the environment

liquid–liquid extraction, solvent extraction, ion exchange, ozonation, chemical oxidation, etc. that are employed to remove these toxicants from aqueous media. Adsorption is thought to be the best one in the field of separation technology, as it offered significant benefits such as design simplicity, high separation, ease of operation, and proficiencies compared to other techniques. In this regard, diverse adsorbents have been used for the removal of aqueous phase pollutants (Afroze and Sen 2018) (Fig. 8.2).

8.2 Chemistry and Toxicity of Heavy Metals

In human beings, heavy metals can cause severe health issue contingent upon the nature and amount of the metal ingested. Their toxic effect is associated with complex formation with proteins, where amine (− NH2), carboxylic acids (− COOH), and thiol (− SH) moieties are utilized. Such kind of metal bindings influences important protein and enzyme structures. The most hazardous toxic metals that human beings encounter are cadmium, lead, mercury, aluminum, and arsenic. Aluminum has been related to senility, presenile dementia, and Alzheimer's and Parkinson's diseases. Arsenic can produce skin lesions, sickness or cancer, and abdominal problems. Cadmium can harm kidneys and can cause hypertension. Lead

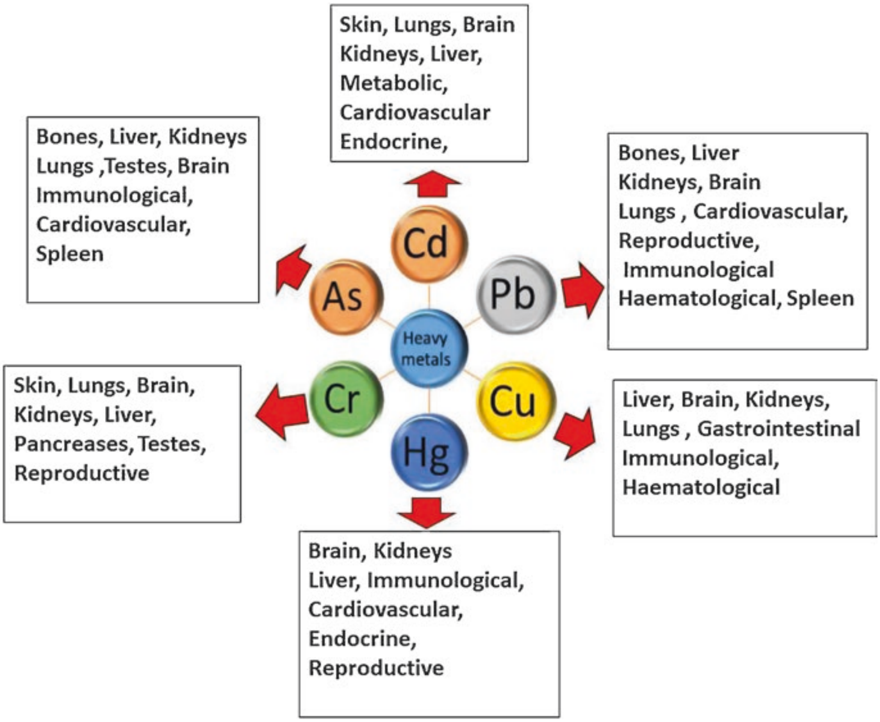


Fig. 8.2 Health impacts of heavy metals

is known to be a potential human cancer-causing metal and commutative toxicant (Zhao et al. 2014), while mercury toxicity results in impairment of speech, mental disturbance, and hearing and vision problems (Budnik and Casteleyn 2019). Additionally, lead (Pb) and mercury (Hg) may result in autoimmunity development, a disease in which immune system of a person tend to destroy its own cells, which ultimately can cause joint-related illnesses, kidney damage, and ailment of the neurons and circulatory system. Higher quantities of lead and mercury may also result in incurable brain impairments.

The source, toxicity, and chemistry of some heavy metals are discussed below.

8.2.1 Arsenic (As)

Arsenic is a tasteless and odorless element that occurs naturally. Arsenic occurs in the aquatic environment in an inorganic form which comes from the disintegration of solid compound including AsS_2 (realgar), As_2O_5 (arsenolite), and As_2O_3 (arsenic anhydride) (Saint-Jacques et al. 2018). Arsenic may found in various valance states, i.e., +1, +3, −3, and +5, and infrequently in elemental phase. It is found in underground rocks and soil, from where it makes its entry toward hydrosphere and go in the food chains by polluted water intake, and affected plants and cereals ingestion. Higher concentration of arsenic in drinking water can cause long-term skin problems and other circulatory and nervous systems issues. Its accumulation in human beings can cause open lesions, tissue destruction, and neural sicknesses and can develop cancer (Pal 2001).

8.2.2 Copper (Cu)

In the aqueous media, copper (Cu) can exist in three major forms: colloidal, particulate, and dissolved. The dissolved form may have either free ions or ions complexed with inorganic and natural ligands or may contain both free and combined states. Commonly, copper forms complexes/compounds with hard bases including nitrate, sulfate, chloride, hydroxide, ammonia, carbonate, and humic materials. The development of stable malachite ($Cu_2(OH)_2CO_3$) plays a major role to control free copper (II) ion level in aqueous media.

Copper has gained specific attention due to its harmfulness and its prevalence and occurrence in industrial process including electroplating, paint industries, and metal finishing. Cu in drinking water may result in hand and sole keratinization, dermatitis, and many other serious illnesses. In this way, the level of copper in drinking water should be decreased to the limits that fulfill the ecological guideline for different waterways. Disintegrated copper grants undesirable, metallic, harsh taste to drinking water. Therefore, the copper concentration in water should be lowered based on the environmental guideline for different water bodies. Copper in dissolved form can cause an unpleasant, metallic, bitter taste in drinking water (Kwikima and Lema 2017).

8.2.3 Cadmium (Cd)

Cadmium (Cd) is mostly found in carbonate ($CO^{2-}{}_3$) and sulfide (S^{2-}) ores. Cadmium is also gained as a by-product during refining of other metals. In aqueous media, the dominated cadmium forms are $CdCO_3$(s) (otavite), Cd^{2+}, and $Cd(OH_{)2}$(s). The cadmium water solubility is affected by its acidic nature. In groundwater, cadmium may found in different complexes; however, at lower pH, such complexes are not found in significant amount.

Cadmium can enter in water bodies from a variety of sources in the environment and from industry. It may occur naturally in groundwater, or contaminates groundwater from fertilizers, sewage sludge, or mining wastes can cause higher cadmium level in aqueous media. Cadmium does not play any important biological role. It is very poisonous to human being. It can accumulate in the body especially in the liver and kidney upon chronic exposure. Acute toxicity from inhalation and ingestion can cause severe issues, and death has been reported from self-poisoning of cadmium chloride ($CdCl_2$). It also caused itai-itai (ouch-ouch) disease, associated with chronic cadmium poisoning.

8.2.4 Lead (Pb)

Lead contamination can occur in groundwater due to different human activities, including mining, smelting, leaded fuel spills, automotive emissions, incinerator ash disposal, municipal landfill, and industrial leachates, and other products containing leads, such as lead paint, lead batteries, and dust. The behavior of lead in water is affected by pH range. The lead binding with negatively charged organic surfaces enhances profoundly above pH 5. The groups that are more susceptible to lead toxicity are children and fetuses. It can cause serious nervous system illness. In children, it can affect the development of the central nervous system, thus causing irritability, headache, and hyperactivity. Additionally, it can cause learning and concentration difficulties (Kwikima and Lema 2017).

8.2.5 Chromium (Cr)

Chromium is found in aqueous media in two forms, i.e., chromium (III) oxide (Cr_2O_3) and chromium dioxide (CrO_2). Numerous chromium, particularly chromium (III) oxide, complexes are not water-soluble. The only water-soluble chromium compounds are chromium (III) oxide and hydroxide. The occurrence of most prevailing Cr(III) form in water relies on pH. Cr does not involve in complex formation with anionic particulate matter due to its negative charge. Chromium is an essential component of diet for many living organisms. This, however, only relates to trichrome (trivalent chromium). Hexavalent chromium (*chromium* (*VI*)) is extremely poisonous to plants, animals, and humans. Chromium (VI) is an abundant ecological toxicant, posing a seriously harmful effect on public health. Various studies are conducted to analyze the health impacts of Cr(VI). It was found that chromium (VI) can cause mitochondrial damage and ultimately can lead toward cell death (Zhong and Zhong 2017) (Fig. 8.3).

8.3 Heavy Metal Remediation Methods

In order to comply with the standards and to make water safe and contamination-free, heavy metals should be removed. A number of extensive industrial researches have been conducted for the safe elimination of pollutants and metallic elements from industrial runoffs and unwanted species from water. As some metals are expensive such as platinum and gold, so attempts have been made for recycling and reusing them for large-scale usage.

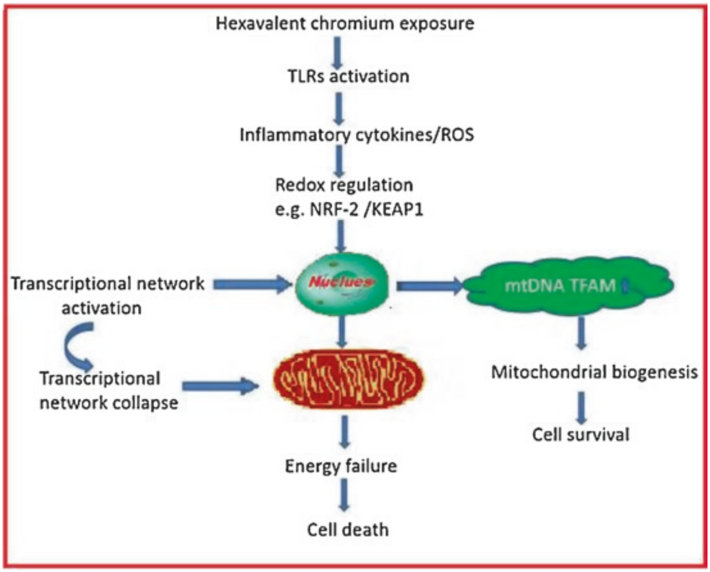


Fig. 8.3 Chromium toxicity. (Modified Zhong and Zhong 2017)

The conventional methods used for decontamination of heavy metals include chemical (chelation), mechanical (such as ion exchange, reverse osmosis, and adsorption), and electrochemical (deposition). Each method has its own pros and cons. Chemical precipitation or chelation requires large number of chemicals which themselves are not easy to remove from water; it also produces huge quantity of sludge which itself has negative impact on the environment as well as its disposal (Sud et al. 2008).

The ion-exchange method although is an outstanding method for decontamination has its limitations as well, for example, ion-exchange rinse can contaminate easily by the organic particulates and other toxicants in the water as well. Like chemical method, the ion-exchange method also produces highly concentrated metal solution which is difficult not only to handle but also to dispose of (Carolin et al. 2017).

The detail description of some conventional methods (Fig. 8.4) for decontamination of heavy metals is given below:

8.3.1 Chemical Precipitation

In this method, chemical reagents are added, which lead to separation of metals by precipitation, leaving the clean water on top. This precipitation is achieved by adding salts that coagulates such as iron salts (Akbal and Camcı 2010; Matlock et al. 2002). Gopalratnam found that 80% of heavy metals that include zinc, coper, and lead and up to 96% of the industrial wastewater that contained oil can be removed by combined hydroxide precipitation and air filtration (Gopalratnam et al. 1988).

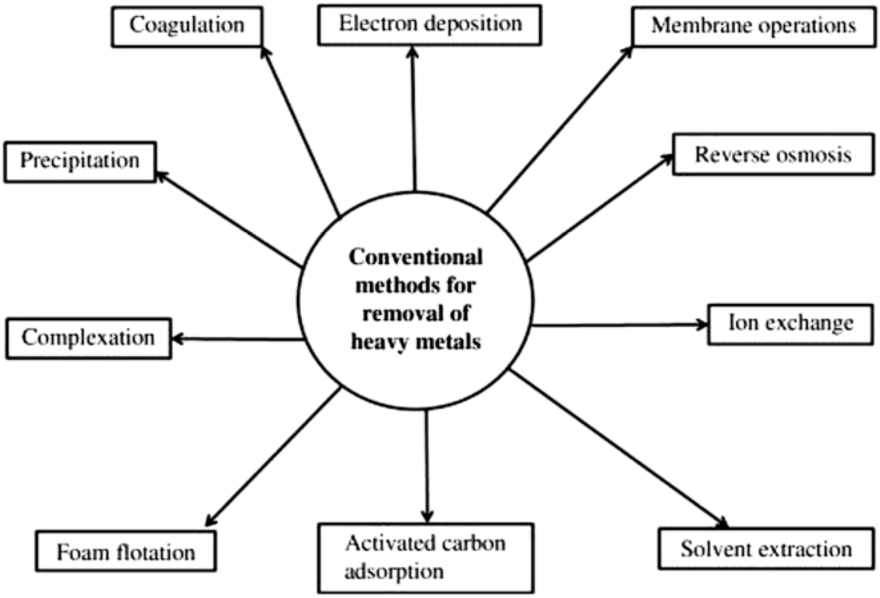


Fig. 8.4 Conventional methods for removal of heavy metals

8.3.2 *Ion-Exchange Method*

It is a reversible procedure in which an ion or a radical present in a solution is removed by simple exchange. The exchange is done with the help of similarly charged particle that is attached to a stationary solid phase. These exchanged particles may occur naturally as zeolites and clays or synthetically produce organic resins or ion-exchange membrane made up of high molecular mass polyelectrolytes that have the capability to exchange ions of similar charge. The number of mobile sites is unique to each rinse that determines the capacity of ions that per unit of the rinse can exchange. Synthetic rinse is preferred as they can be tailored according to need and application. The ion-exchange rinse is categorized based on the charge that it carries. Both ion-exchange and synthetic rinses are prepared from the same -based polymer. The only difference is the ionizable group is attached to the network of hydrocarbon chains. It is basically the functional unit of the rinse that determines its behavior (Sud et al. 2008).

8.3.3 *Electrodialysis*

It is a membrane-based procedure where ions are moved due to the difference in electro-potential gradient across a semipermeable membrane. Like ion exchangers, these are also selective membrane for cations or anions, i.e., either cations or anions will permeate through the membrane. For example, the polyelectrolytes on cation-selective membranes are negatively charged and repel anions, allowing flow of cations only (Satapathy and Natarajan 2006).

8.3.4 Coagulation/Flocculation

Coagulation is a chemical process in which a chemical (coagulant) is added into water. These coagulants cling the colloid material in the water, making small masses of the “flocs.” The suspended matter is caught by flocs and hence removed easily (Sillanpää et al. 2018).

Flocculation is a slow gentle mixing of the water to aid the flocs to develop and grow in size as well which settle down easily leaving clear water behind. The basic mechanism that removes the organic contaminants by coagulation was studied by Fernandez and coworkers (Fernandez et al. 1997), while Kuo et al. studied the influence of various controllable parameters including initial pH, turbidity, and per ozonation doses as well as flocculation time on the removal of organic material dissolved in water during alum coagulation. (Kuo and Amy 1988).

8.3.5 Ultrafiltration

The principle behind ultrafiltration is size exclusion; in this process, simple mechanical (pressure) filtration is done using membranes with pore size ranging from 0.1 to 0.001 μm. This process removes colloids, high molecular weight molecules, as well as organic and inorganic molecules. When pressure is applied, water and low molecular weighted substances pass through the filter membrane, while colloids and macro-solutes are retained by the membrane. Factors affecting this efficiency of filtration include surface chemistry of particles as well as the membrane itself and their electrical charges (Landaburu-Aguirre et al. 2009).

8.3.6 Membrane Filtration

This method has gained great deal of consideration for water remediation since it is not only used to remove inorganic effluent and suspended particulates (organic and inorganic) but also effectively utilized for heavy metal treatment. Various types of membrane filters are used these days such as ultrafiltration and nanofiltration membranes depending upon the size of particle that can be engaged. These unique specialties of the ultrafiltration enable the passage of low molecular weight solutes while blocking macromolecules, whose size is larger than membrane pore’s size.

8.3.7 Reverse Osmosis

In reverse osmosis, cellophane-like semipermeable membrane is used to purify water from contaminations. In reverse osmosis, the particles move across a selectively permeable membrane under the effect of osmotic gradient created across the semipermeable membrane. The process is augmented by external pressure. When the pressure is provided at the concentrated side, it forces the water molecules to move to the dilute side and retain the impurities on the other side, making water pure and contamination-free. The impurities left behind on the concentrated side are going away with released water. The use of reverse osmosis for water purification includes decontamination of water from electroplating industries, fisheries, wastewater containing organic impurities, industrial waste including food processing, textile, petrochemical, paper and pulp preparation as well as municipal and radioactive wastewater. It is also reported to be used for decontamination of groundwater and preparing pharmaceutical and reagent grade water (Chen et al. 2018).

Most of the abovementioned conventional processes are unsuitable and unsatisfactory due to the disposal of dirt, their excessive operational price, less productivity, and less effectiveness. The major drawback is that these methods are not applicable for large number of pollutants and less efficient for the handling of small quantity of metallic ions and problems of further treatment because of the production of toxic sludge.

8.3.8 Adsorption

Among all filtration processes, adsorption is considered the most suitable for wastewaters, not only being cost-effective but also being simple. Adsorption is the most popular, convenient, superior, and beneficial strategy above any other processes for the remediation of polluted industrial wastes and elimination of contamination from water supplies. It has many advantages such as practicality, pliancy, or malleability in design and simplicity of working or performance and producing supercilious emission capable for reuse free from other pollutants (Fig. 8.5).

The major advantage related to adsorption is regeneration of sorbents with appropriate desorption process, and most of such regenerations need low maintenance cost with excess efficiency and is easy to operate. It is accepted as one of the productive, effective, labor-saving valuable, and reasonable methods. Thus, adsorption is the most promising technique that can be utilized to eliminate certain types of pollutants by the selection of appropriate adsorbent.

Adsorption is a process that occurs when a liquid or gaseous solute accumulates on solid or liquid phase i.e. the adsorbent, forming an atomic or a molecular filum i.e. the adsorbate. It takes place in almost all chemical, natural, physical and biological systems. It is mostly applied for treatment of industrial waste using a variety of

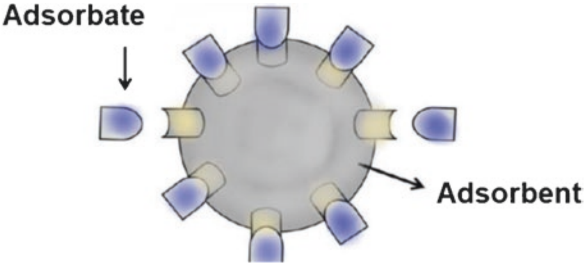


Fig. 8.5 Adsorption

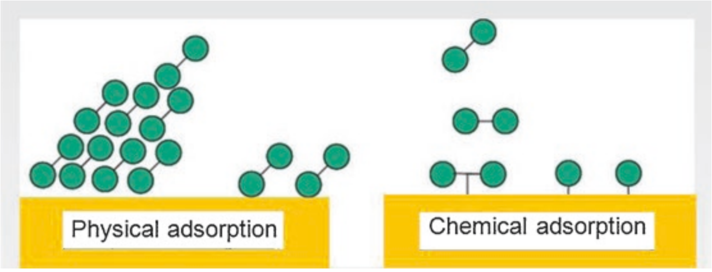


Fig. 8.6 Kinds of adsorption

adsorbents such as activated charcoal, activated carbon, etc. for purification of water (Burakov et al. 2018).

Adsorption processes for removal of pollutants in aqueous media are done either in a discontinuous way by batch reactors or in a continuous manner by fixed-bed reactors or columns (Gong et al. 2018). The Fixed bed systems are mostly used for industrial scale, while batch is utilized on laboratory purpose as, due to their easiness and easy handling they are restricted for treating of small concentration of solution (Crini et al. 2019).

8.3.9 Kinds of Adsorption

Adsorption, at molecular scale, is related to the mutual attractive forces of the surface among adsorbent and adsorbed particle. Molecules are interacted with surfaces due to some forces creating either from van der Waals forces (physical) or from the hybridization of their orbitals with substrate atoms (chemical), reliant on which involvement dominates adsorption may be either physisorption or chemisorption (Fig. 8.6).

- Physisorption (physical adsorption): It occurs as a consequence of physical intermolecular attractive forces between the adsorbing molecules and substances to be adsorbed (adsorbate). Physisorption happens only if attractive forces between adsorbate and adsorbents become stronger than the intramolecular attraction of adsorbent itself. Moreover, it occurs at lower temperature, which is in general near the critical temperature of material to be adsorbed.

- Chemisorption (chemical adsorption): It occurs due to the interaction of adsorbed surface and the solid. This process is irretrievable and is of great concern in catalysis. Therefore, the energy of the process of chemisorption is considered similar to that of any chemical reaction, i.e., it may be either exothermic or endothermic of variable magnitude varying from negligible to huge. The elementary steps of the process are often highly endothermic processes (requiring high adsorption energy) (Andreev et al. 2019).

8.3.10 Adsorbent Properties

In order for commercial applications, the sorbent is supposed to have the following qualities:

- It should be highly selective, enabling sharp separations.
- The adsorbent capacity should be high, hence utilizing least amount of sorbent.
- Kinetically favorable.
- Transport properties enabling speedy sorption.
- Thermal stability, i.e., stable at extreme temperatures.
- Chemical stability, i.e., inertness toward contacting fluids, preserving not only the amount but also the chemical integrity of the sorbent.
- Mechanical strength and its hardness increasing its life.
- Lacking the tendency to enhance or reinforce any chemical reactions.
- The ability of regeneration when applied for commercial purposes (Singh and Gupta 2016).

8.3.11 Factors Affecting Adsorption

Various factors that influence adsorption procedure are given below:

- The composition of an adsorbent also plays major role in its adsorption capacity. Adsorbents with specific functional groups can adsorb anions and cations from solution. The degree of adsorption relates to kinds and density of the adsorption sites available.
- Surface area is a major factor affecting adsorption behavior of filter media; it is directly related to adsorption capacity of an adsorbent. Nanostructured adsorbents showed more adsorption capacity compared to micro and macro one due to large surface area.
- Adsorption is affected by many other several physicochemical characteristics of an adsorbate, such as the size of adsorbate molecule, solubility, surface charge,

molecular weight, and ionic radius. Solubility is a very important parameter influencing the adsorption capacity.

- The size and the polarity of adsorbate also influence adsorption both positively and negatively.
- pH is also a major factor affecting adsorption capacity of an adsorbent. This factor is more influencing in case of heavy metal adsorption from aqueous media.
- Efficient sorbents should be harmless and possess high sorption efficiency and sensitivity to lower the amount of toxicant.
- The desorption of sorbent should be easily possible and finally recycled able.
- It should have fast rate of adsorption.

8.3.12 *Various Adsorbents Used in Adsorption Processes*

There are varieties of materials that are used for adsorption purpose. Some conventional and nonconventional adsorbents used for remediation of heavy metals are shown in Figs. 8.7 and 8.8 respectively.

- Activated Carbon

It is amorphous solid in nature, highly porous, and consistent of graphite microcrystal lattice. It is prepared in either powdered form or small pallets usually. It has the capacity to remove various kinds of heavy metals (Crini et al. 2019; Xu et al. 2018).

Ferrous chloride (FecCl$_2$) solution is utilized to impregnate iron in the activated carbon for removing heavy metals including Cr, Zn, and Pb from synthetic wastewater. Different studies proved the use of AC for adsorption of heavy metals from aqueous solution (Fig. 8.9).

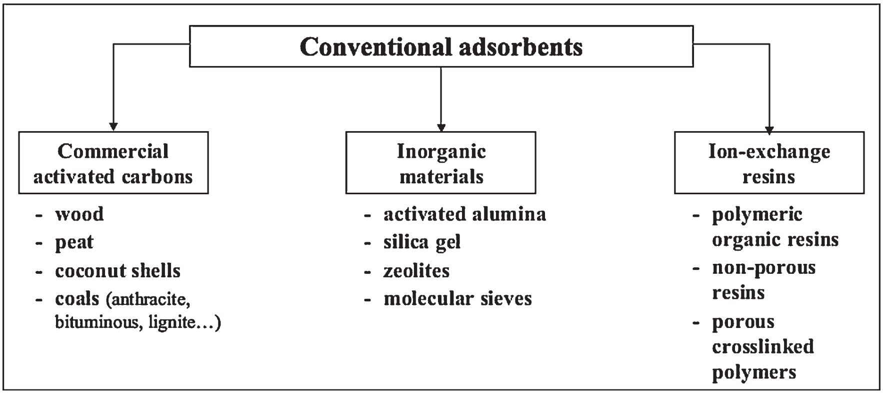


Fig. 8.7 Various types of conventional adsorbents

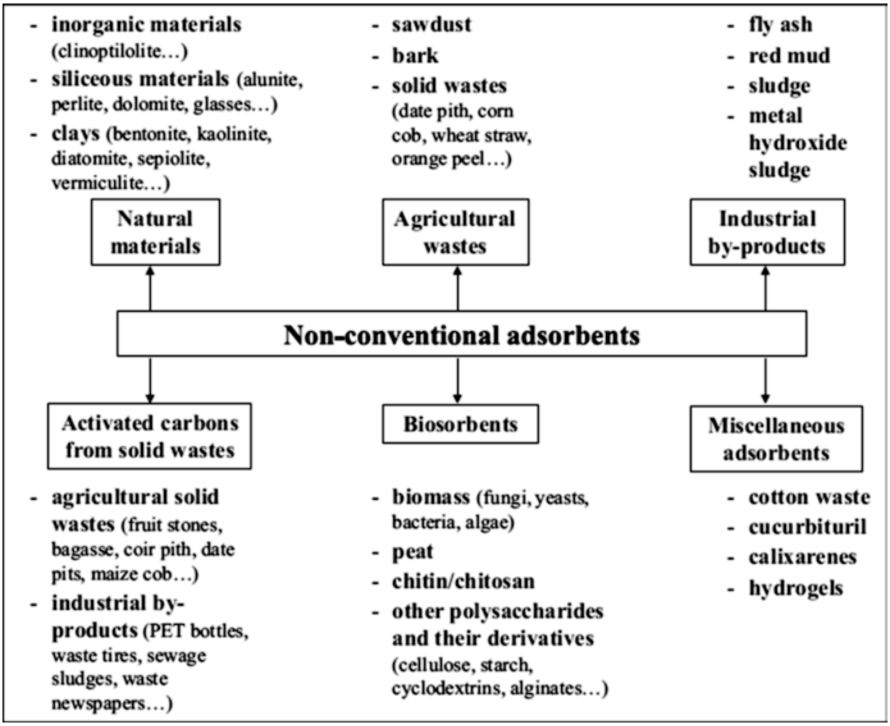
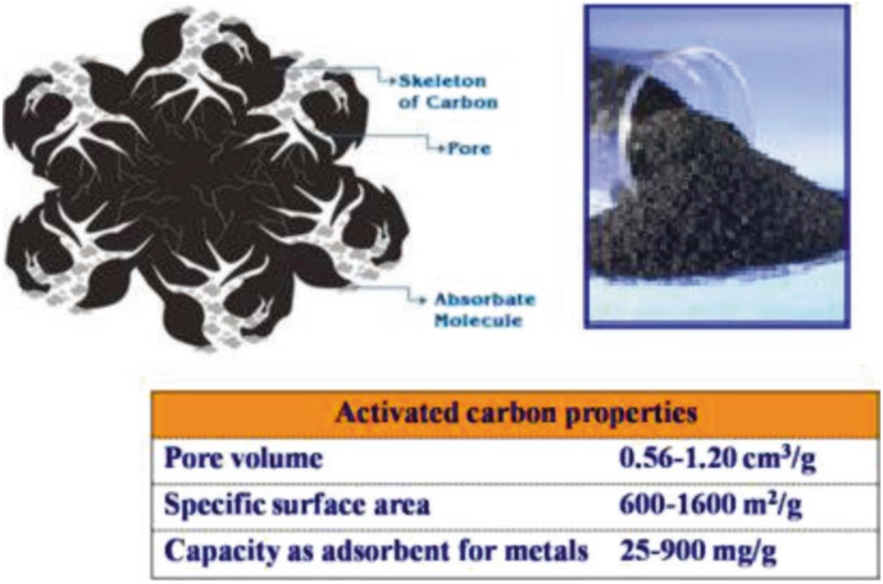


Fig. 8.8 Various types of nonconventional adsorbents



Activated carbon properties	
Pore volume	0.56-1.20 cm³/g
Specific surface area	600-1600 m²/g
Capacity as adsorbent for metals	25-900 mg/g

Fig. 8.9 Activated carbon based adsorbent for heavy metal treatment. (Modified Jain et al. 2018)

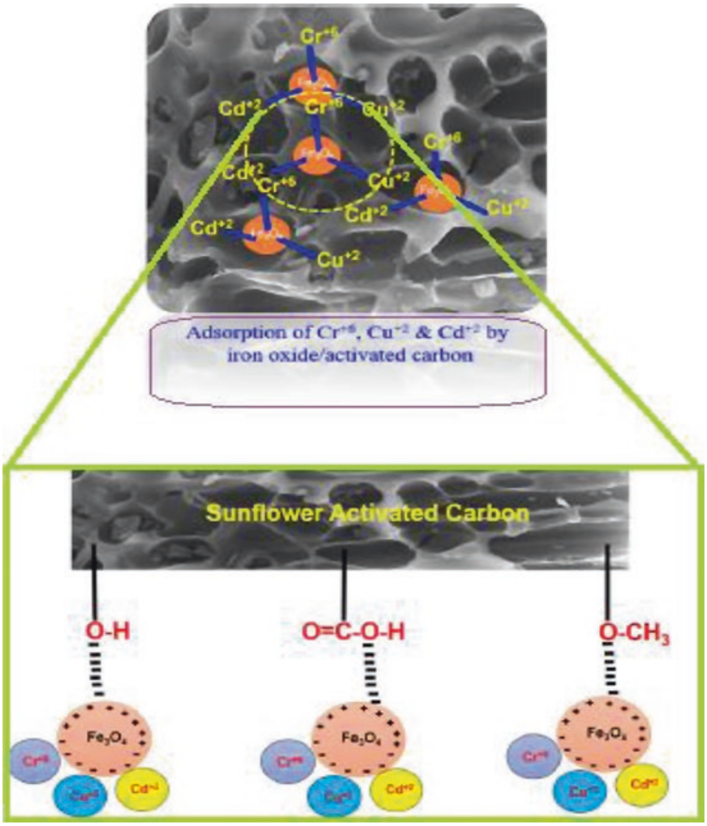


Fig. 8.10 Removal of chromium (VI), Copper (II) and cadmium (II) by iron activated carbon nanocomposite. (Modified Jain et al. 2018)

Jain et al. analyzed the elimination of chromium (VI), copper (II), and cadmium (II) ions from water by applying activated carbon-based nanocomposite (Fig. 8.10). They found excellent adsorption and desorption results (Jain et al. 2018). Activated carbon is applied as sorbents, but it needs complexion agents in order to increase its removal efficiency toward toxic materials. Some other disadvantages also related to their usage including high adsorbent cost, complications of regeneration, and laboriousness of detachment or uncoupling of powdered activated carbon from aqueous solution for recreation.

- Activated Alumina

It is a filter media prepared from aluminum ore so that it becomes pours and possesses lent adsorptive feature. The activated alumina has a tendency to remove pollutants. It needs washing with a suitable regenerator like alum or an acid periodically in order to remain operative effectively. The greatest disadvantage of this system is that its efficiency is maximum only at low pH, hence requiring treatment of

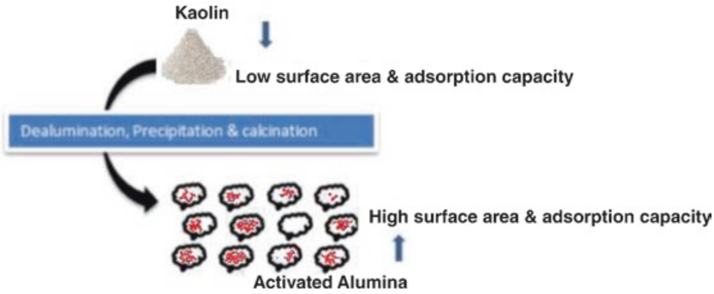


Fig. 8.11 Activated alumina. (Modified Salahudeen et al. 2015)

contaminants with peroxides. Its main application is in reduction of contaminants like arsenic that are of health concern. Salahudeen et al. synthesized kaolin-based activated alumina nanoadsorbents and compared its properties with commercial activated alumina (Fig. 8.11).

The adsorption behavior of as prepared activated alumina adsorbent was done using Langmuir, Freundlich and D–R isotherm models (Fig. 8.11). Results showed prepared material has adsorbent ion properties comparable to commercially available activated alumina. The adsorption features of the newly prepared activated alumina have coefficient of determination value of 0.963 best fit for Langmuir model, while the commercial one had coefficient of determination value of 0.707 (Salahudeen et al. 2015).

- Iron Acetate Coated Activated Alumina

The potential to remove arsenic from water of activated alumina can further be augmented by coating it with iron acetate. The percentage adsorption of iron acetate activated alumina is determined by pH, contact time, and adsorbent dose.

- Cast Iron Filings and Steel Wool

Cast iron filing and steel wool are two iron alloys that are low cost and in some cases waste as well from workshops and for cleaning of food prior to polishing. These two low-cost materials have potential of removing arsenic from water by adsorption. Series of studies showed that almost 90–95% of the arsenic was cleared at favorable pH, which is another favoring factor for these materials to operate in normal range pH environment.

- Nanocomposites Adsorbents

The use of nanocomposites as adsorbents to remove toxic materials from water is beneficial in many aspects. Wide variety of nanoadsorbents are applied to adsorb and eliminate toxicants from aqueous media including carbon nanotubes, carbon-based nanoadsorbents, nanoadsorbents from metal or metal oxides, and polymeric sorbents (Wang et al. 2012).

- Carbon-Based Nanoadsorbents

Carbon-based nanomaterials (inorganic materials) are mostly used for removal of heavy metals because they are nonpoisonous and innocuous. These materials also have high adsorption capacities (Zhang et al. 2009). It is also not easy to eliminate heavy metals at lower level (ppb). With the progress of nanotechnology, fullerene, graphene, and carbon nanotubes are prepared and applied as nanoadsorbents (carbon nanotubes) that are widely used for adsorption purposes because of their unique properties (structural, semiconductor, and mechanical, chemical, and physical) which play vital role in the adsorption of toxicants. Carbon nanotubes are applied as nanoadsorbents separately or modified using other materials (metal ions or metal oxides, organic compounds) in order to increase their sorption capacities.

- Nanoadsorbents from Metal and Metal Oxides

Nanocomposites prepared from metal or metal oxides (such as silver (Ag) metal nanoparticles, ferric oxides (FeO), titanium oxides (TiO), magnesium oxides (MgO), and copper oxides (CuO)) are also widely used for the elimination of aqueous phase toxicants and treatment of industrial effluents. As these metal ions possess high surface area and particular attraction, these metal oxides exhibit efficient adsorption capacity, but their separation from the wastewater is not easy because of their high surface energy and nano-size (Wang et al. 2012).

- Polymer Clay Supported Nanoadsorbents

An efficient sorbent should possess specific functionalities and must have high surface area. Inorganic sorbents showed large surface area but deprived of adsorbing functionalities. Organic polymeric materials contain large amount of functional groups ($-NH_2$), and –OH group) could efficiently adsorb heavy metal ions but their small surface area and less adsorption capacity restrict their uses. To vanquish and control this imperfection, newly encouraging organic–inorganic hybrid materials have been applied to eliminate pollutants from environmental compartments (Samiey et al. 2014). Therefore, new sorbents that not only contain polyfunctional groups but also have high surface area have been synthesized. In such composite, the functional organic substance is coupled to the benefits of a heat-resistant, tough, and long-lasting inorganic material causing well-built bonding harmony for desired pollutant ions. Modified organic–inorganic compounds as sorbent are known as the best efficient approach because of toxicant ions that form complex with them. Such types of products offer combination of beneficial characteristics (physical, chemical, and mechanical properties).

The formation of these hybrid adsorbents has open new doors for deep elimination of pollutants from aqueous media. Polymer clay nanocomposites are used as nanoadsorbents in which clay provide surface area and polymer moiety provide functional groups so hybrid materials with desired application have been prepared and used for the adsorption of toxic metals such as Cu^{2+}, Pb^{2+}, etc. (Liu et al. 2010). Variety of polymer/organoclay composite have been reported in literature such as clay/polystyrene (Okamoto et al. 2000), and poly(methyl methacrylate)/clay composite showed performance toward removal of metals from contaminated water (Şölener et al. 2008).

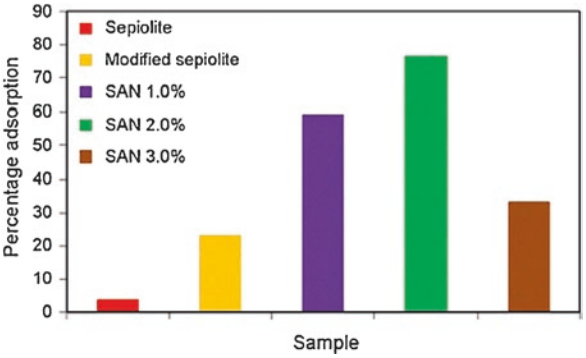
Metal adsorption efficiency of the nanocomposite material can be increased through additional modification. Various types of complexing groups (thiol, amidoxime, mercaptoimidazole. and ionic species including phosphate, carboxy, and carboxymethyl groups), are utilized for this purpose. These groups are introduced on solid adsorbents (polymer/clay adsorbents) to enhance their adsorption capacities (Ulusoy et al. 2003). For example, dithiocarbamate-anchored polystyrene/organosmectite has been used to adsorbed mercury from aqueous solutions with high rate (Say et al. 2008). Similarly, amidoximated polyacrylonitrile/organobentonite composite has been prepared and used for the elimination of copper (II), zinc (II), mercury (Hg), and cadmium (II) from wastewater and industrial affluent (Anirudhan and Ramachandran 2008).

The polymeric chelating materials are synthesized by attaching a functional group to a polymeric backbone (synthetic polymer) (Kato et al. 2003). This functional group shows higher selectivity toward some metal ions. The specific property of metal-chelating ligands is beneficial in many applications, especially in this context. Among different kinds of chelating ligands, the poly(amidoxime) is the most popular chelating ligand. It has the ability to bind the wide variety of metal ions (Raman et al. 2012).

Faizah et al. prepared amidoximated polyacrylonitrile/clay nanoadsorbents to remove copper from prepared wastewater at lab scale (Figs. 8.12 and 8.13). They studied copper removing capacity of nanocomposites using atomic absorption spectroscopy. The prepared nanoadsorbents removed 86% Cu from solution. They also analyzed influence of contact time on adsorption capacity of adsorbent and concluded that the adsorption percentage was increased by increasing contact time (Altaf et al. 2018).

The major disadvantage related to these sorbents including their small sorption potential comparatively poor complexation with toxicants. So researches have been conducted to prepare other nanoadsorbents.

Fig. 8.12 Adsorption percentage of copper at contact time of 120 minutes (Altaf et al. 2018)



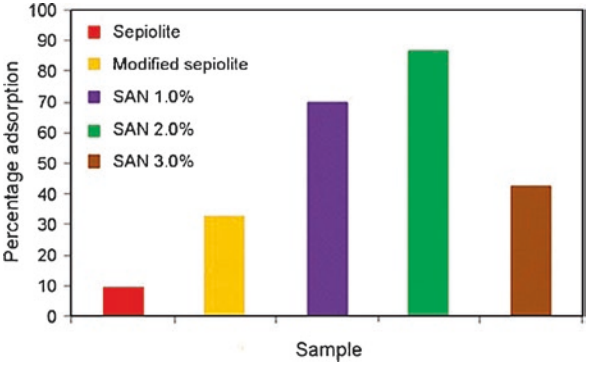


Fig. 8.13 Adsorption percentage of copper at contact time of 240 minutes (Altaf et al. 2018)

8.3.13 Low-Cost Adsorbent

The adsorbent is considered to be low cost if it is found abundantly in nature and does not need much processing or is produced as a by-product from industry. The main sources regarded as low-cost absorbent providers include natural mineral or agricultural and industrial by-products. Usually, these materials are abundantly available and in huge quantities, hence having little economic value making them inexpensive (Lim and Aris 2014).

Some low-cost adsorbents are discussed as follows:

- Chitosan

Chitosan and its derivatives are inexpensive value-added materials. These are made from deacetylation of chitin, which is a naturally occurring material obtained from exoskeleton of arthropods and crustaceans. It is also found in the cell wall of some fungi. Different studies proved that chitosan adsorbent has the ability to remove heavy metals from wastewater and industrial affluent (Liu et al. 2019; Sun et al. 2019).

In chitosan, the presence of amino groups (NH_2-) may undergo protonation to form protonated amine which have the ability to adsorb metal by different kinds of interactive mechanisms including chelation and electrostatic attractions. Pu et al. prepared (Fig. 8.14) magnetic chitosan nanopowder for removal of heavy metals.

The prepared magnetic chitosan nanopowder had high surface area, specific functionalities, and greater adsorption capability. The maximum lead (II) and copper adsorptions were 113.38 mg/g and 92.34 mg/g, respectively. The use of Fe3O4 nanoparticles enables prepared magnetic chitosan nonabsorbent to detach easily via magnetic separation. (Fig. 8.15) nano-Fe3O4 t also enables chitosan to retain excellent adsorption capacity over a pH range. Moreover, the nanocomposite exhibited effective recyclable features of up to several cycles.

They found that magnetic chitosan nanocomposite can be reproduced by ethylenediaminetetraacetic acid 2 Na washing method and showed superior stability and reusability upon five times usage. Overall, the prepared nanocomposite exhibited

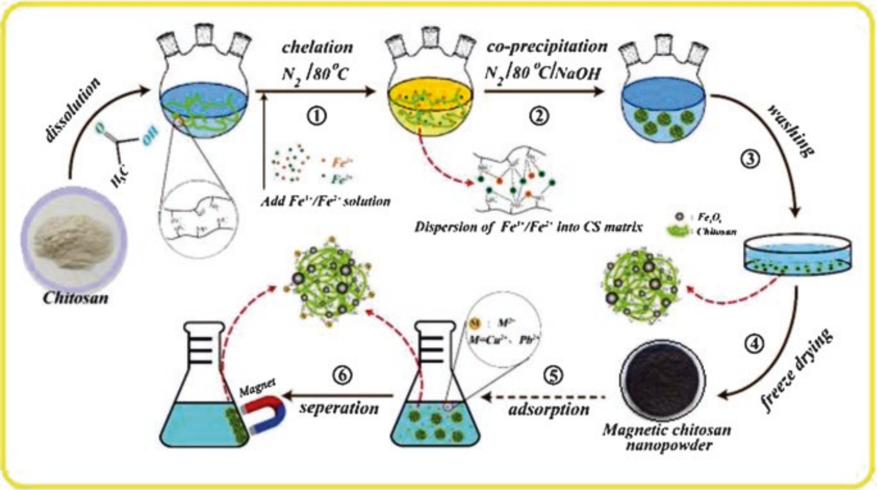


Fig. 8.14 Illustration of synthesis, adsorption, and desorption of magnetic chitosan nanopowder composite for heavy metal adsorption. (Modified Pu et al. 2018)

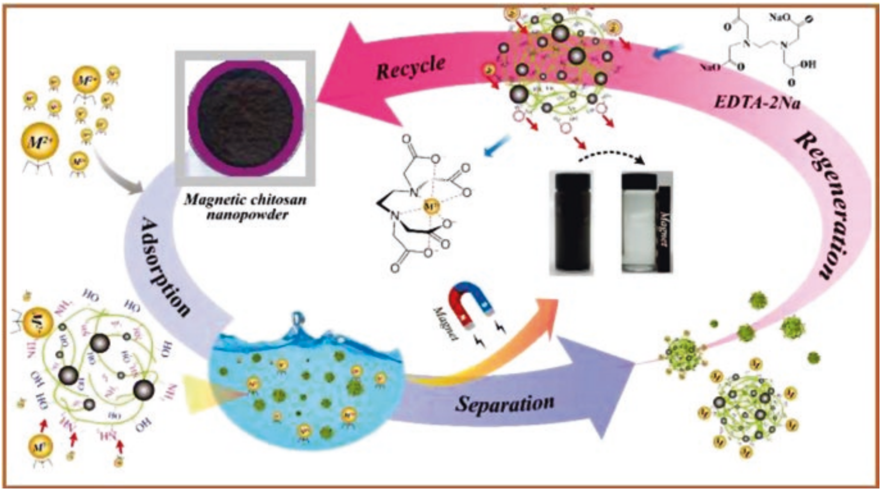


Fig. 8.15 Representation of adsorption and regeneration of magnetic chitosan nanopowder. (Modified Pu et al. 2018)

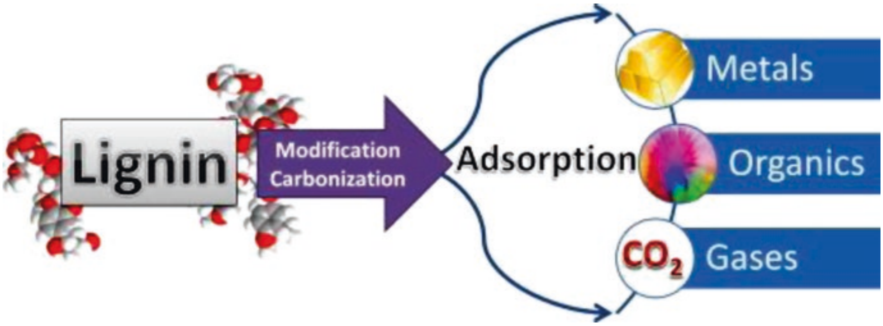


Fig. 8.16 Lignin based adsorbent

greatest regenerating ability and stability in the aquatic environment and outstanding capacity toward heavy metals removal (Pu et al. 2018).

- Eggshell

Eggshells are crystalline calcium carbonate. The natural and boiled hen and duck eggshells are washed several times using tap water and then allowed to dry in air and incubated in hot air oven at 40 °C. Consequently, egg shells were ground to prepare fine a powder. Literature proved that eggshells can be used as adsorbent to treat heavy metals. Eggshells can be converted into nanoporous materials which increase their surface area and improve absorption capacity. Setiawan et al. performed a study to evaluate the adsorption capacity of various eggshell toward heavy metal ions. They found that the nanoporous eggshell showed improved adsorption capacity as activated carbon and can be applied in reducing heavy metal from aqueous media (Setiawan et al. 2018).

- Lignin

It is a complex compound derived commonly from wood. It is a basic building block of plant cell wall and algae. It is the second most widely distributed organic adsorbent polymers available after cellulose (Fig. 8.18). It is an unusual biopolymer due to its heterogeneity in primary structure. Its primary function is to strengthen the wood of the tree. Structurally, it is a three-dimensional aromatic polymer with functional groups, making it effective adsorbent for heavy metal removal aqueous solution (Guo et al. 2008) (Fig. 8.16).

Shweta and coworker prepared nanocomposites composed of carboxymethylated lignin–tetra-ethoxysilane for adsorption of heavy metals. The adsorption of metals was analyzed using atomic adsorption spectroscopic analysis. The obtained results showed carboxymethylated lignin–tetra-ethoxysilane composite adsorbed nickel and cadmium with 70.72 and 81.79%, respectively (Shweta and Jha 2016).

8.4 Agricultural Wastes

Agricultural waste is the reaming product that comes from the growing and initially processed agricultural stuff, for example, organic products, vegetables, fruits, meat, poultry, dairy items, and harvests. Figure 8.17 illustrates different types of agricultural waste This term incorporates both natural and nonnatural waste materials generated by different cultivating exercises, for example, grazing land, dairy farming, breeding, livestock, seed growing, market gardens, even woodlands, and nursery plots. Agricultural waste may be fluid or slurries or solid relying upon the nature of agricultural activities. Agricultural waste may be natural waste, animal waste, and plant waste (Sud et al. 2008) as shown in Fig. 8.18.

The term agricultural waste is associated with all leftover and residual products of the agricultural activities which are needed to dispose of as they do not have direct economic value for the farmers. In order to convert these wastes into valuable products, special process and techniques are required. In some case, mainly in field crops and vegetables, the removal, transport, and processing of wastes are economical. Although the amount of waste material generated by the agronomic activities is considerably small in comparison with wastes produced by other industrial activities, the pollution potential of agricultural waste is high on a long-term basis. For example, the land dispersion of composts and slurries may result in water and soil pollution. In the case of animal excreta, a plethora of toxicants and pathogens can cause severe surface and groundwater pollution (Naidoo and Olaniran 2014).

Nowadays, agricultural waste materials have been used as economic and environment-friendly adsorbents (Bhatnagar and Sillanpää 2010; Dubey and Gopal 2007; Kaliannan et al. 2019; Rehman et al. 2019). Agricultural wastes especially those that contain cellulose have a high biosorption capacity. Adsorbents from plant wastes can be used with or without modification for the reduction of a pollutant from aqueous media. Generally, chemical modification of plant wastes enhances their adsorption capacities as compared to unmodified (Kaliannan et al. 2019; Ngah and Hanafiah 2008).

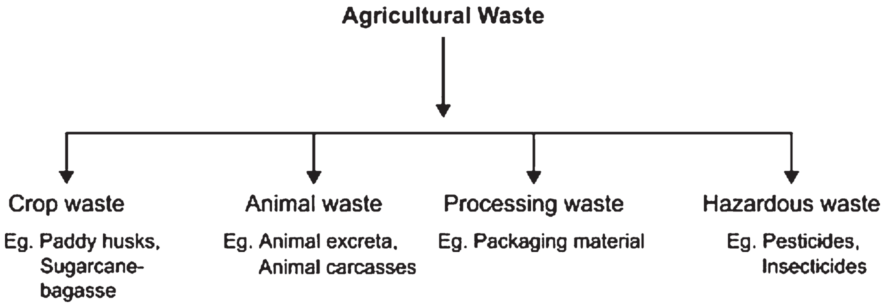


Fig. 8.17 Types of agricultural waste materials

Fig. 8.18 Agricultural waste materials

8.4.1 Agricultural Waste as Low-Cost Adsorbents

The idea of using various agricultural waste materials for the remediation of heavy metal from water has been explored in number of studies (Bhatnagar and Sillanpää 2010; Bilal et al. 2013; Farooq et al. 2010). Scientists examined the effectiveness of different organic waste products as sorbents for heavy metals. The major plus point of this strategy in contrast with others is lower cost when natural waste materials are utilized. Due to these benefits, the utilization of different waste products for metal remediation from wastewater has been highlighted. These waste materials ranged from industrial materials and natural waste materials such as agricultural product and by-product (Inyang et al. 2016; Tripathi and Ranjan 2015).

Agricultural products and by-products is an abundant waste material, and needs to be disposed of properly. There are different methods that can be used for agricultural waste disposal, among them in situ burning is mostly used which produces CO_2 and some other toxicants, thus are harmful for environment. This motivates the alteration of agricultural waste and by-products into beneficial and value-added products. One promising solution is to use this waste as low-cost ion exchange or sorbent material that can expel toxicants from aqueous media (Morin-Crini et al. 2019).

Different agricultural wastes such as coconut husk and rice husk, palm oil, nutshell, and fruit bagasse have been used as adsorbents as reported in many studies. Sawdust and wood dust are promising adsorbents. The dust is comprised of fine wood items, which is made up of lignin, cellulose, and hemicelluloses that are polyphenolic compounds having a great tendency to bind heavy metals through different mechanisms. Seaweeds are natural and abundant source of biosorption materials. Biosorption has shown promising results toward toxic metal removal from industrial effluents and is remarkably low cost. Other sorbents such as carbon anode dust (cad), rice husk, and coconut husk are used for heavy metal removal (Crini et al. 2019) (Fig. 8.19).

There are various factors affect the adsorption process. These are namely the characteristics of adsorbent, the nature of adsorbate, ionic concentration, organic matter, pH and temperature contact time, and kinetics of adsorption (Crini et al. 2019; Sud et al. 2008).

Kazemipour analyzed the removal of copper, zinc, lead, and cadmium in industrial wastewater using activated carbon prepared from hazelnut, pistachio, nutshells of walnut, almond, and apricot stone. The activated carbons generated from such materials showed high surface areas. Adsorption studies conducted on such kinds of activated carbon indicate good adsorption ability toward copper, zinc, cadmium, and lead (Kazemipour et al. 2008).

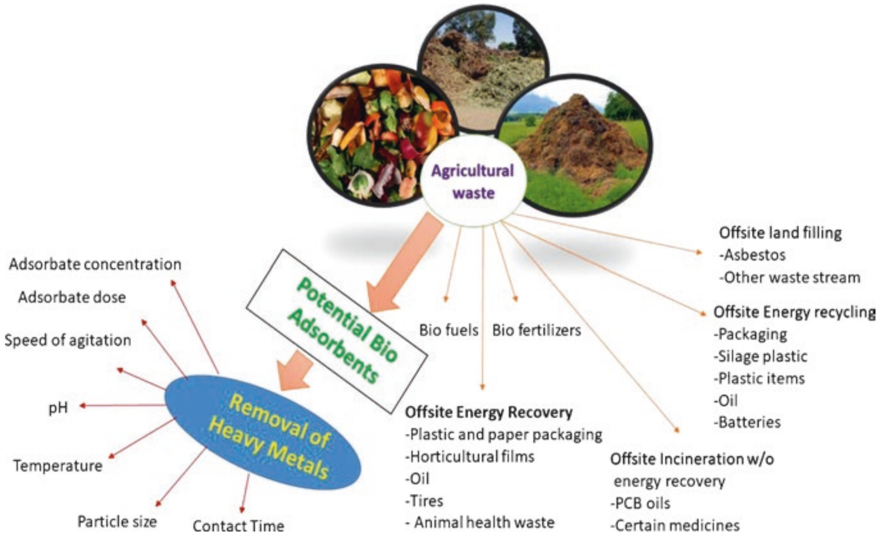


Fig. 8.19 Agricultural waste as adsorbents for removal of heavy metals

- **Removal of chromium**

Different anthropogenic activities release toxic Cr in natural environment (Bhatnagar and Sillanpää 2010). Extensive research work has been devoted to the elimination of heavy metals using waste agricultural materials. A number of agricultural materials including hazelnut shells (Bulut and Tez 2007), orange peels (Annadurai et al. 2003), maize cobs (Ma et al. 2019), soybean hulls (Demirbas 2008), jackfruit (Inbaraj and Sulochana 2004), wheat bran (Kaya et al. 2014), and soybean hulls in pristine or modified form has been applied for aqueous media remediation. Different plants including coconut fiber pith, *Acacia arabica*, pine, cactus, and eucalyptus and various parts of some specific plants such as leaves and needles have also been reported for chromium adsorption. Such materials showed 90–100% efficiency at optimum pH range (Das and Mathew 2011). Rice husk in pristine form and in activated rice form was utilized for chromium (VI) removal, and the obtained data were compared with commercially used activated carbon (Mohan et al. 2006).

Fan et al. prepared nanocomposite using tea waste and Fe_3O_4 nanoparticle and analyzed its adsorption capacity for removing hexavalent chromium aqueous solution. The prepared composite tea waste/Fe3O4 showed maximum adsorption capacity of 75.76 mg g1 based on the Langmuir model. The desorption and regeneration capacity of TW/Fe_3O_4 adsorbent was also analyzed. Their results showed tea waste/Fe_3O_4 composite had excellent recycling potential. Almost 70% of the hexavalent chromium was converted to Cr(III) in this study. This study proved that tea waste/Fe3O4 composite can be used as effective sorbent for Cr(VI) adsorption from waste stream industrial affluent (Fan et al. 2017).

Additionally, beech sawdust, sugarcane, and bagasse were also analyzed for Cr removal. Utilization of mustard oil cake for chromium adsorption has also been studied. Literature showed that chromium adsorption rate using agricultural waste is quite high and ranged from 50 to 100% (Sud et al. 2008).

- **Removal of Lead (Pb)**

The removal of Pb from environmental compartment is of great concern as it develops strong binding with some particles including oil, sewage sludge, and sediments. Different kinds of agricultural waste materials including peanut shells, soybean hulls, rice straw, bagasse, sugarcane, and walnut shells have been applied for lead adsorption (Mishra and Patel 2009; Saka et al. 2012; Singh et al. 2006). Activated carbon synthesized from agricultural waste was also used by many scientists, and its excellent power for lead adsorption has been reported (Abbaszadeh et al. 2016; Noor et al. 2017). Other agricultural wastes such as bagasse fly ash (Golbad et al. 2017; Nguyen et al. 2018), sawdust (Acharya et al. 2018), and rubber wood sawdust (Biswas and Mishra 2015) have been also checked for lead removal.

- **Removal of Cadmium (Cd)**

Cadmium and its compounds as compared to other heavy metals are relatively more water soluble and therefore are mobile and tend to bioaccumulate in environmental compartments. Various agricultural wastes are used to adsorbed Cr and its compounds from aqueous solution. In some studies, rice and wheat bran were analyzed for cadmium adsorption, and excellent results were reported (Motaghi and Ziarati 2016). Studies were conducted on use of other agricultural waste including rice husk and rice polish in both pristine and composite forms for effective cadmium removal. The bark of some plants including *Picea glehnii* and *Abies sachalinensis* and biomass of dried plants (*Parthenium*) were checked for cadmium removal. Adsorption experiments performed using hazelnut shells, green shell, walnut shells, and peanut hulls exhibited good results toward cadmium adsorption. Some other adsorption studies conducted using activated carbon prepared coir pith, bagasse pith, and dates and peanut shells. Their cadmium adsorption capacity was found to be up to 98% (Sud et al. 2008).

Ansari and coworker conducted as a study to produce a valuable absorbent of walnut agricultural waste. Walnut shell has characteristics including large carbon contents, low humidity, and availability and is successfully used as a cadmium adsorbent. Preparing activated carbon with less heat energy usage can be considered as an alternative adsorbent for industrial activated carbon. The activated carbon derived from walnut shell was significantly effective in removing cadmium from the aquatic environment. They obtained maximum cadmium adsorption at pH 6. The Cd adsorption by activated carbon produced from walnut shell was described in two adsorption isotherms, Langmuir and Freundlich. These results showed that walnut shell as an agricultural waste can be used for the synthesis of effective cadmium absorbent (Ansari et al. 2018).

- **Removal of nickel (Ni)**

Adsorption experiments for Ni removal were conducted using *Cassia fistula* biomass, and the obtained results showed 99–100% adsorption capacity (Alam et al. 2018). Nickel removal and sequestering efficiency of waste tea leaves were also analyzed. Excellent results were obtained in this regard (Shah et al. 2015). Other agricultural wastes including hazelnut, sawdust of maple, peanut, cotton seeds, walnut, black locust and oaks, pecan, soybeans, and corncobs have been reported as promising materials; round nutshells in natural or altered form were also used for nickel removal from aqueous media (Sud et al. 2008). Sugarcane bagasse in unmodified form showed more than 80% adsorption capacity (Garg et al. 2008). In one study, agricultural waste, such as rise husk, and industrial waste, such as fly ash, were analyzed for adsorption of heavy metals in electroplating industries. The obtained result showed that rice husk was effective in the simultaneous removal of iron, leads, and nickel, while fly ash removed cadmium and copper. This study concluded that the percentage of heavy metal removal is affected by many factors including dose adsorbent, contact time, and optimum pH range (Fan et al. 2017).

8.5 Conclusion

The Earth's crust naturally consists of heavy metals (including Pt, Pd, Ag, Cu, Cd, etc.) and their components. Abrasion and dissolution of mother rocks also contribute to their presence in the environment. In addition to natural sources, these pollutants also enter in ecosystems through wastewaters generating from human-induced activities such as the operation of chemical preparing and tanning and from various industries such as leather industries, electronic and electric industries, etc. Some of the organic pollutants are vulnerable toward biological degradation, but metal ions cannot degenerate into harmless end product and are persistent in the environment. These pollutants are the chief source of environmental pollution, and their removal from various environmental components is necessary. These metallic ions (toxic elements) even in less concentration pollute drinking water and can be easily accumulated by living organisms (human body), causing different lethal disorders and illnesses. Therefore, it is inevitable to eliminate these toxicants from industrial slug and wastewater. A large number of approaches such as coagulation, solvent extraction, chemical and electrochemical techniques, ultrafiltration, and reverse osmosis have been used for the removal of toxicants. However, most of these processes are unsuitable and unsatisfactory due to the disposal of dirt, their excessive operational price, less productivity, and less effectiveness. Additionally, they are not applicable for large number of pollutants, and are less efficient for the treatment of small quantity of metal ions and other treatment problems because of continuous production of toxic sludge hinder their effective utilization for wastewater treatment. The process of adsorption is one of the most popular, convenient, superior, and beneficial strategies above any other processes for the treatment of polluted industrial effluents and removal of contamination from water supplies.

The main advantage of adsorption is the regeneration of sorbents with appropriate desorption process, and most of such regenerations need low maintenance cost with excess efficiency and is easy to operate. Various conventional and nonconventional adsorbents are used for this purpose such as activated carbon, activated alumina, carbon nanotubes, polymer clay composite, metal oxide-based nanoadsorbents, clays, zeolites, lignin, chitosan, eggshell, etc. The main downside related to these sorbents including their small sorption potential comparatively poor complexation with toxicants. Recent endeavors are devoted to using agricultural waste as low-cost adsorbent. There are many kinds of agricultural waste such as rise husk, coconut husk, hazelnut, sawdust of maple, peanut, cotton seeds, walnut, black locust and oaks, pecan, soybeans, and corncobs that have been reported as promising materials. Round nutshells in natural or altered form were also used for nickel removal from aqueous media. Literature showed that chromium adsorption rate using agricultural waste is quite high and ranged from 50–100%. Similar excellent results were obtained for other heavy metal remediation using low-cost agricultural waste adsorbents.

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Chapter 9

Biosorption of Metal Ions Present in Industrial Wastewater

Dhanya Vishnu, Kannappan Panchamoorthy Gopinath, and Balaji Dhandapani

Contents

Abstract Immobilization of magnetic nanoparticles and enzymes with the aid of chemicals and metals as their major support is extensively used in numerous applications, owing to their superparamagnetic nature, surface interaction, alteration, and binding specificity with the appropriate proteinaceous substances. The metal nanoparticles are widely accepted as the antioxidants, and their prevalent usage inadvertently releases toxic metals that contribute as a major threat to our environment. This leads to the development of the integrated biocatalyst that acts as the robust carrier in the removal of hazardous pollutants in the wastewater. Heavy metals are considered to be a major threat to our environment due to industrialization and urbanization.

Among various metals, International Union of Pure and Applied Chemistry has termed the heavy metal based on their intensity of toxicity and hazardous effects. The agency for toxic contaminants and disease registry has listed the various metals

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like Be, Ba, Cu, Co, Cr, Ni, Zn, Mn, As, Pb, Hg, Cd, Pd, U, and V as the toxic pollutants responsible to damage the genetic mechanisms of both flora and fauna community via free radical production. Superparamagnetic support nanomaterials are prepared via Fe, Cu, Ni, Mn, and Mg and coated with the distinct materials like mesoporous and amorphous silica, polyvinyl alcohol and pyrrolidine, polyethylene glycol, polystyrene, chitosan, dextran, starch, gelatin, polystyrene, polyacrylic acid, and poly(methyl methacrylate). These surface-modified superparamagnetic support nanomaterials tend to possess the enhanced stability and specific reactivity in the system and are used in the elimination of organic and inorganic hazardous contaminants in the industrial wastewater.

Keywords Immobilization · Nanoparticles · Plant extracts · Pollutants · Contaminants · Industrialization · Urbanization · Organic · Inorganic · Hazardous

9.1 Introduction

Industrialization and urbanization mainly elucidate the discharge of major hazardous pollutants like heavy metals and polyhydrocarbons into the water and pollutes the ecosystem. By implementing the different phenomena of clean technology, these pollutants are prevented from contaminating the numerous sites of the environment. Figure 9.1 gives the details about the numerous contaminated sites. Nevertheless, these toxic contaminants prevail in the soil as sediments and pollute the major part of the aquatic organisms that exist in the environment. These contaminants play a prominent role and cause severe health problems to the flora and fauna that remains in our ecosystem (Muthukrishnan et al. 2015). Agriculture too

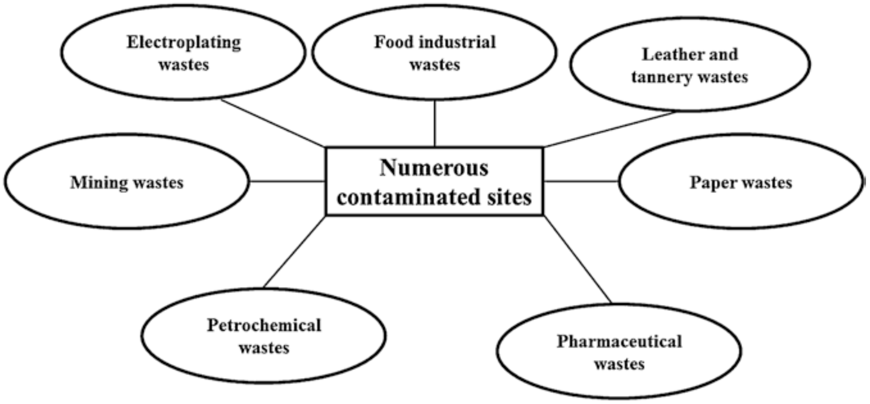

Fig. 9.1 Sources of numerous hazardous pollutants. The various contaminated sources that pollute the environment. (Modified after Mishra et al. 2018)

causes a severe threat to the environment as pesticides and fertilizers get accumulated in the ecosystem contaminate the major part of the groundwater. Also, several other activities like silviculture, aquaculture, toxic pathogens, fertilizers, hazardous chemicals, and numerous metals decrease the quality of surface water (Naushad 2018). Accumulation of the toxic metals in the tissues of the human beings above the certain permissible limits results in the numerous diseases and disorders. Also, heavy metals get accumulated in the soil also pollute the environment with the major effects. These pollutants are nonbiodegradable in nature, and their prevalent existence causes and affects many humans, animals, and microbial sources that exist in the ecosystem. Above the certain permissible limits, these heavy metals and other pollutants cause the deadly effect to both the flora and fauna that exists in our ecosystem (Table 9.1).

Table 9.1 Heavy metal pollutant sites and its health effects

Hazardous pollutants	Allowed permissible range (mg/L)	Contamination sites	Vulnerable health effects
Arsenic	0.05	Production contaminants from industries of glass and electronics	Cancer, vulnerable effect in the circulatory system and skin problem
Antimony	0.006	Various pollutants from petroleum waste refineries, electronics, and ceramic waste materials	Decreased sugar contents in the blood and increased cholesterol amount
Cadmium	0.005	Contaminants arise from galvanized pipes, numerous waste from metal refineries, batteries, and paints	Kidney issues
Chromium	0.1	Contaminants from steel, leather, and tannery sources	Dermatitis issue
Copper	1.3	Contaminants from plumbing and wood industrial sources	Kidney- and liver-related issues with gastrointestinal health problems
Lead	0.015	Numerous pollutants from the plumbing industry and natural deposits getting eroded from the ecosystem	Physical and mental problems and kidney-related issues with increased blood pressure
Mercury	0.002	Contaminants from factories and various industrial refineries and also leaching from landfills	Kidney-related issues
Selenium	0.05	Pollutants discharged from various petroleums, mines, and metal refineries	Blood circulation issues and hair damage
Nickel	0.20	Electroplating waste pollutants	Human toxic carcinogen, asthma, cough, dermatitis issue, and nausea

9.2 Different Methods for Metal Pollutants Removal: Overview

Researchers have found numerous physiochemical methods like hydrolysis, membrane process, pyrolysis, precipitation, floatation, electrocoagulation, adsorption, and ion exchange for the removal of these hazardous contaminants from our environment (Al-Shannag et al. 2015). Figure 9.2 gives the conventional methods in the removal of hazardous contaminants from the wastewater. In both the technical and management concerns, conventional techniques have the most significant importance in compared to the traditional methods, where the removal of metal pollutants and other hazardous components is considered as the major drawback of the system. High operational cost, degeneration of sludge, and applying the various laborious techniques are considered to be the major disadvantages of the system (Calvo et al. 1997; Padil and Černík 2013). The above listed methods are applicable only to remove the high concentrations of the heavy metals, whereas at low concentrations, they are not more efficient which is the major drawback to look for the cost-effective alternative technologies to remove the hazardous components from the system (Demirbas 2008).

9.2.1 *Adsorption: Magnetic Nanoparticles as Adsorbents in the Elimination of Hazardous Metal Contaminants*

Adsorption is the physical phenomena used to get rid of the toxic hazardous metal and other pollutants in the various industrial effluents. Adsorption may occur in two ways: physisorption and chemisorption. Numerous forces like van der Waals,

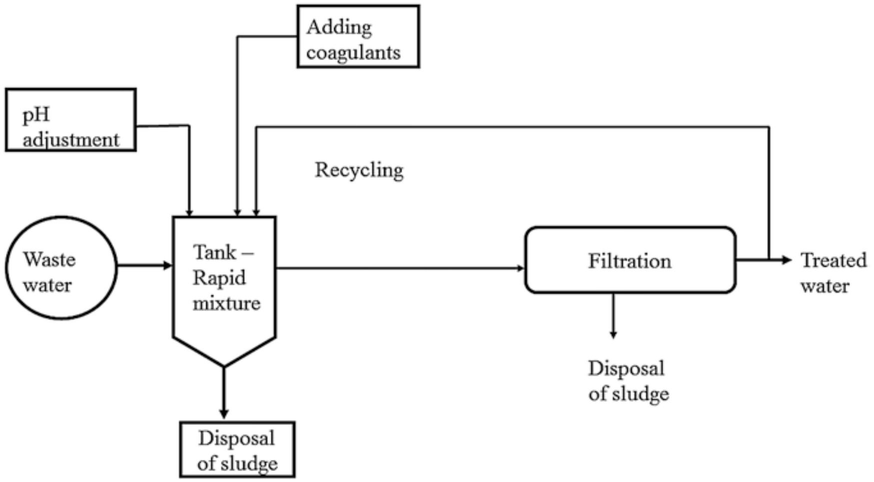

Fig. 9.2 Modified schematic representation on conventional treatment on the removal of metal contaminants

electrostatic and covalent involved in the transfer of these pollutants across the different phases of solid and liquid (Mishra et al. 2018). Recently, magnetic nanoparticles impregnated with the enzymes and metallic sites have been widely utilized for the formation of numerous valuable products and also in the degradation of many toxic components like phenolic substances, dyes, heavy metals, and polyhydrocarbons eliminated from harmful pesticides and insecticides (Vishnu et al. 2017). Also, metallic sites added as the second catalytic site have widely extensively improved their adsorption efficiency which was extensively applied in the various hazardous dye degradations from the industrial effluents. The unique colloidal feature of nanoparticles are extensively used as the biological probes in the synthesis of nanozymes, as device in the electronic system and sensory platforms (Sardar et al. 2007). Due to the distinct features of simple recovery and reusability, these magnetic particles are considered as the primary support for producing the bioactively catalytic substances. But the high cost, greater energy consumption, and chemical contamination which results in the elimination of major secondary pollutants are considered to be the major drawbacks of following these methods (Guo et al. 2014). Nanoparticles modified with the addition of unique functional sites are majorly used in the bioseparation field, owing to their special morphological and topographical characteristics of their high specific area, porosity, structural composition, and determined size. During enzyme immobilization, loading enzymes upon these particles exhibit the enhanced activity recovery and enzymatic activity with the greater operational and thermal stabilities (Kumar et al. 2014). The carbon particles integrated with the magnetic particles are found to be the most compendious approach where the above nano-aggregates have shown the enhanced adsorption capacity with the highest purity upon the bulk production in the suitable appropriate conditions (Ji et al. 2018). The approach of integrating the plant extracts with the nanoparticle for their unique characteristics of the polyphenolic constituents, combined with the numerous polymers and oligomers enhanced the stability of these nano components. These multifunctional characteristics cause a great boom in the growth of green chemistry (Arasu et al. 2019). Nanoparticles owing extensive physiochemical characteristics, which are used in many applications like drug delivery, electro sensing process, bioremediation where they are considered as the prominent carrier molecules in the heavy metal removal as well as in the dye degradation. The green nanoparticles are prepared with numerous methods like enzymatic, chemical, physical, and biological process. The physical phenomena include adsorption, pyrolysis, desorption using laser technologies, ball milling, diffusion flame synthesis, epistasis using a molecular beam, plasma arching, and thin-film techniques (Joerger 2000). The chemical phenomena include coprecipitation, hydrolysis, electrodeposition, sol–gel process, Langmuir–Blodgett method, chemical vapor, catalytic routes, and solution deposition method in the presence of high beam of radiation and enhanced concentrated reagents (Herizchi et al. 2016; Herizchi et al. 2016). The biological phenomenal system is considered to be the greater efficient system due to the presence of many natural constituents like saponins, tannins, alkaloids, tannins, steroids, and other primary nutrients that weed out the hazardous secondary contaminants from the ecosystem through the bioreduction process (Kuppusamy et al. 2016).

9.3 Preparation of Nanoparticle

The different materials like numerous polymers, polysaccharides, and proteins are used to synthesize the nanoparticles that usually increase the treatment. The various factors like the surface characteristic feature of charge, intensity over the degree of toxic nature, biodegradable and biocompatible nature, size, and solubility decide the nanoparticle preparation (Zimmer and Kreuter 1995). The different methods used to produce nanoparticles include are polymerization, solvent evaporation and diffusion, supercritical fluid technology models, and coacervation techniques. The different hydrophilic and hydrophobic drugs are prepared using both the solvent evaporation and the diffusion method where different solvents like ethyl acetate, dichloromethane, and chloroform are used to mix the polymer with continuous stirring. Finally, ultrasonication is done to reduce particle size (Zambaux et al. 1998). Ultrasonication is followed with the polymerization technique where the particles are allowed to suspend in a specific medium, and the mixture is allowed to settle, and the end products are obtained after ultracentrifugation. Appropriate stabilizers are used with the definite concentration which has been considered as the major role in the formation of nanoparticles (Puglisi et al. 1995). The nanoparticle synthesis of hydrophilic polymers that includes gelatin, sodium alginate, and chitosan is prepared using coacervation method. Here the formation of two-aqueous phases occurs where one phase results in the formation of di-block ethylene oxide copolymer, and the other phase results in the formation of polyanion sodium triphosphate. These particles are found to interact with the electrostatic forces in the room temperature (Calvo et al. 1997). The disadvantage of this method is the usage of excessive chemicals, hence an alternate method is superfluid technology, could be used to prepare the nanoparticles with biodegradable nature are considered to be safe to the environment. This method is normally preferred for the large-scale production where solvent used is at their constant pressure and critical temperature. The major disadvantage was the complex design and cost of the equipment (Sun et al. 2005).

9.4 Characterization of Nanoparticle

Based on the distinct functional entities and various elemental components with the morphological characteristics of size, structure, and shape, the synthesized nanoparticles are characterized by numerous analytical techniques as follows. Fourier transform infrared spectroscopy is to assess the specific functional entities on the nanoparticle surface that are obtained by infrared adsorption and spectral emission. Transmission electron microscopy identifies the shape, distribution, and size of the distinct nanoparticles. When a beam of electrons are passed to the scanning electron microscope, based on the reacted components, the size of the nanoparticles is evaluated, and energy dispersive spectroscopy is used to identify the reacted components when X-rays are pass into the spectrum. The crystalline structured product is determined using powder X-ray diffraction when the monochromatic ray gets passed into the structure of the particle. Based on the distinct wavelength, the size of the particles is evaluated using UV-visible spectrophotometer. Dynamic light scattering determines the charge and hydrodynamic structure of the particle based on the scattered rays of an incidental photon (Rajeshkumar et al. 2019).

9.5 Removal of Pollutants Using Different Nanoparticles

9.5.1 Silver Nanoparticles

Silver nanoparticles have a different task in the physical, biological, and chemical properties with the specific electrical and plasmon resonance at their surface. Since nanotechnology has a distinct property to remove the hazardous pollutants from industrial wastewater from other methods like colloidal, electrochemical, oxidation, thermal decomposition, sonochemical, microwave, and photocatalytic degradation, silver particle production emerges as the boom in the removal of these toxic pollutants (Sobana et al. 2006). The major disadvantage is the elimination of these nanoparticles to the ecosystem upon their synthesis, integration, production, and percolation into the soil. Such particles get accumulated and pollute the environment due to their nonbiodegradable nature. So it affects the ecosystem from the primary microorganisms to the higher level flora and fauna in the aquatic environment (El-Kassas et al. 2016). To reduce the toxicity, these silver particles were integrated with the various plant extracts where the polyphenolic constituents play a distinct part as the natural capping and reducing agent. Also, it enhances the overall system stability (Lingamdinne et al. 2017) (Table 9.2).

9.5.2 Magnetic Nanoparticle

Due to their specific characteristic feature of recovery and reusability, magnetic nanoparticles are probably considered in most of the industries. It has numerous advantages such as specific interstitial pores that help the prolonged reactivity among them when compared to other particles and are extensively used in the environmental remediation process. Both top-down and bottom-up approaches which include machining, milling, and etching have been promoted for the growth of these nanomaterials. But other factors like capital expensive, high utilization of energy, their operational cost, irregular surface features, and the elimination of toxic pollutants due to the component reactivity lead to the alternate method that paves the way for the plant extracts to be integrated with the magnetic nanoparticles (Syafiuddin et al. 2017). The polyphenolic components of the various plant extracts due to their specific properties are widely integrated with these nanoparticles and have been extensively studied in the various bioremediation aspects (Machado et al. 2013).

Table 9.2 Nanoparticle type and its source used in the removal of toxic pollutants

Type of nanoparticle	The extract used in the synthesis	Size of the nanoparticle (nm)	Morphological characteristics analysis	Extensive applications	References
Silver	*Eucalyptus citriodora* and *Ficus Benghalensis*	20 nm	Scanning electron microscope, transmission electron microscopy, UV-visible spectroscopy, and thermogravimetric analysis	Fabrication of antibacterial textiles and finishing	Iravani (2011)
Silver	*Mussaenda erythrophylla*	50–80 nm	Fourier transform infrared spectroscopy, scanning electron microscope, energy dispersive X-ray analysis, X-ray diffraction, and zeta potential	Degradation of azo dye and methyl orange using sodium borohydride as the reductant	Varadavenkatesan et al. (2016)
Silver	*Tamarind* extract	100–500 nm	Transmission electron microscopy, atomic force microscopy, UV-visible spectroscopy, X-ray diffraction.	Chemical vapor sensing	Ankamwar et al. 2005)
Magnetic nanoparticle	*Cnidium monnieri*	49.45 nm	X-ray diffraction, Fourier transform infrared spectroscopy, field emission scanning electron microscope, Brunauer-Emmett-teller, atomic force microscopy, and X-ray photoelectron spectroscopy	Removal of lead, chromium	Lingamdinne et al. (2017)
Silver nanoparticle	*Stevia rebaudiana*	2–50 nm	Transmission electron microscopy, and X-ray diffraction	Formation of aromatic compounds	Yilmaz et al. (2011)
Silver nanoparticle	Sorghum bran	10 nm	Field emission scanning electron microscope, high- resolution transmission electron microscopy, X-ray diffraction,and energy dispersive X-ray analysis	Degradation of bromothymol blue	Njagi et al. (2011)

Magnetic nanoparticle	*Eucalyptus tereticornis*, *Melaleuca nesophila*, and *Rosmarinus officinalis*	50–80 nm	Fourier transform infrared spectroscopy, scanning electron microscope, energy dispersive X-ray analysis, and X-ray diffraction	Decolorization of azo dye	Wang et al. (2014)
Zinc nanoparticle	*Tabernaemontana divaricata*	20–50 nm	Fourier transform infrared spectroscopy, scanning electron microscope, transmission electron microscopy, and X-ray diffraction	Photocatalytic degradation of methylene blue in the presence of sunlight, methylene blue, and methyl orange	Raja et al. (2018)
Silver nanoparticle	*Aconitum violaceum*	20 nm	Fourier transform infrared spectroscopy, transmission electron microscopy, X-ray diffraction	Calorimetric detection of lead using silver nanoparticle	Khan et al. (2018)
Titania nanoparticle	*Aganonerion polymorphum*	10–20 nm	X-ray diffraction, transmission electron microscopy and scanning electron microscope, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, gas chromatography – mass spectrometry	An organic protective film which is a cointegration of titania nanoparticle and the *Aganonerion* plant extract acts as protective coverage and organic corrosion inhibitor in a simulated ethanol fuel bend	Hoai Vu et al. (2019)

(continued)

Table 9.2 (continued)

Type of nanoparticle	The extract used in the synthesis	Size of the nanoparticle (nm)	Morphological characteristics analysis	Extensive applications	References
Titania and copper nanoparticle	X-ray diffraction, HR-TEM and SEM, FTIR, UV-visible absorption, and photoluminescence studies	2D phase mesoporous characterized leaf extract integrated with cu and TiO_2 enhances the photocatalytic conversion of benzene to phenol (97%).	X-ray diffraction, high resolution-transmission electron microscopy and scanning electron microscope, Fourier transform infrared spectroscopy, UV-visible absorption, and photoluminescence studies	2D phase mesoporous characterized leaf extract integrated with cu and TiO_2 enhances the photocatalytic conversion of benzene to phenol (97%).	Devaraji and Jo (2019)
Magnetic nanoparticle	Oolong tea extracts	40–50 nm	Fourier transform infrared spectroscopy, scanning electron microscope, energy dispersive X-ray analysis, X-ray diffraction, and absorbance spectroscopy	Degradation of malachite green	Huang et al. (2014)

9.5.3 Other Metallic Nanoparticles

The various metals and its integration with an external substance form nanoparticles at different environmental conditions such as pH, temperature etc. The various metallic nanoparticles produced from the *Gum kondagogu* biopolymer have been assessed at different time interval and pH. This biopolymer considerably has a greater proportion of uronic acid with the distinct functional groups of hydroxyl, carbonyl, acetyl, and carboxylic. Silver nanoparticles are synthesized with the time of 60 min at the various pH 3, 4, 5, and 7 at 45 °C. Gold nanoparticles are synthesized within 60 min at the various pH 4,5,6,8, and 10 at 75 °C, whereas the platinum nanoparticle is produced within 15 min at the pH 4,5,6,8, and 10. These nanoadsorbents are prominently used to remove the toxic metal contaminants and also in the degradation of polyhydrocarbons and phenolic compounds that are present in the pharmaceutical industry (Vinod et al. 2011). Gold nanoparticles are synthesized via Turkevich–Frens method with specific reducing agents under the appropriate reaction conditions of temperature, the concentration of salt, the reducing agents, and the pH. The usage of the stabilizing agent's concentration under the appropriate reaction conditions is considered to be the major disadvantage in the production system (Herizchi et al. 2016). The Brust-Schiffrin method is to synthesize the gold nanoparticle with the specific thiolate group that enhances the stability and reusability, and this present method has the disadvantage of using stabilizing agents with biocompatible nature in the system (Oliveira et al. 2005; Puglisi et al. 1995). Also, the morphological features of size and shape of the gold nanoparticles are concerned with the various concentrations of the bioreducing derivatives of the numerous plant extracts (Gonnelli et al. 2015). Gum karaya is an acid polysaccharide widely used as a thickener and emulsifier. When copper gets combined with this component upon their nanoparticle synthesis, they act both as the capping and reducing agent (Padil and Černík 2013). The extensive antioxidant property of aloe vera extracts upon integration with the zinc particle increases their stable nature and is widely used in the pharmaceutical (Elia et al. 2014).

9.6 Agricultural Residues: As the Adsorbent in the Removal of Pollutants

Agro-industrial wastes are predominantly constituted as the numerous industrial by-products due to the excessive amount of carbon and oxygen contents with the existence of numerous bioactive components. The department of energy from the United States has evaluated that more than 500 million tons of the numerous agro-based residues are available as the raw material with the considerable price limit of 20–50$/ton (Singh Nee Nigam and Pandey 2009). Due to their excessive availability with cheap cost, they are considered as the key component to producing numerous and valuable by-products. Also, these feedstocks are subjected to undergo various phenomena of physical, chemical, and biological treatment for the production of valuable by-products (Okabe et al. 2009). The different kinds of agricultural waste products obtained from rice, sugarcane, cereals, wheat, and beet act as the primary sources since they are rich in starch content. Also, the carbohydrate-rich residues are mostly preferred in the food and the numerous chemical industries (Shin et al. 2009). These agro-based residues have the major constituents of lignin and cellulose entities with the specific functional polar constituents of phenolic, alcoholic, carboxylic, aldehydes, ketones, and ether components. These major groups play a major role in the integration of metal complexes upon their interaction with the different metals (Syafiuddin et al. 2017). Also, numerous organic acids based on the specific functional group react with the metal from the metal complex and play a vital role in the removal of various metal contaminants from the soil (Yang et al. 2006).

9.7 Conclusion

Numerous methodologies have been followed in the removal of polluted toxic contaminants from the wastewater effluents. Though both the conventional and traditional methods are followed in the system, nanoparticles integrated with the plant extracts are extensively used in numerous applications. Different metallic nanoparticles especially the silver nanoparticles are not only used in the antimicrobial applications; they are also mainly used in the bioremediation process. The flavonoids and the other constituents present in the integrated metallic particles not only play a prominent role in the pharmaceutical applications; they are also used in the degradation of various pollutants such as aromatic compounds, polyhydrocarbons, and the different metal removal. Silver nanoparticles and other metallic nanoparticles with plant extracts are known for its wide applications such as antimicrobial activity; they are preferred to be used in the bioremediation especially in the removal of various metal pollutants. Magnetic nanoparticles are preferred for their high surface area and different catalytic reactive sites. They are also preferred for their easy recovery and reusability. Due to the easy separation with the help of magnets, the cost of other cofactors and enzymes is less. The usage of the integrated plant extract adsorbent reduces secondary pollutants generation, hence they are considered as the boom in the growth aspects of green chemistry. The main disadvantage of the system is to consider the fate of the above nanoparticles getting into the environment. These particles may cause a severe threat to the flora and fauna in the aquatic environment. The low cost and excess availability of agricultural residues are used as the major adsorbents in the annihilation of toxic contaminants.

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Chapter 10
Heavy Metal Removal by Low-Cost Adsorbents

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Contents

Abstract Water pollution is one of the foremost environmental issues to deal with worldwide. Heavy metal remediation from water bodies is of particular concern as it persists in environment. Toxic heavy metals released in the water bodies from different sources like fertilizer manufacturing industries, mining, and electroplating which are causing pollution in water and soil systems. Metals like arsenic, lead, and

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cadmium in drinking water cause several health hazards like skin cancer, allergic dermatitis, hypertension, etc. Increase in industrial activity has headed to enhancement of toxic metal contamination in lakes, rivers, and many other water bodies. Thus it is necessary to develop an eco-friendly, cheap, and efficient method to eliminate heavy metals from the effluent water.

Different improved techniques such as chemical precipitation, adsorption, membrane separation, etc. have been designed to decrease the effect of heavy metals. But the most efficient and economically feasible process among them is adsorption. This chapter covers on low-cost adsorbents and their sources and applications in removal of toxic heavy metal ions from effluent. This chapter also includes a brief summary of readily available cheap adsorbents like zeolite, clay, peat moss, chitosan, and their applications.

Keywords Adsorbent · Heavy metal · Pollution · Water treatment · Remediation

10.1 Introduction

The heavy metal can be defined as "any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations." Such elements possess higher atomic weights (Srivastava et al. 2008). Metals such as arsenic, lead, and chromium are able to provoke toxicity at trace level when come in contact with living organisms. Heavy metals are not biodegradable and can easily enter inside human body through drinking water, air, and intake of food. Although some of the heavy metals are essential for proper functioning of body metabolism system. Insufficient supply of these nutrients results in number of diseases. Some of the major threats has been shown in Fig. 10.1. Due to the contamination of these toxic metals in aquatic streams several disasters had been faced in past decades. Accumulation of mercury in fish gradually poisoned human beings indirectly. In the last few decades, there has been a rise in public health globally because of contamination of environment by such toxic metals. Due to increasing demand of energy and their use in different industrial, agricultural, domestic, and technological applications, human exposures to such heavy metals have risen drastically. Heavy metals are recognized as priority pollutants. The maximum contaminant level of different metals and associated health hazards are enlisted in Table 10.1.

Major heavy metal disposal sources are geogenic, pharmaceutical, agricultural, industrial, domestic discharges (Tchounwou et al. 2012). These metals are mainly released to the environment from mineral extraction process. Thus mining actions are measured as the key source of toxic heavy metals. Volcanic actions have also been measured as a contributing source to heavy metal discharge to environment. Toxic metal ions are released into water system from various industries like electroplating industries, electronic equipment manufacturing industries, coal burning plants, petroleum industries, nuclear power plant, leather industries, steel plants,

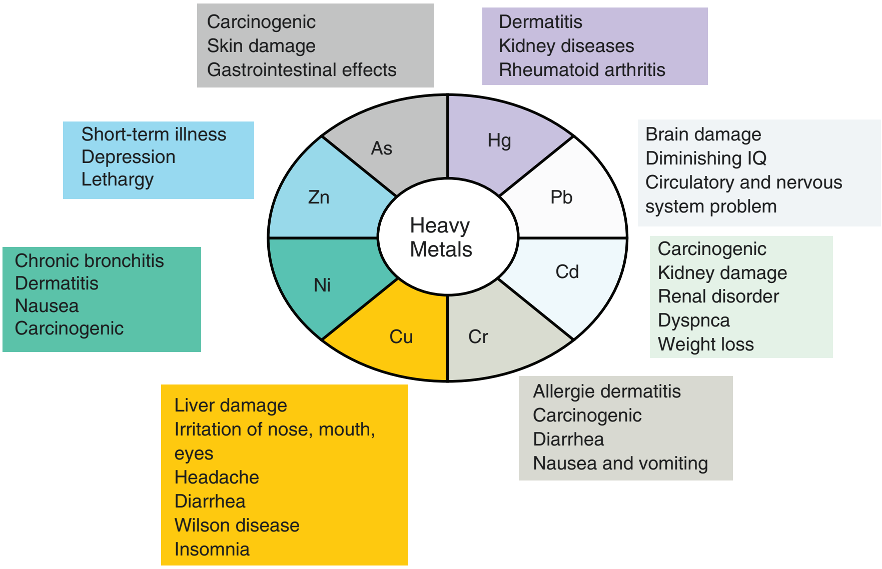


Fig. 10.1 Human health hazards associated with exposure to toxic heavy metals such as lead, cadmium, mercury, arsenic (Sud et al. 2008)

Table 10.1 Limits and health threats related to toxic metals (Sud et al. 2008)

Metal	Standard limits (μg/l)		Health hazards
	WHO[a]	USEPA[b]	
Arsenic	10	10	Carcinogenic, skin damage, gastrointestinal effects
Mercury	6	2	Dermatitis, kidney diseases, rheumatoid arthritis
Lead	10	0	Brain damage, circulatory and nervous system problem
Cadmium	3	5	Carcinogenic, kidney damage, renal disorder, dyspnea, and weight loss
Chromium	50	100	Allergic dermatitis, carcinogenic, diarrhea, nausea, and vomiting
Copper	2000	1300	Liver damage, long-term exposure causes irritation of nose, mouth, eyes, headache, diarrhea, Wilson disease, insomnia
Nickel	–	–	Chronic bronchitis, dermatitis, nausea, carcinogenic
Zinc	–	–	Short-term illness, depression, and lethargy

WHO World Health Organization, *USEPA* United States Environmental Protection Agency
[a] Values denoted by World Health Organization (WHO 2017a, b)
[b] Values denoted by United States Environmental Protection Agency (USEPA 2019)

and many more chemical industries (Strater et al. 2010). Table 10.2 indicates the major sources of heavy metal.

According to World Health Organization, about one billion people do not get pure drinking water and that number is increasing day by day. Thus millions of people are suffering from different types of diseases due to contact with poisonous metals. Clean water scarcity is the second most vital issue after oxygen worldwide.

Table 10.2 Different sources of metal contamination (Uddin 2017)

Contaminant	Usage	Natural sources	Industrial sources
Nickel	High resistive nickel alloy and steel, catalyst for metallurgy, coating element, manufacturing battery, food pigment	Dust volcanoes, fissure in the earth's crust, sea salt, wildfires, ore mining	Smelting operations, electroplating, thermal power stations, battery industries, incineration of solid waste
Lead	Automotive batteries, pigments of oil paints, stabilizers in plastic, fuel additive, crystal glass, cosmetics	Lead aerosols, prairie fire volcanic eruptions	Mining of metal ores, smelting process, incineration of lead acid batteries, combustion of fossil fuels, ceramic, and glassware
Zinc	Galvanic cell, die-casting alloys, plastic and paints, cosmetics pharmaceuticals, batteries, textiles electrical equipment	Rock, surface water	Poultry manures, electroplating, smelting
Copper	Wiring, electronic devices, transmission wires, copper alloys, and ornaments	Wind-blown dust, sea spray	Mining, electroplating, smelting operations
Cadmium	Steel electroplating, computer, laptop, Ni-Cd batteries, nuclear reactor	Mining and smelting, coal combustion, anthropogenic sources	Metal plating, industrial wastewater, soldering, phosphate fertilizers, plastic stabilizers
Mercury	Thermometers, barometers	Geologic deposits of Hg, volcanoes, volatilization from the ocean	Hydroelectric, coal-based thermal power plants, incineration of medical waste
Arsenic	Insecticides, rat killer, doping agent in semiconductor, bronzing, wood preservation	Ground water, earth crust, volcanic activities, geothermal processes	Fuel combustion, smelting, geogenic processes, thermal plants
Chromium	Electroplating, stainless steel, catalyst, pigments, food processing equipment, medical and dental tools	Rocks, soil, and in volcanic dust and gases	Mining, chrome plating, airborne emissions from chemical plants, cement plants, solid wasteland filling
Cobalt	Corrosion/wear resistant alloy for aircraft, batteries, and electroplating, permanent magnet, radioactive in treatment cancer	Soil, dust, seawater, volcanic eruptions, forest fires, surface and underground water	Ore smelting, processing of superalloys and coating, nuclear power plant operations, vehicular exhaust, radioactive waste landfills, combustion of coal and oil

Therefore it is high time to develop easy and simple method for reclamation of wastewater using low-cost adsorbent materials for our sustainable development on earth.

10.2 Different Techniques Available for Heavy Metal Removal: Pros and Cons

Due to known impacts of heavy metals on living organism as well as environment, a major number of research have been done on developing different methods for removal of heavy metals from water sources along with industrial wastewater, municipal wastewater, and other wastewater sources. Methods which are most common on removing toxic metals from contaminated water sources are as follows: ion-exchange, flocculation, chemical precipitation, coagulation, electrochemical treatment, adsorption, membrane separation, and electro-dialysis (Carlos et al. 2013).

10.2.1 Chemical Precipitation

In chemical precipitation, heavy metals are either removed as hydroxide or sulfide precipitate which is formed via the chemical reaction with hydroxide (such as NaOH, $Ca(OH)_2$), and sulfides (such as Na_2S and FeS). Firstly, heavy metals are coagulated by lime, alum, iron salts, and other organic coagulants. These coagulants lead to formation of insoluble precipitate which can be easily settled down by sedimentation and then separated by filtration. Finally treated water can be discharged or reused (Pehlivan and Altun 2006). Copper and Chromium ions are eliminated from effluent by hydroxide precipitation process (Mirbagheri and Hosseini 2005). Cu^{2+}, Cd^{2+}, and Pb^{2+} ions are removed by using pyrite and synthetic iron sulfide by sulfide precipitation (Ozverdi and Erdem 2006). The main disadvantage of chemical precipitation is the large amount of toxic sludge produced during the process (Kurniawan et al. 2006).

10.2.2 Ion Exchange

In ion-exchange process, metal ions from dilute solution are exchanged with the ion-exchange resin by electrostatic forces. Because of many advantages like high removal efficiency and fast kinetics, ion exchange process has been broadly applied to eliminate toxic metals from effluent. It is one of the most effective process for the removal of toxic metals released from chemical industries into drinking water at very low concentration making it the most promising process to be used (Dabrowski et al. 2004). Among the varieties of ion-exchange resins, the most common cation exchangers like sulfonic acid groups containing resins are strongly acidic and carboxylic acid groups contaning resins are weakly acidic. Dowex 50 W is one such resin which contains RSO_3^- group and was applied for removing of cadmium ions from aqueous solutions (Pehlivan and Altun 2006). The disadvantages include very high cost of ion exchange resin and partial removal of certain ions.

10.2.3 Membrane Filtration

Membrane filtration is very simple and easy technique to remove various heavy metals by using various membranes. This process mainly depends on particle size. This technique is used in different forms which are described as the following.

Ultrafiltration

Ultrafiltration technique uses a semipermeable membrane to eliminate dissolved molecules and metal ions in low transmembrane pressure based on molecular size. The membrane offers passage for low molecular solutes and separates out the larger molecules and heavy metals. Ultrafiltration technique is of three types: complexation – ultrafiltration, micellar enhanced ultrafiltration, and chelating enhanced ultrafiltration. Chitosan and synthetic carboxymethyl cellulose both have strong influence on enhancement of nickel rejection provided that adequate amount of polymer is used. Amicon YM10 Ultracel regenerated cellulose which was applied as the ultrafilter, is highly efficient in removal of copper and zinc ions at a high pH 8.5–9 (Juang and Shiau 2000). These experiments revealed that heavy metal elimination ability is enhanced by using chitosan ultrafiltration membranes. Large amount of production of sludge is the main limitation of this technique as it is tough to manage such huge amount.

Nanofiltration

Nanofiltration is the in-between process between ultrafiltration and reverse osmosis. It is an efficient technique for the separation of heavy metal ions such as Ni^{+2}, Cr^{+6}, Cu^{+2}, and As^{+3} from wastewater. Advantages of nanofiltration process are simple operation, consistency, low energy consumption, and high pollutant removal efficiency. In nanofiltration, soluble elements cannot be separated from the water, which is a major limitation of this process.

Reverse Osmosis

In reverse osmosis, when hydrostatic pressure is higher than osmotic pressure, solvent passes through semipermeable membrane in direction opposite to that of osmosis process. Heavy metals like zinc and copper removal using low pressure below 690 kPa with a reverse osmosis membrane has been studied by researchers which showed that Zn^{2+} and Cu^{2+} removal was improved in the presence of polysulfone reverse osmosis membrane (Ujang and Anderson 1996). The major disadvantage of this technique is it is not cheap (Kurniawan et al. 2006).

Electrodialysis

Electrodialysis is a process in which separation of metal ions across charged membranes from one solution to another in the presence of an electric field which acts as driving force. Membranes applied in this process are of two types: anion exchange membrane and cation exchange membrane. This technique is generally used for making drinking water from seawater and brackish water, for recovery of valuable materials from effluents, and for salt production. Limitations of this process are such that organic matter and colloids cannot be removed by electrodialysis and stack selection is necessary for compatibility guarantee with the feed stream.

10.2.4 Electrocoagulation

Electrocoagulation is an electrochemical approach which utilizes electrical current for not only removal of heavy metals from aqueous solution but also capable of removing suspended solids, dissolved metals, tannins, and dyes from wastewater. The metal ions become destabilized and precipitate in a stable form when they are neutralized with ions of opposite electrical charges provided by coagulates such as ferrous sulfate, aluminum, and ferric chloride. Heavy metals like cadmium, copper, and nickel removal from an artificial wastewater was performed with an efficiency of 99.78%, 98.90%, and 99.98%, respectively, using electrocoagulation method at neutral pH 7. The formation of metal hydroxides leads to clogging of the membranes which is the main limitation of this method (Pedersen 2003).

10.2.5 Flotation

Flotation is used to separate heavy metals from a liquid phase by bubble-metal attachment process. The common flotation processes for the removal of metal ions from solution are dissolved air flotation, ion flotation, and precipitation flotation. Among these, dissolved air flotation process is mostly used than any other flotation processes in removing toxic heavy metals. In dissolved air flotation process, floating particles in the water attach to air microbubbles which further develop agglomerates producing flocs which rise through the water and accumulate on the surface of water and thus can be separated easily as sludge. Disadvantage of this process is its high operating cost.

10.2.6 Phytoremediation

Phytoremediation is the process in which plants and their associated microorganisms treat pollutants in soil, water, and air. In this process, natural plants or genetically engineered plants are used to eliminate pollutants like toxic metals, antibiotics, and pesticides. The benefits behind this technique over conventional techniques are such that this process is cheap and environment friendly. But there are some limitations which can be overcome by using high biomass plants with faster growth rate. Table 10.3 shows some other advantages and limitations of phytoremediation process. For environmental remediation, plants are chosen selectively which can accumulate pollutants thereby controlling pollution.

The disadvantages of this method are the following: it is a slow process, and plant regeneration is challenging which subjects to poor heavy metal removal and requires high energy. Also a large amount of harmful sludge is created which results in difficulty in disposal (Feng and Aldrich 2004). Various experiments have been done for the elimination of heavy metals from environment using variety of plant species which is listed in Table 10.4.

10.2.7 Photocatalysis

Basically heavy metal removal involves reduction reactions from higher oxidation state to lower one to produce elemental metals or metal ions. This mechanism is applicable for all heavy metal ions except for arsenic, which exists in anionic form and needs to be converted to higher oxidation state via oxidation reaction. Therefore TiO_2 with ultraviolet radiation has the capability to endure both oxidation and

Table 10.3 Advantages and limitations of phytoremediation

Advantages	Limitations
1. Environment-friendly and cost-effective	1. Process is limited to the depth reached by roots
2. It can treat site with more than one pollutant type	2. It depends on the tolerance capacity of plants used
3. Precious pollutants can be collected from accumulating plants after end of process	3. Because of their biodegradable nature, there is chance of reentering of heavy metals

Table 10.4 Removal of heavy metals by phytoremediation strategies

Heavy metals	Plant species	References
As	*Cynara cardunculus*	Baldwin and Butcher (2007)
	Pteris vittata	Thayaparan et al. (2013)
Pb	*Azolla pinnata*	Ali et al. (2012)
	Pelargonium roseum	Assuncao et al. (2003)
Cd	*Thlaspi caerulescens*	Qiu et al. (2014)
Zn	*Helianthus annuus*	Hegazy et al. (2011)
	Typha domingensis	Pandey et al. (2009)

reduction reaction and is widely applicable in removal of metal ions as well as metalloids.

Chromium enters into our body naturally through fruits, vegetables, grains, and meats in form of Cr^{+3}, but in higher oxidation state as Cr^{+6}, it becomes very toxic and demands reduction to lower oxidation state. Several photocatalysts are used for degradation of Cr^{+6} such as TiO_2, ZnO, WO_3, ZnS, CdS, and $SnIn_4S_8$. Degradation of Cr^{+6} under ultraviolet radiation depends greatly on pH. In a photodeposition method, the platinum precursor $[Pt^{+4}Cl_6]^{2-}$ was reduced by the photogenerated electron at the valance band of TiO_2, and the sacrificial organic reagent acts as hole scavenger (Chowdhury et al. 2013). The Pt–TiO_2 photocatalysts have extensive applications in water treatment as well as in photocatalytic hydrogen generation. Photoreduction of Cd^{+2} in the presence of formate ion was much faster compared with Zn^{+2} photoreduction (Chenthamarakshan et al. 2000). It was reported that photoreduction of Hg^{+2} is significantly improved by 45% with TiO_2 in absence of oxygen (Khalil et al. 2002). Photocatalytic conversion of As^{+3} to As^{+5} can be achieved both by the mechanism with a superoxide anion such as $HO_2^{\cdot}$ or O_2^-, and via a valance band hole or HO (Fei et al. 2011). The cost-effective photoreactor development is the key issue involved with photocatalysis system. It also takes long duration for photoremediation.

10.2.8 Adsorption

Adsorption process is an efficient and environment-friendly process for effluent treatment. It is a mass transfer process in which a substance is carried from a liquid phase to the surface of a solid and bounds with the solid surface by physical and/or chemical interactions. In addition, regeneration of adsorbents is possible as it is sometimes reversible using suitable desorption process. Depending on intermolecular forces, adsorption is of two types which are described in the following.

Physical adsorption: It is one such process in which adsorbate binds on adsorbent surface by van der Waals attractive force. It can only be observed in low temperature for solid–liquid or solid–gas system, and under appropriate conditions, gas phase molecules can form multilayer adsorption.

Chemical adsorption: In this type, interaction between adsorbent and adsorbate occurs through chemical reactions by creating new bonds such as covalent and ionic bond, etc. Adsorption technique has many advantages over other usual methods such as efficient, effective, regenerative, eco-friendly, and metal selectivity.

Activated carbon materials are undoubtedly popular and commercially used adsorbents throughout the world because of having large pore size and pore volumes. Nowadays, it becomes very expensive due to its depleted source of coal as well as needs complex agent to improve its efficiency toward inorganic matter. An alternate source of activated carbon which is abundant and inexpensive becomes our prime concern which leads us to the solution that transforms carbonaceous materials into activating carbon for elimination of toxic metals. Many of the researchers come up with the interest for production of activated carbon from waste materials. The binary component adsorption of copper and lead by activated carbon produced from eucalyptus bark was found with maximum adsorption capacities for lead and copper of 0.53 and 0.45 mmol g^{-1}, respectively (Kongsuwan et al. 2009). Poultry-based activated carbon shows higher adsorption efficiency for heavy metals than commercial activated carbon produced from coal and coconut shell.

10.3 Low-Cost Adsorbent

Most of the abovementioned techniques have many disadvantages such as higher cost of operation and sludge disposal problem caused by these techniques. But adsorption is the most efficient technique in wastewater treatment due to the advantages like eco-friendly, cost-effective, simple technique and very less maintenance required (Bhattacharyya and Gupta 2008).

10.3.1 Zeolite

Zeolites are naturally occurring three-dimensional hydrated aluminosilicate mineral. They belong to the class of minerals known as "tectosilicates." The structures formed by the interaction of alumina and silica and are commonly referred as molecular sieves. The chemical formula of zeolites has been shown below:

$$M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$$

where:

M – metal (sodium, lithium, potassium, calcium, and magnesium)
n – valence of metal cation
y – number of water molecules present in zeolite structure

Zeolites can provide adsorption sites for heavy metal ions by exchanging the cations. Other than ion exchange and adsorption, many more mechanisms involved in removal of heavy metals by zeolite are surface precipitation, destruction, or dissolution of natural zeolite structure. Zeolites have large surface areas in the range of 600–800 m^2g^{-1}, and because of its ion-exchange capability, it is an efficient adsorbent for heavy metal removal. The price of zeolite considered itself very cheap depending on the quality of the zeolites. It was found that clinoptilolite gives high selectivity and cation exchange capacity for metal ions like Pb^{2+}, Cd^{2+}, Zn^{2+}, and Cu^{2+} which are greatly influenced by pretreatment procedure (Babel and Kurniawan 2003). The adsorption parameter such as pH plays important role on selection of heavy metal. 4A zeolite synthesized from kaolin showed good result in Cu^{+2} and Zn^{+2} removal at both neutral and high pH, while Cr^{+6} was better adsorbed at low pH (Barakat 2008). It was reported that zeolites in both forms clinoptilolite and chabazite, have significant removal efficiency for treating effluent contaminated with Pb^{+2}, Cd^{+2}, Cu^{+2}, Zn^{+2}, Ni^{+2}, and Co^{+2} (Ouki and Kavanagh 1997). Therefore both the ions have greater opportunity to exchange with Na ions of zeolite. Magnetically modified synthetic zeolite with Fe_2O_3 showed high Pb^{+2} adsorption capacities for and good chemical resistance at a wide pH range 5–11 (Nah et al. 2006). Overall we can say that zeolite has a great potential to remove metal ions from various industrial effluent.

10.3.2 Clay

Clays as an adsorbent have many advantages compared to other adsorbents such as its abundant availability, low cost, high specific surface area, excellent adsorption ability, non-toxic nature, and large ion-exchange potential. Usually clay minerals are very efficient and widely used to adsorb metal cations as they are negatively charged by a number of adsorption mechanisms like ion exchange and metal cations and with clay surface bonding. Clays are mainly mixture of clay minerals composed of hydrous aluminum phyllosilicates with an average particle size of less than 2 μm, crystals of other minerals, and metal oxides. Clays are classified into groups like smectites such as montmorillonite and saponite; mica such as illite; kaolinite; vermiculite; serpentine; pyrophyllite such as talc; and sepiolite (Shichi and Takagi 2000).

Montmorillonite, a subgroup of smectites is considered to be most efficient for adsorption due to its availability, adsorption capacity, high specific surface area, and compatible cation exchange capacity among all of the clay families (Kennedy 1990). Copper and nickel removal using raw montmorillonite claimed that internal solute pore diffusion at clay wall was more essential than external mass transfer for the adsorption mechanism (Ijagbemi et al. 2009). The other study reported that sodium-montmorillonite is potentially more effective for adsorption of Cu^{+2}, Pb^{+2}, Zn^{+2}, Cd^{+2}, and Co^{+2} ions than calcium–montmorillonite (Chen et al. 2015). Because of hydrophilic nature of clay mineral, it cannot be used without certain modification. Organically modified montmorillonite appeared to be better adsorbent than the raw one showing remarkable selectivity and removal efficiency toward Cu^{+2} ions (Abou-El-Sherbini and Hassanien 2010). Most of the studies on adsorption revealed that main operating parameter which influenced the surface complexation mechanism is pH. At a high pH, adsorption of copper and arsenic reduces, while it was found to be optimum at pH 6 (Uddin 2017).

Bentonite clay consists of volcanic ash named as “montmorillonite” with high silica, iron, magnesium, sodium, and potassium concentration. It has a very unique quality to produce electrical charge upon hydration. Chemical treatment with acids such as HCl, HNO_3, and H_3PO_4 followed by washing with NaOH made it negatively charged material which can easily bind to cations (Shawabkeh et al. 2007).

Kaolinite clay has poor ion-exchange capacity. Varying concentrations of electrolyte from 0.01 to 0.1 molar and adsorption of various metal ions like Ni^{+2}, Cu^{+2}, Pb^{+2}, and Cd^{+2} were significantly reduced (Jiang et al. 2010). The maximum adsorption by kaolinite observed for nickel of amount 140.84 mg g^{-1} (Jiang et al. 2010). It has been well predicted that adsorption of metal ions decreased with increasing concentration of electrolyte because of screening effect of negative charges on surface (Coles and Yong 2002). The parameter also influences the adsorption behavior of different adsorbents. With the increase in temperature, adsorption of metal ions decreased. A comparative study on adsorptive nature of As^{+5} ions with montmorillonite, kaolinite, and illite concludes with similar result as aforesaid (Mohapatra et al. 2007). Though natural untreated form of kaolinite provides good results, modified form of kaolinite gives enhancement of adsorption properties. The adsorption capacities of natural raw siderite and kaolin materials have been increased with the surface-coated MnO_2 particles via chemical precipitation due to increase in specific surface area (Dankova et al. 2015). Nanomagnetic Fe_3O_4 composite with kaolinite increases its adsorption capacity for heavy metals such as cadmium, copper, chromium, lead, and nickel with increase in pH over time.

The natural raw form of vermiculite showed excellent potential for removal of metal ions via adsorption. Pb adsorption by vermiculite was strongly affected by pH (Liu et al. 2007). It is important to know during studying about adsorption of positively charged metals onto clay mineral that ionic strength of inbuilt salts impart a great role on formation complex metals and thereby competing for the adsorption site. It was reported that competitive adsorption behavior by pure vermiculite was investigated for different heavy metal ions like Cr^{+3}, Cu^{+2}, Ni^{+2}, and Co^{+2} (El-Bayaa et al. 2009). Another experiment showed that lead always adsorbs on vermiculite in comparison to other metal ions such as Ni^{+2}, Ag^{+1}, and Cd^{+2} because lead sorption involves more than one mechanisms (Liu et al. 2010). A comparative study of Cu^{+2} adsorption on different adsorbent like vermiculite and clinoptilolite leads to the conclusion that adsorption of copper on vermiculite is possible via two mechanisms: ion exchange and surface complexation (Dizadji et al. 2013).

Heavy metal removal using goethite requires appropriate assessment of environmental hazards. The first successful prediction comes with extended triple layer model, which was experimented with As^{+3} and As^{+5} (Kanematsu et al. 2013). The metal adsorption of Cd, Cu, Pb, and Zn on raw goethite significantly increased in presence of sulfate in liquid phase (Swedlund et al. 2009). Various studies are

Table 10.5 Different clay minerals with remarkable adsorption capacities for heavy metals

Heavy metals	Adsorbent	Adsorption capacity (mg/g)	References
Cd^{+2}	Smectite	971.00	Mhamdi et al. (2014)
$Cr^{+3/+4}$	Polyaniline/montmorillonite composite	308.60	Chen et al. (2014)
Hg^{+2}	Montmorillonite	385.50	Uddin (2017)
Co^{+2}	Chemically treated bentonite	138.10	Shawabkeh et al. (2007)
Cu^{+2}	Immobilized bentonite	54.07	Erdem et al. (2009)
Zn^{+2}	Kaolinite	250.00	Arias and Sen (2009)
Pb^{+2}	Illitic clay	238.98	Ozdes et al. (2011)
Ni^{+2}	Kaolinite	140.84	Jiang et al. (2010)

experimented to evaluate the effect of temperature, ionic strength, and surface acidity of goethite in aqueous medium (Mamindy-Pajany et al. 2009; Kersten and Vlasova 2009). The result leads to the conclusion that adsorption of arsenate on goethite is an exothermic process and thereby weaken with increase in the temperature (Kersten and Vlasova 2009). The adsorption behavior of different microstructure of goethite with addition of multiple metal ions, e.g., Pb^{+2}, Cr^{+3}, Zn^{+2}, and Cd^{+2}, was investigated (Kaur et al. 2009). It was very evident from the result that Cr^{+3} and Cd^{+2} are significantly removed mutually and incorporation of Pb^{+2} also gives positive result in the goethite structure but for Zn^{+2}, it was not the same. Therefore critical results conclude that goethite might not be right choice to the circumstances where multiple metal ions are present (Kaur et al. 2009).

There are loads of research studies on heavy metal removal using clay mineral as a cheap, readily available, and efficient adsorbent material. Table 10.5 shows comparative studies available in literature on best adsorption capacities of few clay minerals. On the basis of relative study on adsorption capabilities among various clay minerals, it can be stated that montmorillonite, in both natural and modified form, exhibits higher adsorption of chromium and mercury as compared to the other heavy metals. Kaolin has better adsorption compatibility of lead, zinc, and nickel; bentonite performed pretty well for adsorption of cadmium; remarkable arsenic adsorption is achieved with goethite clay.

10.3.3 Peat Moss

Peat moss is one of the inexpensive, naturally abundant adsorbent materials having high surface area greater than 200 $m^2\ g^{-1}$ and porosity more than 95% (McLelland and Rock 1988). The major constituents of peat moss are lignin and cellulose which have polar functional groups like -OH, -CHO, ketones, acids, phenolic hydroxides, and ether to form chemical bond with the metal ions, therefore enabling peat moss as an efficient adsorbent for removal of hazardous heavy metal through simple cation exchange mechanism. There are a variety of peats such as eutrophic and oligotrophic peat. Eutrophic peat has less cellulose content, but has high humic acid, and oligotrophic peat such as sphagnum is more acidic than eutrophic peat (Babel and Kurniawan 2003).

10.3.4 Chitosan

Chitin is readily available natural adsorbent which exists in exoskeletons of arthropods and cell walls of some fungi (Ren et al. 2008). Chitosan is deacetylated chitin derivative and the second most abundant biopolymer after cellulose. Chitosan is not only efficient and abundant but also cheap (Kumar 2000). Chitosan has some special characteristics such as hydrophilicity, biocompatibility, biodegradability, and non-toxicity, and it also offers ease of derivatization (Huo et al. 2009). It can form chelate complex due to the presence of amino and hydroxyl groups with heavy metals (Hu et al. 2011). In spite of having such advantages, chitosan has its own limitation as because it is mechanically weak, pH sensitive, and soluble in acidic medium and may remove carbon sources when applied in raw form (Kumar 2000; Hu et al. 2011). Therefore, to improve its stability as well as adsorption performance, various cross-linkers like formaldehyde, glutaraldehyde, and ethylene glycol diglycidyl ether have been used (Wang et al. 2011). A group of researchers also developed "ion imprint technology" for the same purpose which involves the technology to develop a novel adsorbent like urea-modified magnetic ion embossed chitosan@TiO_2 composite for Cd^{+2} removal. The result with this adsorbent at pH 7 showed an adsorption capacity of 256.41 mg g^{-1}. Chitosan also help in coating on ceramic alumina composite through which active binding sites of heavy metal increases. There has been a wide application of ceramic or chitosan – alumina composites as an adsorbent to eliminate heavy metals like arsenic, chromium, copper, and nickel. Nano-chitosan synthesized by ionotropic gelation of tripolyphosphate and chitosan was experimented for lead adsorption with an adsorption capacity of 398.0 mg g^{-1} (Qi and Xu 2004). It was reported that metal ion adsorption is relatively high with the order of $Cd^{+2} > Cu^{+2} > Pb^{+2}$ on chitosan and sulfhydryl-functionalized graphene oxide composites due to the increase in selectivity and specific surface area (Li et al. 2015). However, recovery of these materials limits its large-scale application as they require complex separation procedures. To solve this issue, researchers now focused on chitosan composite which can give magnetic response. Magnetic chitosan composites exhibit high potential ability for removal of toxic metal ions such as Ni^{+2}, Cu^{+2}, and Pb^{+2} with maximum uptakes of 108.9, 216.8 and 220.9 mg g^{-1}, respectively. Recently a very interesting research work was done which is not only economic but also versatile method to remove multiple metal ions from natural or

Table 10.6 Performance of chitosan as adsorbent for remediation of toxic metal-contaminated wastewater

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	References
Chitosan/alumina	Cr(VI)	153	Boddu et al. (2003)
Chitosan/perlite	Cu(II)	128.20	Swayampakula et al. (2009)
Chitosan/perlite	Cu(II)	196.07	Kalyani et al. (2005)
Chitosan/cotton fibers	Hg(II)	104.31	Qu et al. (2009)
Magnetic chitosan	Cr(VI)	69.40	Huang et al. (2009)
Chitosan/magnetite	Pb(II)	63.30	Tran et al. (2010)
Chitosan/magnetite	Ni(II)	52.55	Tran et al. (2010)
Chitosan/calcium alginate	Ni(II)	222.2	Vijaya et al. (2008)
Chitosan/silica	Ni(II)	254.3	Vijaya et al. (2008)
Chitosan/PVC	Ni(II)	120.5	Popuri et al. (2009)
Chitosan/PVA	Cd(II)	142.9	Kumar et al. (2009)
Fe_3O_4/chitosan films	Pb(II)	114.9	Lasheen et al. (2016)
Chitosan nanoparticles	Pb(II)	398.0	Qi and Xu (2004)
Chitosan nanorods	Cr(VI)	323.6	Sivakami et al. (2013)
Cross-linked chitosan	Hg(II)	269	Zhou et al. (2010)
Coconut shell/chitosan	Zn(II)	60.41	Amuda et al. (2007)

PVC polyvinyl chloride, *PVA* polyvinyl alcohol

industrial wastewater. Chitosan and gelatin spherical hydrogel particles were prepared by inverse emulsion method and revealed that for single ion solution, it shows maximum adsorption efficiency of 98% for Hg^{+2} ion whereas 73–94% for multiple ions such as Pb^{+2}, Cd^{+2}, Hg^{+2}, and Cr^{+3}. Some of the chitosan composite with its application are enlisted in Table 10.6.

10.3.5 Coal

Raw hard coals are cheap and exist in large deposits in many countries. They do not lose their properties after use and also represents a highly calorific fuel. Thus raw hard coals are one of the promising adsorbents. The adsorption of gases such as CO_2, CH_4, and acetylene on raw hard coals has been widely studied (Li et al. 2010; Gensterblum et al. 2014). The application of raw hard coals as low-cost adsorbents for water treatment has been described in only a few works for the removal of heavy metal ions (Lakatos et al. 2001, 2002), dyes (McKay et al. 1999; Venkata Mohan et al. 2002). The most important parameters affecting the adsorption process of metal ions by coal include pH and ionic strength.

10.3.6 Agricultural Waste

Agricultural waste defines the waste generated by human beings after processing of agricultural activity. Agricultural waste is a promising biosorbent for remediation of hazardous metals from contaminated water because of its enormous availability, cost-efficiency, superior adsorption ability and selectivity, and ease of processing, separation, and regeneration of adsorbent. Nowadays researchers are highly concerned about the utilization of agricultural waste which can act as a good alternative of commercially available activated carbon adsorbent and therefore achieving the global concern to reduce environmental pollution by "treating waste by waste".

Agricultural wastes are mainly lignocellulosic biomass consisting of lignin, pectin, cellulose, and hemicellulose. The functional groups like carbonyl, hydroxyl, and ether are responsible for binding heavy metals via chelating, coordinating, and hydrogen bonding. In spite of having noticeable characteristics of good adsorbent, use of untreated agricultural wastes indulges with severe problem. These wastes cannot be disposed of randomly as it elevates chemical and biological oxygen demand as well as total organic carbon to the water systems.

Rice husk is readily available, cheap adsorbent consisting of cellulose followed by lignin, hemicellulose, and mineral ash. The utilization of rice husk is a major concern for developing countries like India, China, and Indonesia where rice is the main food crop for livelihood. The presence of functional groups like hydroxyl, silanol, and siloxane in rice husk reflects strong affinity toward heavy metal cations. Rice husk was found to be effective low-cost adsorbent in the removing metal like Ni, Cr, Zn, Pb, and Cu. A study on adsorption efficiencies of nine different toxic heavy metals by rice husk found adsorption capacity with the values ascending in subsequent order nickel $<$ zinc $\approx$ cadmium $\approx$ manganese $\approx$ cobalt $<$ copper $\approx$ mercury $<$ lead. Natural rice husk and rice husk modified by activated carbon using O_3 were used for the removal of chromium showing that by modification higher removal efficiency was achieved. Though rice husk is efficient adsorbent, it still needs modification to enhance its adsorption capacity. It was reported that modified rice husk removes 125.94 mg g^{-1} of cadmium when stirred with NaOH for 24 h, whereas non-modified one gives only 73.96 mg g^{-1} adsorption at an optimum pH of 6.5. Biochar which is a byproduct from pyrolysis of rice husk can be used for chromium removal with the adsorption capacity of 95%. Another experimental study on the copper removal observed an adsorption capacity of 17.9 mg g^{-1} using rice husk. Rice husk can act as a promising adsorbent for the adsorption of lead because of the following mechanisms: surface complexation with –COOH and –OH groups, ion exchange with calcium and magnesium, and forces of attraction.

Coconut shell is well-known common low-cost adsorbent under agricultural waste which is very abundant in tropical countries. Heavy metals such as Cu, Pb, Ni, Zn, and Cr are efficiently removed from wastewater by coconut shell. 7.5 million tons of coconut per year is produced in India, and the waste has been used as adsorbent for treatment of effluent. Coconut coir pith comprises cellulose 35%, fats 1.8%, lignin and resin 25.2%, pentosans 7.5%, ash 8.7%, moisture 11.9%, and the rest other substances which enable sorption properties toward heavy metal ions. An experimental study on activated coconut shell with phosphoric acid revealed that adsorption of Pb is higher than inactivated coconut shell (El-Deen and El-Deen 2016). Another research work converts coconut shell into activated carbon, and the result shows maximum adsorption capacity of 26.41 mg g^{-1} for cadmium ion at pH 5.5 (Jin et al. 2013).

Peanut shells are also found to be a good adsorbent for heavy metal removal. An effective Cr^{+6} removal at low pH values was also achieved by researchers (Ahmad et al. 2017). Peanut husk seemed to have efficient adsorption properties toward heavy metals.

Pistachio hull waste is also considered as a susceptible adsorbent for various toxic metals. It was reported that Cr^{+6} from waste was removed with 98% of efficiency using pistachio hull (Moussavi and Barikbin 2010). Another study explored adsorption capabilities of pecan shells with different metal ions such as Pb^{+2}, Cu^{+2}, and Zn^{+2} by applying a number of modification methods to improve removal efficiency which includes carbon dioxide, steam, and acid activation (Bansode et al. 2003).

Fruit waste material like peel shows remarkable adsorption capacity for various heavy metals in treatment of different wastewater. Orange peel acts as an efficient bioadsorbent as it contains cellulose, pectin, hemicelluloses, and lignin in high amount. Different heavy metals like Zn, Pb, Ni, Cu, and Cd were significantly removed using orange peel. Studies have stated that chemically modified orange peel enhances adsorption capacities metal like Pb, Cd, Cu, and Ni. Mosambi or sweet lime peel dust was capable to adsorb Cr^{+6} ions from an aqueous solution (Saha et al. 2013). Banana peel also shows different degrees of heavy metal removal for Zn^{+2}, $Pb^{+}2$, Cd^{+2}, Cu^{+2}, and Ni^{+2}. A maximum adsorption capacity of 46.1 and 42.1 mg g^{-1} for the removal of Ni and Cd was achieved by grapefruit peel (Torab-Mostaedi et al. 2013).

10.3.7 Industrial Waste

Industrial waste is another cheap source of adsorbent which can be used for heavy metal removal from wastewater. Synthesis of adsorbent from industrial waste mainly by-products requires very small processing. Some of the industrial wastes capable of removing heavy metals from wastewater are fly ash, red mud, lignin, blast furnace sludge, grape stalks waste, and battery industry waste.

Fly ash, a residue product of coal combustion, has high potential for adsorption for which it is used in wide range of applications. It can be used as a good substitute of commercial adsorbents such as zeolite and activated carbon. Adsorption capacities of fly ash depend on the origin from which it is derived as because it has a variety in chemical composition. Mainly the chemical compositions of fly ash are silica 60–65%, alumina 25–30%, and magnetite 6–15% which makes it compatible to be used as an adsorbent. Raw fly has low adsorption capacity which can be improved by proper physical and chemical treatment. Fly ash has been used for different applications in wastewater treatment. Mainly Cr, Pb, Ni, As, Hg, Cd, and Cu adsorption by fly ash has been studied. Study on Zn^{+2} and Ni^{+2} removal ability by activated carbon and fly ash showed that maximum metal removal depends on concentration of Zn^{+2} and Ni^{+2} and pH of solution (Cetin and Pehlivan 2007). Zeolite can be synthesized from natural resources like fly ash, red mud, and clay which can be further used as an adsorbent for treatment of wastewater. Studies on fly ash-derived nano-zeolite X sono-sorptive for the elimination of methylene blue have been done (Sivalingam et al. 2018). Maximum methylene blue removal of 64.52% by coal fly ash, 99.30% by highly pure nanozeolite X, and 96.57% by commercial zeolite X was achieved at a certain pH.

Red mud is also serving as good source low-cost adsorbent which is very abundant industrial waste. It is a residue of bauxite ore processing during caustic leaching in alumina production process, also known as Bayer's process. About half tons of red mud produced one ton of alumina. Red mud is mainly composed of aluminum, silicon oxide, calcium, and iron which are the reason behind its high surface reactivity. Therefore they have been used widely for the extraction of heavy metals in the treating process of wastewater. Arsenic which causes several health hazards can be removed by red mud. Thermal and chemical modification on red mud increases its adsorptive capacity. Like other adsorbents, red mud activity is also dependent upon pH. As^{+3} was adsorbed at alkaline pH 5.8–7.5, while As^{+5} was significantly reduced at acidic pH 1.8–3.5 (Selvaraj et al. 2003). Red mud can be used as liquid phase too for As^{+5} removal, and it was proved to be more advantageous over solid phase.

10.3.8 Bioadsorbent

Bioadsorption is a new area in the field of wastewater treatment having a high efficiency in extraction of heavy metal. The major benefits of using this process are use of inexpensive bioadsorbent because of their natural origin as well as fast and reversible. The three main sources of bioadsorbent are algal biomass, microbial biomass, and non-living sources such as crab shell, lignin, shrimp shell, and bark.

The most abundantly available biosorbent on earth crust is algae. The algae or marine algae are mostly used in different fields such as food processing and pharmaceutical applications. Owing to its remarkable adsorption capacity and renewable availability, it can be used as a promising bioadsorbent. Figure 10.2 shows the number of documents published in the area of heavy metal removal by biosorption.

There are three types of marine algae: green algae, brown algae, and red algae. They consist of certain active functional groups, like amine, hydroxyl on the surface of the cell wall which possesses chemical bond with metals, and selective binding in the adsorption process.

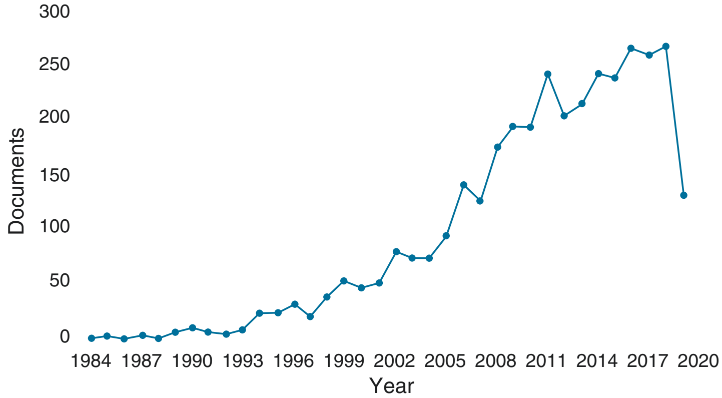


Fig. 10.2 Number of documents published by year in the field of adsorption of toxic heavy metals by bioadsorbents (Scopus Data as on October 2019)

The mechanism behind the heavy metal adsorption is *ion-exchange process:* ion exchange occurs because of the presence of functional group on the surface of the biomass which proved to be potentially active substrate for removal of toxic elements. *Uptake mechanism:* This is a complex mechanism in which organic matter form complex compound with inorganic metal ions through a covalent bond or electrostatic force. *Chelation:* This mechanism occurs when more than one e^- doner is present in the functional group which helps the biomass to form a chelate cage-like complex structure with metal ions. *Precipitation:* Precipitation is highly dependent upon conjugate metal ion concentration and pH.

10.4 Mechanisms of Heavy Metal Removal

Among all of the remediation techniques for removal of heavy metal from wastewater, adsorption-assisted technique is a very simple and commercial approach to adopt. There are several mechanisms of adsorption like physical and sorption, ion and ligand exchange, chelation, or surface and internal complexation (Dai et al. 2018). Surface and interfacial adsorption are mainly responsible for physisorption which frequently occurs in low-cost adsorbents. In surface adsorption, metal ions are drifted from solution to the adsorbent surface by diffusion. On the adsorbent surface having opposite charge to the adsorbate, metal ions are strongly attracted by some electronic forces such as dipole–dipole interactions, moderate forces of attraction, or H-bonding (Sulyman et al. 2017). Once metal ions crosses boundary layer, they readily attached to adsorbent surface and thereby successively removed from the solution. Figure 10.3 shows pictorial representation of the mechanism. During interfacial adsorption, metal ions after getting diffused from the liquid boundary

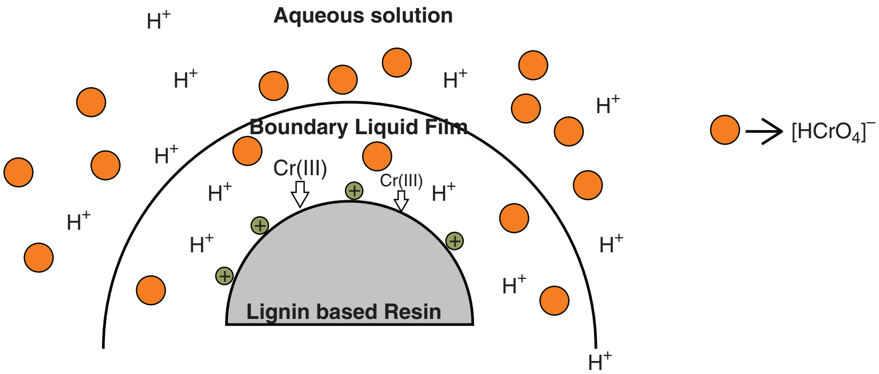


Fig. 10.3 Adsorption of chromium(VI) by adsorbent such as lignin based resin via surface adsorption. (Modified after Liang et al. 2013)

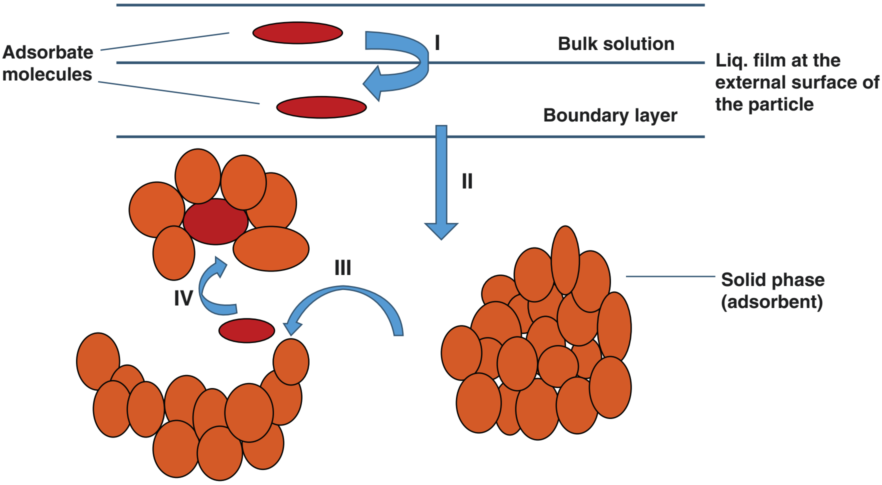
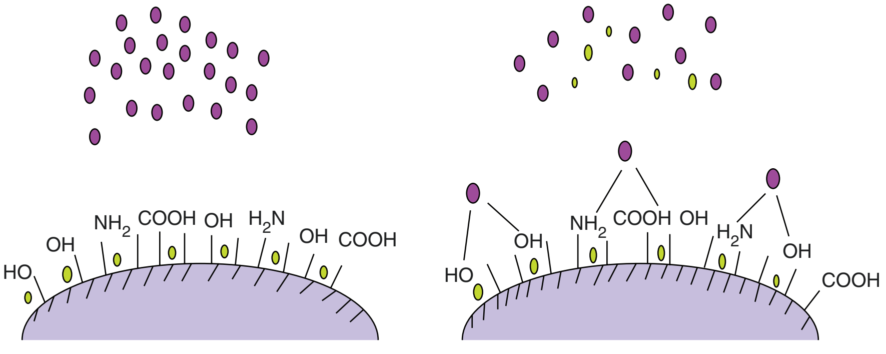


Fig. 10.4 Removal of toxic heavy metal using adsorbent via interstitial adsorption. (Modified after Sulyman et al. 2017)

layer enter into the interstitial pores of the adsorbent. Thereby adsorption occurs on the interior wall of substrate material. Figure 10.4 illustrates this type of mechanism.

Bioadsorbent contain several functional groups such as amide, hydroxide, phosphate, carboxylate, and thiols, which can form chemical bonds with metal ions. Adsorption via ion-exchange pathway is very efficient depending upon activation energies of the reactions. Figure 10.5 represents proposed mechanism. Therefore it was very clear that apart from bioadsorbent the compounds which has phenolic group are capable to interchange protons with metal ions leading to decrease in pH as per the following equation (Bozic et al. 2009):



Before adsorption **After adsorption**

Fig. 10.5 Before and after adsorption of heavy metal such as lead by adsorbent via ion-exchange mechanism. (Modified after Chen et al. 2010)

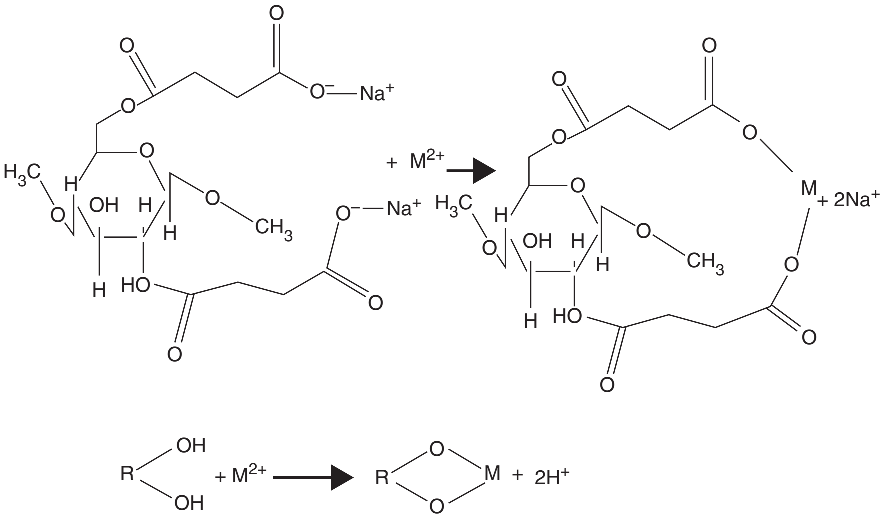


Fig. 10.6 Adsorption of toxic divalent heavy metal cations (M^{+2}) by exchange with Na^+ and H^+ ions. (Modified after Dai et al. 2018)

$$M^{2+} + 2\left(R{-}OH\right) \rightarrow M\left({-}OR\right)_2 + 2H^+$$

A recent study on adsorption of metals by cation exchange mechanism revealed that in presence of -COOH and -OH groups, divalent heavy metal cation present in solution form bond by sharing 2 pairs of electrons and then successively releases 2 H^+ or Na^+ ions in the solution (Dai et al. 2018) which is shown in Fig. 10.6. From the reaction mechanism of ion exchange, it is quite obvious to assume that with decrease in pH, concentration of H^+ ions increases and therefore adsorption decreases because of the absence of vacant sites on adsorbent for metal ions (Demirbas et al. 2009).

Electrostatic forces also have influence on the adsorption mechanism. Electrostatic forces involve attraction between charged clouds of atoms. It is heavily dependent on operating conditions mainly on pH of the aqueous solution. At lower pH, various functional groups like carboxyl and hydroxyl are protonated and much more challenging for metal cations to accommodate active sites of adsorbent over H_3O^+, consequently resulting in electrostatic repulsion as well as preventing adsorption. Adsorption of metal ions increases as pH increases because of the decrease in electrostatic repulsion. The removal efficiency of adsorbent is also influenced by relative value of pH that is point zero charge pH_{PZC}. At the point zero charge, adsorbent surface has no charge at all. When solution pH is less than pH_{PZC}, adsorbent surface gets positively charged, but at pH greater than the pH_{PZC}, surface of the adsorbent became negative (Joseph et al. 2019). Therefore the negative charge density of adsorbent surface at $pH > pH_{PZC}$ enhances cation adsorption capacity, and reverse is true for $pH < pH_{PZC}$.

10.5 Conclusion

Environmental pollution becomes main hurdle for our sustainable development. Remediation of toxic hazardous metal is one of the concerned issues to be dealt with. Therefore there are load of studies available in literature on heavy metal removal from domestic, municipal, and industrial wastewater. In this chapter we restrict our studies only on low-cost adsorbents capable of eliminating risk of environmental contamination by heavy metals. Adsorbents like clay, coal, peat moss, zeolite, and chitosan are indeed very cheap and effective for this purpose. Along with conventional adsorbents, agricultural and industrial wastes are emerging out as efficient alternative for heavy metal removal. Most of the research study shown keen interest for enhancement of adsorption capabilities of these waste materials by chemical or thermal modification. The vital facts indulge with metal adsorption are adsorbate concentration, temperature, pH, extent of surface modification, and adsorbent characteristics. In spite of considerable adsorption performance, low-cost adsorbents seek for proper studies in terms of technicality and overall process efficiency to be commercialized.

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Chapter 11
Characteristics and Adsorptive Treatment of Wastewaters Containing Dyes

Anna Wołowicz and Monika Wawrzkiewicz

Contents

Abstract High usage of dyes by textile, paper and pulp, tannery and paint, plastic, cosmetics, and food industries generates effluents containing hazardous dyes and auxiliaries. In order to eliminate this problem, it is desirable to look for effective, sustainable, and efficient methods for wastewater treatment containing dyes. Overview regarding disposal of dyes by adsorption using such material as carbonaceous sorbents (commercial activated carbons, fullerenes, nanotubes, activated carbons prepared from wastes), naturally occurred substances (clays, zeolites, siliceous materials), nonconventional low-cost adsorbents (agriculture wastes, e.g., leaves, fruits, straw, rice husks, chaff, vegetable fibers, sunflowers stalks, or wastes from industry such as red mud, metal hydroxide sludge, fly ash, as well as biosorbents

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such as living or dead biomass, e.g., algae, yeast, bacteria, fungi), composites and nanocomposites, nanomaterials, as well as ion-exchange resins. The physicochemical properties of the above mentioned sorbents and their sorption capacities were compared toward different types of dyes based on a literature review.

Keywords Dyes · Adsorption · Activated carbons · Low-cost adsorbents · Composites · Anion exchangers · Textile wastewaters · Dyes removal

11.1 Introduction

11.1.1 Dyes: Definition and Classification

The definition of dyes as chemical substances taken from a popular science encyclopedia states that they are organic substances of natural or synthetic origin which are able to have selective absorption of light within visible region (400–700 nm) and coloring miscellaneous materials such as fabrics, plastic, leather, food, wood, cosmetics or paper. In their molecule, two basic types of groups can be distinguished: chromophore and auxochrome (Fig. 11.1).

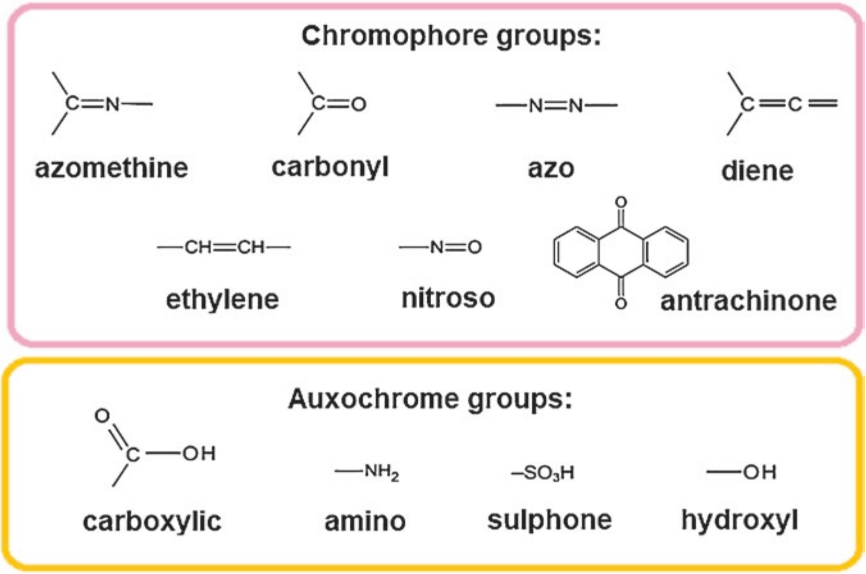
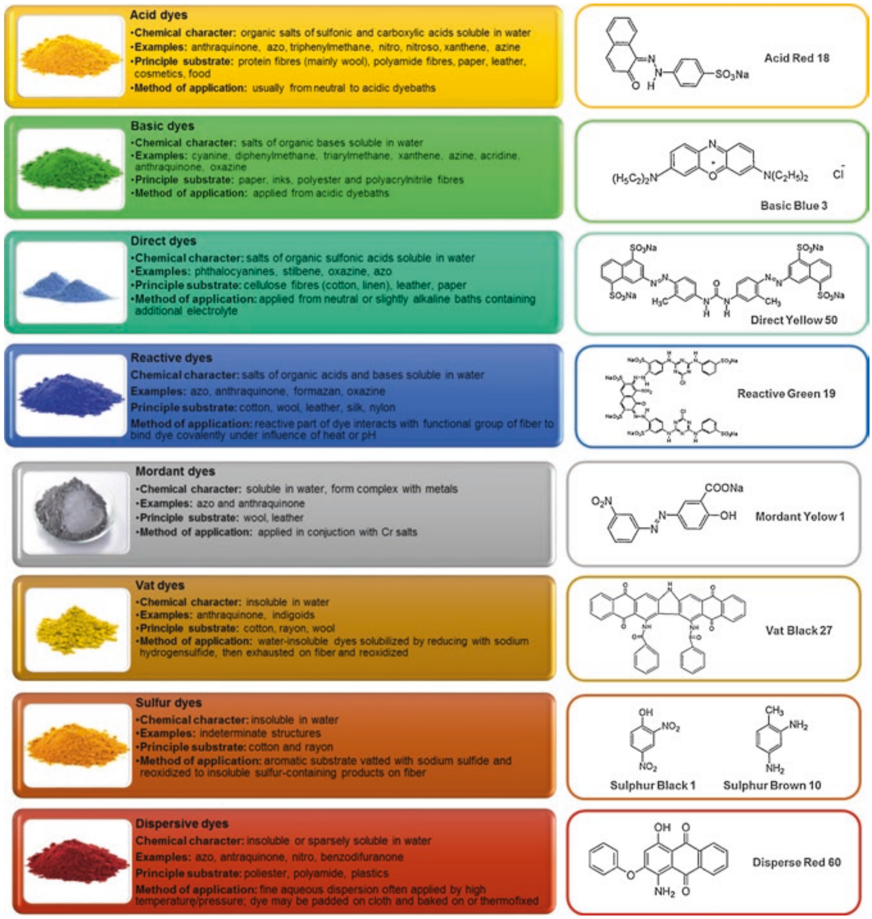


Fig. 11.1 Chromophores and auxochromes of dyes



Acid dyes
- **Chemical character:** organic salts of sulfonic and carboxylic acids soluble in water
- **Examples:** anthraquinone, azo, triphenylmethane, nitro, nitroso, xanthene, azine
- **Principle substrate:** protein fibres (mainly wool), polyamide fibres, paper, leather, cosmetics, food
- **Method of application:** usually from neutral to acidic dyebaths

Basic dyes
- **Chemical character:** salts of organic bases soluble in water
- **Examples:** cyanine, diphenylmethane, triarylmethane, xanthene, azine, acridine, anthraquinone, oxazine
- **Principle substrate:** paper, inks, polyester and polyacrylnitrile fibres
- **Method of application:** applied from acidic dyebaths

Direct dyes
- **Chemical character:** salts of organic sulfonic acids soluble in water
- **Examples:** phthalocyanines, stilbene, oxazine, azo
- **Principle substrate:** cellulose fibres (cotton, linen), leather, paper
- **Method of application:** applied from neutral or slightly alkaline baths containing additional electrolyte

Reactive dyes
Chemical character: salts of organic acids and bases soluble in water
Examples: azo, anthraquinone, formazan, oxazine
Principle substrate: cotton, wool, leather, silk, nylon
Method of application: reactive part of dye interacts with functional group of fiber to bind dye covalently under influence of heat or pH

Mordant dyes
- **Chemical character:** soluble in water, form complex with metals
- **Examples:** azo and anthraquinone
- **Principle substrate:** wool, leather
- **Method of application:** applied in conjuction with Cr salts

Vat dyes
- **Chemical character:** insoluble in water
- **Examples:** anthraquinone, indigoids
- **Principle substrate:** cotton, rayon, wool
- **Method of application:** water-insoluble dyes solubilized by reducing with sodium hydrogensulfide, then exhausted on fiber and reoxidized

Sulfur dyes
- **Chemical character:** insoluble in water
- **Examples:** indeterminate structures
- **Principle substrate:** cotton and rayon
- **Method of application:** aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber

Dispersive dyes
Chemical character: insoluble or sparsely soluble in water
Examples: azo, antraquinone, nitro, benzodifuranone
Principle substrate: poliester, polyamide, plastics
Method of application: fine aqueous dispersion often applied by high temperature/pressure; dye may be padded on cloth and baked on or thermofixed

Fig. 11.2 Technical classification of dyes

The former are responsible for selective absorption of light from visible region and the latter for affinity for being colored materials. Other substituents which impart specific properties of dyes affecting their solubility or stability improvement can also be present (Hunger 2002). Dyes could be divided into few classes taking into consideration their chemical structure (chemical classification) or their usage and application methods (technical classification). The most popular groups of dyes based on chemical classification are azo/azomethine, anthraquinone, polymethine, phthalocyanine, formazan, nitro and nitroso, etc. The technical classification of dyes is given in Fig. 11.2.

All dyes are ordered in a special register, called color index. The international database is run jointly by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists. It was first edited in 1925. Currently, it is published only in the Internet. It serves as a common color list used by producers and consumers. All colors used in trade and industry have their references in this index. Each of the coloring substances listed in the index (both dyes and pigments) has an individual name (generic name) and an individual designation in the form of a number (constitution number) in the case of a known and published structure. The first synthetic dyes were fuchsin and mowein. The demand for dyes and pigments rises year after year, estimated to be 3.9% in 2008–2013; in 2010 the highest consumption of dyes and pigments was observed in Asia. The leading countries in the production of dyes in the last quarter of the century were the United States, Japan, the countries of Eastern Europe and Asia especially China, India, and South Korea. 1990 was a breakthrough year in the textile industry and the production of dyes. Statistical data indicates that for several years now, supply and demand are at a similar level. In present, China is the largest producer and recipient of dyes on a global scale, which consume a larger half of the dyes produced (Katheresan et al. 2018). Dyes are used in many industries, including textile, cellulose and paper, pharmaceutical, food, production of paints and varnishes, cosmetics, and production of inks and toners. Moreover, they are increasingly used in the technology of optical indicators and optical recording, nonlinear optics, and color photography technology.

11.2 Methods of Dyes Removal

Due to the large scale of dye production and the possibility of their penetration into water reservoirs as a result of non-efficient technological processes, they get into the environment from the textile industry in the amount of 2–50%, depending on the chemical group (dyes discharge to effluents amounts: 5–20% acid, 0–5% basic, 5–30% direct, 0–10% disperse, 2–10% metal-complex, 10–50% reactive, 10–40% sulfur, 5–20% vat). Textile sewages composition (Bartkiewicz and Umiejewska 2010) depending on the type of fabrics dyed is presented in Fig. 11.3.

Dyes concentration in effluents can reach up to 300 mg/mL (O'Neill et al. 1999). Many dyes are discernible at 1 mg/L concentration in water (Panday et al. 2007). Besides the aesthetic values, it is also important to mention that they constitute a threat to the environment and living organisms. Their presence in the environment affects adversely the functioning of aquatic ecosystems and poses a threat to human and animal health. Permeation of colored wastewaters into waters causes limitation of photosynthesis, which in turn leads to an oxygen concentration decrease and biological balance disturbance in the environment. Many industrial dyes contain harmful carcinogenic and mutagenic substances, which can enter food chain and move through its individual links (O'Neill et al. 1999; Holme 1984). Analysis of Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers report concerning toxicity of 3000 different dyes allows to state that they are characterized by a high Lethal Concentration$_{50}$ value compared to pesticides, e.g., dichlorodiphenyltrichloroethane (Lethal Concentration$_{50}$ (dyes) = 0.05 mg/L, Lethal Concentration$_{50}$

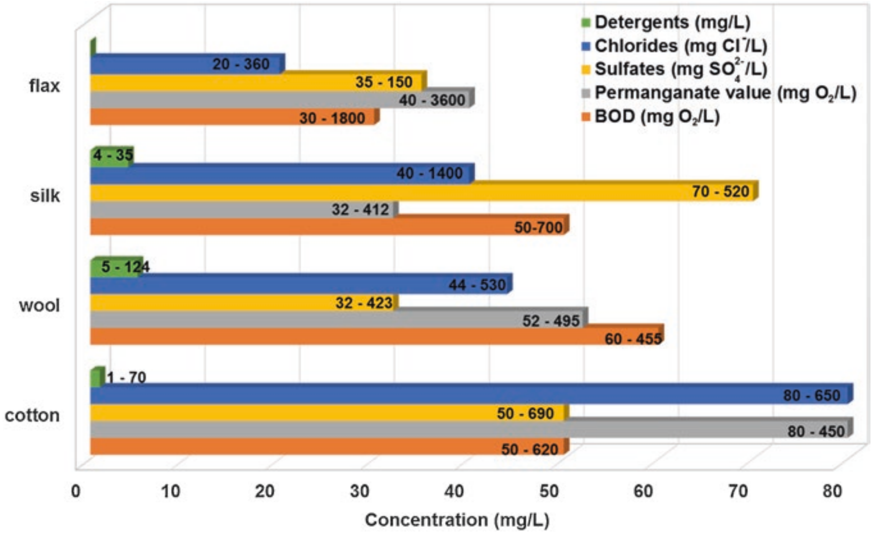


Fig. 11.3 Range of indicator fluctuations in the textile industry wastewater impurities (where *BOD* biochemical oxygen demand)

(dichlorodiphenyltrichloroethane) = 0.006 mg/L) (Holme 1984). 98% of dyes under studies show Lethal Concentration$_{50}$ over 1 mg/L. Particularly high toxicity (Lethal Concentration$_{50}$ = 0.8 mg/L) shows basic yellow 37 (Holme 1984). According to Ventura-Camargo and Marin-Morales (2013), oral exposure of humans to the azo dyes can lead to the formation of aromatic amines by both the intestinal microflora and liver azoreductases. Moreover, some of these amines have exhibited carcinogenic properties.

Difficulties in developing a suitable method (economical, effective, and simple) for synthetic dyes removal are caused by application of different types of dyes in technological process and changes in production technology (Forgacs et al. 2004). In order to control the negative impact of different types of dyes on the environment and living organisms, intensive research is carried out to develop effective and selective methods of their removal and degradation. Textile wastewaters can be treated using biological, chemical, physical, as well as physicochemical combination processes (Fig. 11.4).

The advantage of biological treatment of wastewaters containing dyes is undoubtedly the price and simplicity of operations using microbial biomass, fungal, and microbial cultures, algae degradation, as well as pure or mixed cultures under aerobic and anaerobic conditions. This technique is insufficient to remove dyes form wastewaters completely. It is ineffective method for different types of dyes, and there can be formed methane and hydrogen sulfides as by-products. In addition, it is time-consuming. The efficiency of biological wastewater treatment varies 76–90% (Katheresan et al. 2018).

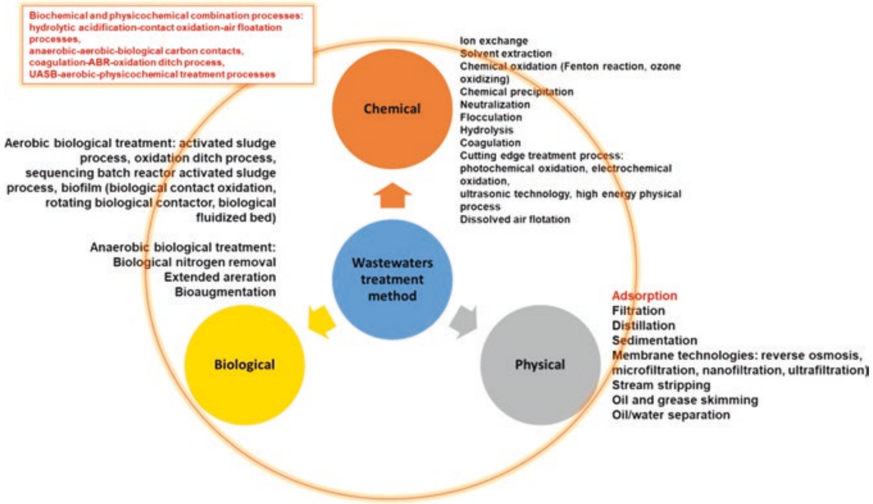


Fig. 11.4 Methods of textile wastewater treatment

The chemical methods of dyes removal are advanced oxidation processes, Fenton reaction, oxidation, ozonation, photochemical and ultraviolet irradiation, and electrochemical decomposition. Most of the above mentioned methods are costly due to high energy consumption and formation of secondary pollution. The most dangerous, however, is the apparent decolorization, which, despite the color removal, does not lead to detoxification of substances present in wastewaters. As a consequence, colorless decolorization products are still found in the aquatic environment. This effect occurs during decolorization, e.g., by chlorination, brown lignin-rich wastewaters generated during pulping of wood in the pulp and paper industry. It leads to the formation of colorless but toxic, mutagenic, and carcinogenic by products of cleavage, i.e., chlorolignins and dioxins (Crini 2006). Other undesirable drawbacks are additional chemicals usage in macroscale and specific equipment. The color reduction yield by chemical treatment ranged from 88% to 99% (Katheresan et al. 2018).

Physical dye removal methods such as coagulation and flocculation, membrane filtration, nano-filtration or ultra-filtration, reverse osmosis, adsorption, and ion exchange are usually straightforward methods. These techniques are often chosen because of its simplicity and 86–99% effectiveness (Katheresan et al. 2018). Physical methods consume a lot less chemicals compared to the biological and chemical ones.

Although many dye removal methods are known and extensively researched, only several of them could be implemented by industries due to their drawbacks and limitations (Bhatia et al. 2017; Gupta and Suhas 2009; Katheresan et al. 2018; Raval et al. 2017; Yagub et al. 2014).

11.3 Adsorption and Sorbents Classification

Adsorption is useful technic for separation, purification, catalysis, and pollution control processes (Rouquerol et al. 1999). Taking into account its advantages, it can be also applied in textile wastewater treatment (Yagub et al. 2014; Seow and Lim 2016; Pavithra et al. 2019). The use of traditional methods of synthetic dyes removal from water and wastewater and thus effective decolorization of wastewater is not always possible, whereas the use of adsorption processes seems to be a beneficial solution.

The term adsorption was coined in 1881 by the German physicist named Heinrich Kayser. Adsorption is defined as the interaction of chemical species such as atoms, ions, or molecules onto the surface of particles and taking place on solid's surface in contact with liquid or gas. In the other words, adsorption is material enrichment or fluid density increase in the vicinity of an interface. Most often adsorption refers to the process of liquid substance binding on the solid surface or gaseous substance binding on the solid or liquid surface (Rouquerol et al. 1999).

Adsorption proceeds using various types of adsorbents (porous insoluble sponge-like substances) which are capable of adsorbate capturing (Fig. 11.5). Such materials should be characterized by a few very important properties. First of all adsorbents should be characterized by low price (Zhou et al. 2019). Nowadays, low-cost adsorbents are frequently applied to reduce the total cost of adsorption process (Gupta and Suhas 2009). Moreover, they are produced from various kinds of waste materials or natural materials. It is essential that these materials should be easily accessible. Fundamental characteristics of a good adsorbent are a high adsorption capacity resulting in quantitative removal of dyes and high adsorption efficiency. The morphological and structural properties of materials such as the surface area and

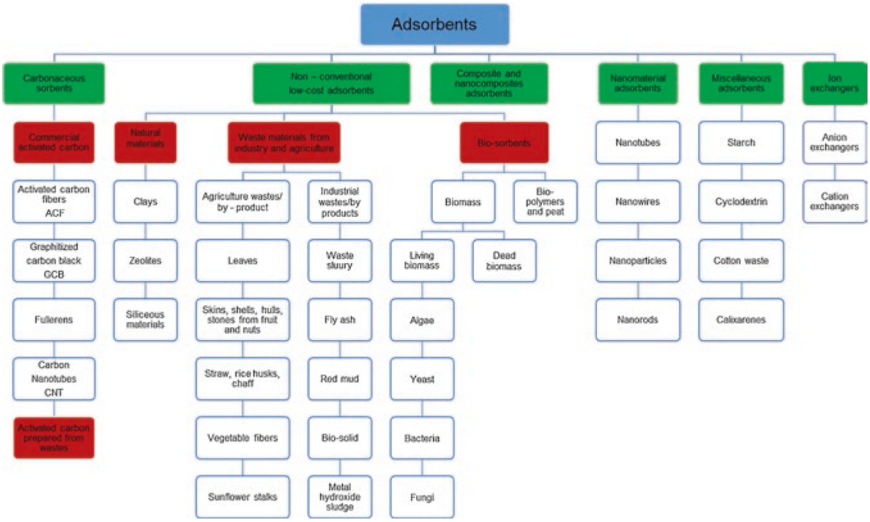


Fig. 11.5 Adsorbents classification

porous structure are likewise important features of adsorptive materials. With increase of surface area and using more porous material, higher adsorption efficiency is obtained. Not only an economical aspect but also the process duration is important. Dyes should be removed with high efficiency as well as in the shortest possible time. Additionally, adsorptive materials should be able to remove various types of pollutants, to be reused and function in a broad range of pH, temperature, as well as dye concentrations.

Solid materials used in wastewaters treatment such as sorbents can occur in different chemical forms and geometrical structure of the surface. Moreover, they are classified in various ways depending on the adopted criterion. Some of them are presented below. Sorbents could be divided into a few classes:

1. Natural materials (wood, peat, chitin, and chitosan, clays, natural zeolites, coal)
2. Modified natural materials with a developed structure and improved properties (activated carbon, silica gel, activated alumina)
3. Manufactured materials (zeolites, aluminosilicates, polymeric resins)
4. Agriculture wastes and by-products
5. Biosorbents (Crini et al. 2019)

The other authors (Dąbrowski 2001) classified sorbents into three categories such as (1) carbon adsorbents (activated carbons, fullerenes, carbonaceous materials, activated carbon fibers, molecular carbon sieves), (2) mineral adsorbents (activated alumina, metal hydroxide and oxide, silica gels, zeolites, clay minerals, pillared clays), and (3) other adsorbents (synthetic polymers, mixed adsorbents, composite adsorbents). Crini et al. (2019) presented classification of sorbents into two categories: (1) conventional adsorbents, activated carbons, inorganic materials, and ion-exchange resin, and (2) nonconventional adsorbents, activated carbons prepared from the solid wastes as well as miscellaneous ones. Activated carbons, silica gels, zeolites, and activated alumina are the most frequently commercially applied sorbents from the conventional adsorbents group for sorption processes.

11.4 Removal of Dyes from Waters and Wastewaters Using Various Adsorbents

11.4.1 Commercial Activated Carbon

The term active carbons includes a wide range of carbonaceous materials (amorphous) that are characterized by a high degree of porosity and surface reactivity as well as the extended interparticle surface area. Active carbons are known to be very efficacious adsorbents. However their production costs are very high. This group includes commercial activated carbons and active carbons produced from agricultural waste materials (Crini et al. 2019).

The commercial activated carbons are one of the oldest materials most widely utilized in industry as adsorbents, catalysts, support for catalysts, or reducing agents. Due to great capacity of commercial activated carbons, they are the most effective adsorbents in organic as well as mineral contaminants removal (Pyrzyńska 2008; Ryczkowski 2012).

Active carbons are substances partly composed of graphite fine crystalline, from elemental carbon in an amorphous form and various substances which are non-carbon, such as mineral substances and heteroatoms, e.g., hydrogen, oxygen, sulfur, and nitrogen or phosphorus. Carbon as a major constituent of active carbons is present in the range 85–95%. The quantity and type of heteroatoms depend on the raw materials used in the production process, production processes, as well as the procedure of their activation (heteroatoms introduced during the activation process). Active, surface functional groups and the delocalized electrons result in acidic or basic surface of active carbons (Shafeeyan et al. 2010; Wołowicz 2013). Good adsorptive properties of carbonaceous materials are associated with their surface chemical and porous structures (Bansal and Goyal 2005; Crini et al. 2019; Wołowicz 2013). They possess a large surface area which is usually in the range from 800 to 1500 m^2/g (for the most widely applied active carbons) which is a result of existence of internal porous structure (micropores, mesopores) and pore volume from 0.2 to 0.6 m^2/g (in many cases pore volume is as large as 1 cm^3/g) (Wołowicz 2013). The examples of surface area of active carbons can be found in Katheresan et al. (2018). The active carbons are often modified in order to improve their sorptive properties using physical activation (two steps, (1) carbonization of the carbonaceous precursors (raw materials) by the pyrolysis process, (2) activation using the agents – air, stream, carbon dioxide, mixture of oxidizing gases, high temperature 600–1200 °C) or chemical activation (one or two steps conducted at the same time, (1) impregnation of the precursor (raw material) by chemicals, (2) heating in the flow of nitrogen gases, low temperature 450–900 °C), e.g., introduction of nitrogen functional groups into the surface of carbon (nitrogen functionalities) by the reaction with reagents containing nitrogen (amines, ammonium, nitric acid) or activation precursors containing nitrogen, oxidation by gases in order to introduce acidic groups containing oxygen such as carboxylic, phenol, lactone, carbonyl, carboxylic anhydride, quinone, pyrone, chromene etc. the acidic, basic and neutral ones etc. (Foo and Hameed 2010; Shafeeyan et al. 2010; Yagub et al. 2014). Active carbons (obtained by combustion, thermal decomposition, or partial combustion) are prepared usually in granular, powder, fibrous, and cloth forms (Bansal and Goyal 2005). The advantages and disadvantages of active carbons are presented in Fig. 11.6.

Active carbons can be successfully applied in dye removal from waters and wastewaters (Crini et al. 2019) but such technology also possesses a few disadvantages. The commercial activated carbons are quite expensive materials and their price increases with developing quality. They can be nonselective and ineffective toward vat and disperse dyes, varied in quality; they create problems with their removal after the use of spent active carbons. They are characterized by rapid saturation and difficulty with regeneration (high cost, loss of the adsorbent, not straightforward) (Crini et al. 2019; Yagub et al. 2014).

Dai (1998) applied commercial activated carbons (powder, 781-A type, the solution pH at zero-point charge = 6.2) for cationic dyes such as methyl green and methyl violet as well as anionic dyes such as phenol red, carmine, and titan yellow

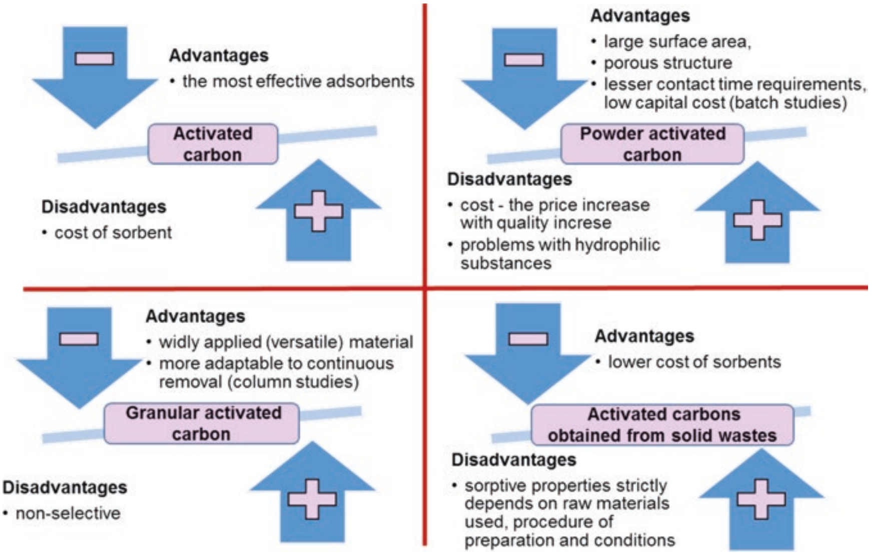


Fig. 11.6 Advantages and disadvantages of active carbons

removal and observed changes of saturated adsorption amounts of dyes with pH of solutions and changes of saturated adsorption amounts with zeta potentials. Methyl green possesses the quaternary ammonium halide group and methyl violet the amine group whereas anionic dyes the sulfuric group. The saturated adsorption amount for anionic dyes reduction was observed with the increase of pH. Moreover, the zeta potential of commercial activated carbons surface showed three distinct states: zeta potential is nearly zero – neutral potential state, dispersion forces are the adsorption forces whereas the electrostatic interactions between commercial activated carbon surface – dyes are negligible (no effect of pH); zeta potential is negative or positive, attractive or repulsive interactions between commercial activated carbon surface and dyes occurred.

Congo red was removed by activated carbon (mass of adsorbent 1 g/L, pH at zero-point charge = 6.6). Efficiency of dye removal was above 90% (initial dye concentration 50–100 mg/L) and close to 80% at pH 7.0. At pH 2 the maximum adsorption (quantitative removal) of dye was observed. Kinetic and equilibrium studies proved that pseudo second-order kinetic model, and Freundlich model fit the experimental results more adequately. Desorption of Congo red was carried out using the surfactant enhanced carbon regeneration method with the anionic and cationic surfactants (Purkait et al. 2007).

Reactive black 5 was removed using grain and powder commercial activated carbons (powders after chopping obtained from the granular form) using three Norit materials such as Norit R008, Norit Darco 12 × 20, and Norit PK 1–3 (used as fine powders of the size from 75 to 125 µm). The effect of pH (2–12) (1 g/L of adsorbent, 20 mL of dye solution, the concentration before sorption C_0 = 500 mg/L) shows that the optimum pH was alkaline and equal to 10. Moreover, the ionic strength (0.001–1 mol/L) or temperature (25–65 °C) increase results in the increasing adsorption capacity. The capacity values were equal to 348 mg/g (for Norit Darco 12 × 20), 527 mg/g (Norit R008), 394 mg/g (Norit PK 1–3) at 25 °C and 564 mg/g (Norit Darco 12 × 20), 796 mg/g (Norit R008), and 474 mg/g (Norit PK 1–3) at 65 °C. The authors pointed out that the size of particles influenced the removal efficiency – a decrease of particle size results in the dye removal efficiency increase, e.g., from 274 mg/g (grain activated carbon, 25 °C) to 348 mg/g (fine powder activated carbon, 25 °C), Norit Darco 12 × 20; from 287 mg/g (grain activated carbon, 25 °C) to 527 mg/g (fine powder activated carbon, 25 °C), Norit R008; and from 195 mg/g (grain activated carbons, 25 °C) to 394 mg/g (fine powder activated carbon, 25 °C), Norit PK 1–3. Desorption of reactive black 5 from the activated carbons conducted by means of sodium dodecyl sulfate (6 g/L) resulted in 18% removal of reactive black 5 from the Norit Darco 12 × 20 sorbent at 25 °C and 83% at 85 °C, whereas the percentage removal for Norit PK 1–3 and Norit R008 was the following: 17% (25 °C) and 67% (85 °C), Norit PK 1–3, and 10% (25 °C) and 42% (85 °C), Norit R008. The Langmuir-Freundlich and the pseudo second-order kinetic equations show better fitting to experimental results. The interaction was the π–π ones between the ring of carbons and that of reactive black 5 molecule (Giannakoudakis et al. 2016).

The commercial activated carbons and that treated with 2 mol/L HCl and 2 mol/L HNO_3 for 24 h (ambient temperature) after washing with ultra-pure water and drying at 103–105 °C were applied for removal of methylene blue, crystal violet, and rhodamine B (5 mg of adsorbent, 200 mL of dye solutions, initial dye concentration 1.2×10^{-5}–4.6×10^{-5} mol/L, temperature (30–50) ± 0.1 °C). Treatment of activated carbons by acids results in negligible increase in the surface area from 972 m^2/g (activated carbon) to 1015 m^2/g (commercial activated carbon treated with 2 mol/L HCl) and 987 m^2/g (commercial activated carbon treated with 2 mol/L HNO_3), whereas pore structure changes are insignificant. The zero-point charge of the tested sorbents is equal to 8.6 for activated carbon, 6.7 for commercial activated carbon treated with 2 mol/L HCl, and 2.98 for commercial activated carbon treated with 2 mol/L HNO_3. Based on the adsorption capacities, the selectivity series were as follows: activated carbon > commercial activated carbon treated with 2 mol/L HCl > commercial activated carbon treated with 2 mol/L HNO_3 for methylene blue or commercial activated carbon treated with 2 mol/L HCl > activated carbon > commercial activated carbon treated with 2 mol/L HNO_3 for crystal violet and rhodamine B. Treatment of activated carbons using HNO_3 results in production of more active acidic groups (lactone, carboxyl) and more homogeneous pore size which leads to sorption capacities reduction, whereas treatment using HCl causes that less active acidic groups are formed resulting in better removal efficiency. According to the authors sorption of dyes proceed by diffusion because after 700 h the system equilibrium is not reached. Sorption of rhodamine B on activated carbon is an endothermic process, and its kinetics can be fitted well by the pseudo second-order model (Wang and Zhu 2007).

More examples of commercial activated carbon without or after treatment applied for dyes removal are presented in Table 11.1.

Table 11.1 Commercial activated carbons for dyes wastewaters treatment

Starting material	Preparation of adsorbents	Adsorbate type and name	Additional information	Results	References
Commercial activated carbon	None	Reactive: reactive turquoise blue QG	Surface area = 618.7 m^2/g	Max. sorption capacity = 140 mg/g (pH = 2, T = 30 °C), the best fit for the kinetic data – pseudo second-order model, process was exothermic, the main mechanism was physisorption	Schimmel et al. (2010)
Panreac, Fagron	None	Mordant: mordant blue 9	Surface area of Fagron = 514 m^2/g Surface area of Panreac = 296 m^2/g	Max. sorption capacities: Fagron – 221 mg/g Fagron – 80,300 mg/g Fagron – 200,490 mg/g Panreac– 213 mg/g	Martins and Nunes (2015)
Panreac, Fagron	Oxidant acid treatment (20 mL of 4.6 mol/L HNO_3), heated at 60 °C, washed with deionized water and dry at room temperature (24 h)			Max. sorption capacities: Fagron – HNO_3 180 mg/g Panreac – HNO_3 93 mg/g	
Norit ROX 0.8	None	Reactive: red, yellow, blue Direct: red, yellow, blue Acid: red, rellow, blue Basic: red, yellow, blue	Surface area = 833–1032 m^2/g	Percentage removal of dyes were following: Reactive: blue 57%, red 47%, yellow 34%; Direct: red 20%, yellow 9%, blue 27%; Acid: red 43 %, yellow 78%, blue 45%; Basic: red 87%, yellow 90%, blue 99%	Pereira et al. (2003)
Norit ROX 0.8	Oxidation with 5 mol/L HNO_3, 3 h, T – boiling				
Norit ROX 0.8	Oxidation with 5 mol/L HNO_3, 3 + 3 h, T – boiling				
Norit ROX 0.8	Oxidation with 1 mol/L H_2O_2, T – room				
Activated carbon	Reduction with NH_3, T = 200 °C				
Activated carbon	Thermal: under N_2 flow, T = 700 °C, +1 h under dry air flow, T – room				
Activated carbon	Thermal: under H_2 flow, T = 700 °C, +1 h under dry air flow, T – room				
Activated carbon	Thermal: under H_2 flow, T = 900 °C, +1 h under dry air flow, T – room				

Granular activated carbon	Purified by water, drying at 120 °C (24 h)	Acid: indigo carmine (other name acid blue 74, food blue1)	Surface area = 1403 m^2/g pH at zero-point charge = 8.0	Effect of dose: 97.2% (dye initial concentration 20 mg/L, dose – 0.2 g/L), effect of pH: pH = 7, max. sorption capacity 38 mg/g, effect of particle diameter (2.5; 3,5; 7 mm): 30 mg/g (2.5 mm), max. sorption capacity 133.8 mg/g at 45 °C, adsorption of indigo carmine – endothermic process, the best fit for the kinetic data – pseudo second-order model	Secula et al. (2011)
Filtrasorb 400 activated carbon	None	Reactive: remazol reactive yellow, remazol reactive black, and remazol reactive red	Surface area = 1100 m^2/g	Max. sorption capacities: remazol reactive yellow 714 mg/g, remazol reactive black 278 mg/g, remazol reactive red 213 mg/g, capacity drops in the multisolute system; Langmuir and Redlich–Peterson models show good fitting of equilibrium data	Al-Degs et al. (2007)
Powdered activated carbon	None	Reactive: reactive black 5	Surface area = 900 m^2/g	Max. sorption capacity: 58.82 mg/g, the best fit for the kinetic data – pseudo second-order model; Langmuir and Freundlich models show good fitting of equilibrium data	Eren and Acar (2006)

Where *T* temperature

Activated Carbon Obtained from Wastes

To overcome deficiencies of commercial activated carbon, agricultural wastes or industrial solid wastes are applied for active carbons production. Over the last several years, more attention was paid to such type materials which are considered in wastewaters purification due to excess of generated wastes, low cost, easy availability, and non-toxicity in nature (Raval et al. 2017; Yagub et al. 2014). As precursors used in activated carbons production for dyes removal leaves, shells, hulls, stones, skin of fruit and vegetables, oil palm fibbers, wood, etc. could be applied (Foo and Hameed 2010). The examples of various precursors used for activated carbons production and application for dye removal are presented below in the following order: precursor of activated carbons production, dye which is removed, and maximum sorption capacity:

- Waste apricot, surface area = 1060 m^2/g, methylene blue 136.98 mg/g (50 °C), methyl green 163.93 mg/g (50 °C), crystal violet 91.74 mg/g (50 °C) (Basar 2006)
- Palm fruit bunch, basic yellow 21 327 mg/g, basic red 180 mg/g, basic blue 92 mg/g (Nassar and Magdy 1997)
- Oil palm shell, methylene blue 243.90 mg/g (Tan et al. 2008)
- Plum kernel, acid blue 74 388.00 mg/g (Tseng and Wu 2009)
- Organic sugarcane bagasse, acid blue 80 391 mg/g (Valix et al. 2004)
- Sunflower seed hull, acid violet 17 107.52 mg/g (Thinakaran et al. 2008)
- Sludge, acid orange 7 and chrysophenine 83–270 mg/g at temperatures 10–60 °C (Chiang et al. 2009)
- Sewage sludge (drying at 105 °C, chemical activation using 98% H_2SO_4 (48 h), dried at 80 °C, pyrolysis under flow of N_2 (heating rate 15 °C/min up to 625 °C), washed using 10% HCl (10% by weight) and drying at 105 °C, then ground and sieved (0.125 and 1.5 mm), surface area = 390 m^2/g, methylene blue 194.3 mg/g, safranine 250.2 mg/g (Rozada et al. 2003)
- Natural cellulose: jute, coconut (physical activation, carbonization at 950 °C under N_2 flow, activation with CO_2; chemical activation, impregnation using 30 wt.% H_3PO_4 (900 °C) for 24 h, washed and heated (20 °C/min) in the N_2 flow at 900 °C for 2 h, purified using ultra-pure water, subsequently dried at 105 °C, acid red 27 113.63–181.81 mg/g (Phan et al. 2006)
- Peanut hulls (chemical activation using 41 wt.% and 85 wt.% H_3PO_4, KOH, 50% $ZnCl_2$, thermal activation by steam pyrolysis), surface area = 80.8–1177 m^2/g, methylene blue 31–38.5 mg/g (Girgis et al. 2002)
- Orange peel, direct blue 86 33.78 mg/g (El Nemr et al. 2008)
- Peach stones (impregnation using 85 wt% H_3PO_4 followed by carbonization (500 °C), soaking overnight at 80 °C, washed with hot water and dried in their own atmosphere of evolving gases, impregnation using 50 wt% H_3PO_4 and carbonization (500 °C) in the N_2 flow, further heating (800 °C) in the air flow), methylene blue 198–412 mg/g (Attia et al. 2008)
- Almond shell, direct red 80 20.5 mg/g, 16.4 mg/g, and 16.96 mg/g for mixture, internal, and external shells (Ardejani et al. 2008)

- Sugarcane bagasse pith, reactive orange 3.48 mg/g (activation using 28% H_3PO_4, 50% $ZnCl_2$, pyrolysis at 600 °C, physical activation 600 °C without air) (Amin 2008)
- Rubberwood sawdust (*Hevea brasiliensis*), bismark brown dye 1456 mg/g (Kumar et al. 2005)
- *Parthenium* biomass (sulfuric acid treatment method), rhodamine B 18.52 mg/g (pH = 7, particle size 0.3–1 mm) (Lata et al. 2008)
- Coir pith (dried in sunlight (5 h), ground; carbonization at 700 °C (1 h) using a muffle furnace under closed conditions, surface area = 167 m^2/g, acid brilliant blue 15.24 mg/g (Kavitha and Namasivayam 2008)
- Rice husk, sawdust, surface area = 272.5–516.3 m^2/g, acid yellow 36 86.9–183.8 mg/g (Crini 2006)

More examples of commercial activated carbons and activated carbons obtained from wastes/by-products precursors could be found, e.g., in Crini (2006) and Gupta and Suhas (2009).

11.4.2 Low-Cost Adsorbents

Natural materials, synthetically prepared materials, as well as industrial or agricultural by-products are included into one group of adsorbents called low-cost adsorbents (Fig. 11.4). As it was mentioned in Sect. 11.4.1. the costs of activated carbons obtained from wastes (agriculture or industrial wastes) production are much lower (0.1 USD/kg) compared to the commercial activated carbons (1.5 USD/kg) (Gupta and Suhas 2009). Similarly, low-cost adsorbents are cheaper alternatives; therefore they can be substitutes for all expensive adsorbents applied for treatment of wastewaters containing dyes. Moreover, they give double benefits such as waste management and treatment (Yagub et al. 2014).

Application of agricultural solid wastes for dyes sorption is an environmentally friendly, economical, and efficient process (Afroze and Sen 2018). Forest industries produce a large amount of solid wastes such as sawdust, bark, and shavings (Fig. 11.7) which due to their physicochemical properties are potential materials capable to effective removal of dyes (Ho and McKay 1998a; McKay et al. 1999; Özacar and Sengil 2005; Shukla et al. 2002; Velić et al. 2018). Such materials contain organic compounds with the polyphenolic groups (cellulose, hemicellulose, lignin) useful for dyes binding or possess a large tannin content (e.g. bark) which enhances dyes removal. Low cost of waste wood materials (transport influences largely their total cost) and broad availability make waste wood materials very promising as adsorbents. Moreover, the sorption results obtained using the wood sawdust depend largely on pH (Garg et al. 2003; Ho and McKay 1998a) and initial concentration of adsorbate (Khattri and Singh 2000). Ho and McKay (1998a) pointed out that the sorption capacity due to the ionic character of sawdust is much higher for basic than for acidic dyes. Raw sawdust usually exhibits lower sorption

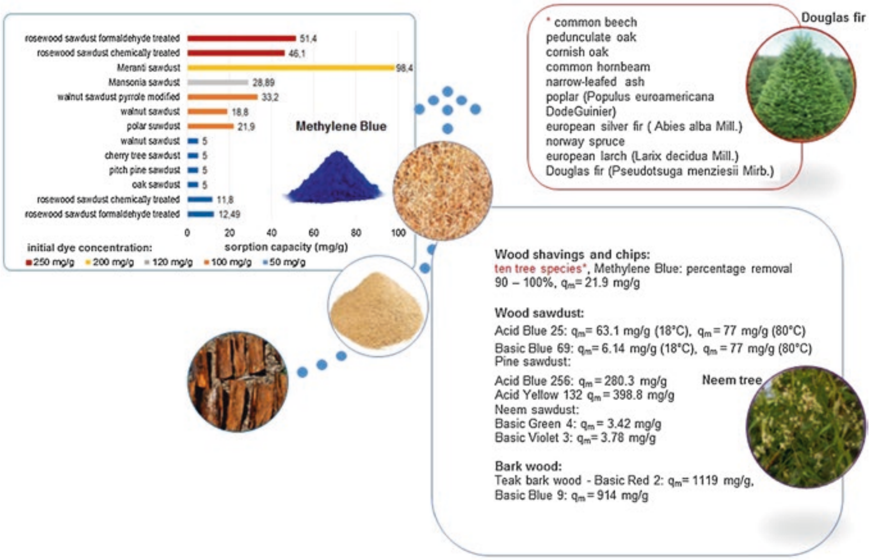


Fig. 11.7 Potential materials capable of effective removal of dyes prepared from waste from the wood industry (where q_m – monolayer sorption capacity)

capacity compared to sawdust after the chemical pretreatment, e.g., sorption of methylene blue and red basic 22 on the beech sawdust treated using $CaCl_2$ (Batzias and Sidiras 2004) or sawdust obtained from the *Dalbergia sissoo* (Indian Rosewood) tree treated by formaldehyde (Garg et al. 2003).

Other solid agricultural wastes were also utilized for the removal of different types of dyes from aqueous solution, e.g., peels such as banana peels (Annadurai et al. 2002), orange peels (Doulati Ardejani et al. 2007; Rajeshwarisivaraj et al. 2001), garlic peels (Hameed and Ahmad 2008), pithes, e.g., banana pithes (Namasivayam et al. 1998), Egyptian bagasse pithes (Chen et al. 2001; Ho and McKay 2003), coir pithes (Namasivayam et al. 2001a, b), and rice husk (Chuah et al. 2005; McKay et al. 1999). The sorption capacities of such materials are collected and compared in Table 11.2.

The other groups of wastes used as adsorbents are by-products come from industry. Red mud, metal hydroxide sludge, as well as fly ash are included in the group of low-cost adsorbents. Sludge comes from the electroplating industry, and it is the dried waste obtained by metal ions precipitation using calcium hydroxide, whereas the fly ash originates in great amounts from combustion processes. Despite the fact that fly ash can contain some toxic substances, e.g., heavy metal ions, it is widely applied in industry and in dyes removal, e.g., the fly ash produced in the sugar industry containing small amounts of toxic metal ions is proposed for efficient dye removal. However, adsorption efficiency and chemical composition of fly ash depend largely on its origin and treatment procedure. Moreover, the high content of silica (60–65%), magnetite, Fe_2O_3 (6–15%), and alumina (25–30%) as well as

Table 11.2 Selected low-cost adsorbents for dyes removal

Waste materials			Dye removed	Sorption capacity [mg/g]	References
Peel	Banana peel		Methyl orange	21	Annadurai et al. (2002)
			Basic blue 9	20.8	
			Basic violet 10	20.6	
	Orange peel		Methyl orange	20.5	Annadurai et al. (2002)
			Acid violet 17	19.88	Rajeshwarisivaraj et al. (2001)
			Basic blue 9	14.3	Annadurai et al. (2002)
			Direct red 23	10.7	Doulati Ardejani et al. (2007)
			Direct red 80	21.1	
	Garlic peel		Methylene blue	82.64 (30 °C) 123.45 (40 °C) 142.86 (50 °C)	Hameed and Ahmad (2008)

(continued)

Table 11.2 (continued)

Waste materials			Dye removed	Sorption capacity [mg/g]	References
Pith	Banana pith		Direct red	5.92	Namasivayam et al. (1998)
			Acid brilliant blue	4.42	
	Egyptian bagasse pith		Basic blue 69	168	Ho and McKay (2003)
			Acid blue 25	14.4	
			Basic blue 69	152 ± 5	Chen et al. (2001)
			Acid red 114	20.0 ± 0.5	
			Acid blue 25	17.5 ± 0.5	
			Basic red 22	75 ± 2	
	Coir pith		Acid violet	1.6	Namasivayam et al. (2001a)
			Acid brilliant blue	16.6	
			Rhodamine B	203.2	
			Rhodamine B	2.56	Namasivayam et al. (2001b)
			Acid violet	8.06	
Husk	Rice husk		Basic red 2	838	McKay et al. (1999)
			Basic blue 9	312	

particle size, porosity, and surface area makes it a potential adsorbent for dye removal (Ahmaruzzaman 2011; Yagub et al. 2014). Red mud is obtained in the alumina production process during the bauxite processing (Yagub et al. 2014).

Namasivayam and Sumithra (2005) applied Fe(III)/Cr(III) hydroxide (particle size 250–500 μm) for direct red 12B and methylene blue removal at different phases contact time, adsorbent dose, dye concentration before sorption, and pH. Equilibrium and kinetic sorption of dyes followed the Langmuir and Freundlich models and pseudo second-order model, respectively. The maximum sorption capacity for direct red 12B was equal to 5.0 mg/g and for methylene blue 22.8 mg/g, and the acidic pH was chosen as favorable for direct red 12B, whereas the alkaline one for methylene blue. The authors pointed out that chemisorption could play a main role in the adsorption process (percentage desorption of dyes was below 10.0 (pH = 3.0–10.0, the dye concentrations 10 and 20 mg/L)).

Metal hydroxide sludge sorptive properties and mechanism of sorption for the azo-reactive dyes such as reactive red 2, reactive red 120, and reactive red 141 containing sulfonic groups from aqueous solution were examined by Netpradit et al. (2003). As it was proved the solution pH influences the sorption process of the abovementioned dyes, and the pH = 8–9 was selected as optimal (at pH = 2 precipitation of dye–metal complexes occurred). The sorption capacity of the metal hydroxide sludge for the azo dyes was in the range from 48 to 62 mg/g and the sorption process proceeded according to the ion-exchange mechanism. Moreover, sorption of reactive red 120, reactive red 141, and reactive red 2 is temperature dependent; the sorption capacities decreased with the increasing temperature (reactive red 2) or increase with the increasing temperature (reactive red 120, reactive red 141) (Netpradit et al. 2004). The adsorption of reactive red 2 was mainly physical, whereas it was chemical for more charged dyes (reactive red 120 and reactive red 141). Adsorption efficiency decreased with electrolyte concentration or valence increase.

The calcium-rich fly ash was utilized for the Congo red sorption. It was observed that with the concentration and temperature increase, the amount of dye adsorbed also increases or negligibly decreases with the increasing pH. The sorption efficiency was from 93% to 98%, whereas the percentage desorption was equal to 29.18% using 0.1 mol/L HCl and 47.21% using 50% v/v CH_3COOH. The pseudo second-order model and Freundlich and Dubinin–Radushkevich ones show the best experimental results fitting (Acemiŏglu 2004).

The bagasse fly ash was applied for Congo red removal from aqueous solutions. The optimal pH_0 was 7.0, the dosage was 1 g/L, and the system reached equilibrium after 4 h. The pseudo second-order and the Redlich–Peterson isotherm models well describe the sorption data (Mall et al. 2005).

Ahmaruzzaman (2010) presented the review paper concerning the utilization of fly ash in which many examples of various fly ash types applied for such dyes such as methylene blue, crystal violet, rhodamine B, acid blue 9, acid blue 29, acid blue 91, etc. removal could be found.

Wang et al. (2005) used the fly ash as well as the red mud for methylene blue removal and shows that the fly ash usually possesses bigger sorption capacity for methylene blue than the red mud. Raw materials show the sorption capacities 1.4×10^{-5} (fly ash) and 7.8×10^{-6} mol/g (red mud), respectively. Heat treatment of fly ash and red mud results in adsorption capacity reduction for both sorbents, whereas the acidic treatment using HNO_3 results in an increase (fly ash) (2.4×10^{-5} mol/g) or decrease (3.2×10^{-6} mol/g) of adsorption capacity. The Redlich–Peterson model proves to be the best for description of the equilibrium data. The methylene blue retention is endothermic.

Gupta et al. (2004) also applied red mud for methylene blue sorption as well as fast green and rhodamine B removal. The percentage removals of dyes on red mud were 92.5 (rhodamine B), 94.0 (fast green), and 75.0 (methylene blue), respectively. The column studies give 95–97% removals of dyes. The adsorption is exothermic in nature.

Namasivayam and Arasi (1997) and Namasivayam et al. (2002) proposed red mud for Congo red (red mud after purification by ultra-pure water, then dried at 60 °C for 5 h) and procin orange removal. They obtained nearly quantitative removal of Congo red at pH 2.0. The adsorption capacity of Congo red was 4.05 mg/g, and the adsorption mechanism is mostly ion exchange, whereas procin orange was removed in 82% (pH = 2).

11.4.3 Natural Materials

Natural materials group include clays, siliceous materials, and zeolites. The oldest and well-known natural ceramic material is natural clay minerals. The clays are minerals possessing fine particles having an average diameter of about 2 mm (colloid fraction containing soils, rocks, sediments, and water suspended in aqueous solutions) which may be mixtures of clay-sized crystals, fine-grained clay minerals, and other minerals, e.g., quartz, metal oxides, carbonate, etc. Clays play a significant role as adsorbents due to its abundance in nature in most continents of the world, low cost (e.g., market price of montmorillonite – 0.04–0.12 $ per kg and is about 20 times cheaper than commercial activated carbons), as well as high sorption ability (layered structure with high surface area, high porosity and open porous structure, rapid kinetics, e.g., Fuller's earth). Presence of exchangeable ions on clay surface makes them strong candidate for ion-exchange results in sorption of cations and/or anions through ion exchange mechanism, e.g., montmorillonites possesses high ability for positively charged ions. Clay materials possess a layered structure and included among others serpentine, sepiolite, vermiculite, mica, kaolinite, smectites, Fuller's earth, etc. (Crini 2006; Shichi and Katsuhiko 2000; Yagub et al. 2014). Clays show a strong affinity for dyes (cationic, anionic), e.g., bentonite (fine powder) is effective sorptive material for different class of dyes (combination of sorption and ultrafiltration gives more better efficiency of dyes removal), and dye clay complexes can be formed. The main limitation of application of clays is the fact that such sorbents are not efficient for pollutants of an acid character, their sorption efficiency strongly depends on pH, and in many cases they required chemical modification or activation, e.g., bentonite (Alexander et al. 2019; Crini and Badot 2011; Shichi and Katsuhiko 2000).

Many researchers, e.g., Alexander et al. (2019), Crini (2006), Raval et al. (2016), and Yagub et al. (2014), show comparison of various clays ability for reactive, acid, basic dyes removal. Hu et al. (2017) reported basic red 2 removal using bentonite. The authors pointed out that the main dye sorption mechanism is cation exchange. The sorption kinetics was very fast, after 2–3 min of phase contact time the adsorption yield was about 80–90%, and the adsorption capacity depends on pH of solutions (increases with pH of solutions increase). Alshammari (2014) applied Saudi bentonite clay for acid dye 25 removal from aqueous phase. The adsorption capacity was 12.7 mg/g and diffusion was a major rate controlling step. Congo red removal on unmodified bentonite as well as surfactant modified bentonite was presented by Aki et al. (2013). Better sorption efficiency was obtained for modified bentonite (adsorption capacity 210 mg/g) than for unmodified (sorption capacity 37 mg/g). The adsorption efficiency increases with the initial dye concentration, bentonite mass, temperature, and pH of solutions (pH from 5 to 9). The system reached equilibrium after 120 min, and the adsorption of dye onto modified bentonite is endothermic and spontaneous in nature. Al-Asheh et al. (2003) reported the results of methylene blue adsorption on unmodified and modified bentonite (modification using anionic surfactant – sodium dodecyl sulfate or thermal treatment at 850 °C bentonite). The methylene blue removal selectivity series was as follows: thermal-treated bentonite > modified bentonite using sodium dodecyl sulfate > natural bentonite. The adsorption capacity increases with temperature. High efficiency of reactive red 223 adsorption using acid modified bentonite (95.15%) and desorption efficiency 78% by alkaline solution was obtained by Tahir et al. (2013). The hexadecyltrimethylammonium bromide-modified bentonite was applied by Fosso-Kankeu et al. (2015) for tartrazine and brilliant blue sorption. Impregnation of bentonite ensures removal of anionic dyes (sorption capacity 24 mg/g) compare to unmodified bentonite (incapable for anionic dyes removal). Kyzioł-Komosińska et al. (2014) applied thermal treated and chemically modified smectite clays for the adsorption of reactive blue 81 and direct blue 74 dyes. At pH above point of zero charge-modified smectite surface is negatively charged; therefore the electrostatic interaction between the molecules of anionic dye and the surface of clay is inherit, and the dye sorption is possible due to the hydrogen bonds formation. Montmorillonite was applied for the removal of methyl red from aqueous solution. The sorption capacity was equal to 30.84 mg/g after 30 min. The sorption of methyl red on montmorillonite can be depicted by the pseudo second-order and Freundlich models (Mohammadi et al. 2017).

Siliceous materials (available, abundant, and low-cost inorganic materials) include silica beads, perlite, glasses, alunite, dolomite, etc., and among these group silica beads deserve particular attention due to its chemical reactivity, hydrophilic surface, and presence of among others silanol groups. Moreover its porous structure, mechanical stability, and high surface area make them very good materials for dyes wastewaters treatment. Other advantages of siliceous materials are availability in many countries, e.g., perlite (amorphous siliceous mineral), not necessary of regeneration, e.g., alunite due to its low cost. The main disadvantage of siliceous materials is the fact that sorption efficiency is strongly depended on pH, e.g., application of silica beads due to low tolerance to base solutions is restricted to pH less than 8, the chemical composition is variable, e.g., perlite and the obtained results strictly depend on types and origin of materials, e.g., perlite (expanded or unexpanded). Siliceous material is promising adsorbents for dye removal, and physical or chemical modification of such materials makes them even more efficient (Crini 2006; Crini and Badot 2011). Özacar and Sengil (2003) show that modification of alunite (jarosite group, 50% of SiO_2) gives better sorption efficiency. Reactive blue 114 and reactive red 124 removal using unmodified alunite gives sorption capacities equal to 2.92 mg/g for reactive blue 114 and 2.85 mg/g for reactive red 124, whereas the sorption capacity of calcined alunite was much higher and was equal to 170.7 mg/g (Özacar and Sengil 2003). Moreover, high sorption capacities were also obtained during the reactive yellow 64 and acid blue 40 sorption on calcinated alunite (reactive yellow 64 236 mg/g, acid blue 40 212.8 mg/g). The capacity obtained for commercial activated carbon was lower (acid blue 40 57.47 mg/g) (Özacar and Sengil 2002). Silica precipitated from sodium metasilicate solution by carbon dioxide in presence of ethylene glycol and modified using silane coupling agents with the amino functionalities for reactive blue 19, acid violet 1, acid green 16, and acid red 18 removal was obtained by Krysztafkiewicz et al. (2002). There was found that except for acid green 16, dye adsorption efficiencies were independent on the type of aminosilane used for modification. Glass powder; dolomite, e.g., charred dolomite; perlite (glassy volcanic rock of high silica content >70%); silica; and modified silica found also applicability for reactive, basic, and acid dyes removal, e.g., for acid red 44 (sorption capacity 4.03 mg/g) (Atun and Hisarli 2003), brilliant red E-4BA (sorption capacity 950 mg/g) (Walker et al. 2003), methylene blue (Dogan et al. 2004), and methyl violet (Dogan and Alkan 2003) as well as for basic blue 9 (sorption capacity of unmodified silica 11.21 mg/g) (Woolard et al. 2002) and acid blue 25 removal (sorption capacity of modified silica 45.08 mg/g) (Phaan et al. 2000). As was pointed out sorption on perlite is physical.

Another group of siliceous materials are zeolites, aluminosilicate minerals of porous structures containing cavities. They possess three-dimensional structure of negative charged balanced by cationic ions able to exchange reaction which other cations present in solutions. The main representative of zeolites is clinoptilolite which is a mineral of the heulandite group and the most frequently tested in terms of its sorption properties. Ghobarkar et al. (1999) review the applications of zeolites and present their useful properties. Zeolites are characterized by open and highly porous structures of easy access, high surface area, and sorption capacity as well as selective affinity for certain pollutants (dyes, phenols, heavy metal ions) and low prices which depends on their quality (0.03–0.12 $/kg) (Crini 2006; Crini and Badot 2011). As was observed by Armagan et al. (2004) and Ozdemir et al. (2004), natural zeolites have restricted applicability for reactive dyes removal such as everzol red, everzol black, and everzol yellow due to the low sorption capacity; therefore they need additional modification. Zeolites surfaces modification with quaternary amines or hexamethylenediamine improved their sorption ability toward reactive dyes, e.g., reactive red 239 and reactive blue 250 (Alver and Metin 2012; Ozdemir et al. 2004). Moreover zeolites are characterized by low permeability; therefore in the continuous systems (column studies), additional artificial support is needed. Retention of dyes on zeolites is the result of ion-exchange mechanism. The yield of removal process is usually lower that in the case clays adsorbents. In literature many examples of zeolites application for dyes removal could be found but here was mentioned only some of them. High sorption capacity toward basic dyes was obtained using zeolites synthesized from electrolytic manganese residue, raw and functionalized by iron oxide clinoptilolite for removal of methylene blue (Li et al. 2015; Wang et al. 2006; Badeenezhad et al. 2018) and crystal violet and rhodamine B (Wang et al. 2006). The adsorption capacity for dyes under discussion is in order of methylene blue > crystal violet ~ rhodamine B. Adsorption of basic dyes could be described well by pseudo second-order model. Film diffusion plays a meaningful role, too. Not only the Langmuir but also the Freundlich isotherms fit good the equilibrium data. Retention of cationic dyes is an endothermic in nature (Wang et al. 2006). Li et al. (2015) also found that pseudo second-order and Langmuir models are proper for methylene blue sorption description. pH and temperature greatly affected the sorption efficiency of methylene blue. The adsorption of methylene blue on electrolytic manganese residue is endothermic and spontaneous process. Methylene blue removal by unmodified clinoptilolite was pH dependent and gives 26.86% and 48% removal at pH 3 and 9, respectively. Methylene blue retention on the impregnated clinoptilolite was much higher (96.4–98.6%) and not pH and initial dye concentration dependent. Freundlich isotherm model fit well the experimental results.

11.4.4 Biosorbents

Biosorption is physicochemical process and is described as accumulation and concentration of pollutants using biological materials (Crini 2006). The use of biosorbents in dyes removal seems to be very promising (Asgher 2012; Crini 2006). It results above all from the fact that biosorbents as low-cost sorbents, with easy accessibility even in large quantities, are sometimes characterized by a much higher sorption capacity in relation to metal ions than commercial activated carbons or ion exchangers (reduction of dyes concentration to ppb levels could be obtained). Chitosan molecule modification by inserting functional groups (grafting) or cross-linking reactions leads to the formation of chitosan derivatives of superior sorptive properties results in enhancement of adsorption capacity and resistance (Kyzas et al. 2017). This process is effective and competitive, requires little processing, and is inexpensive. During the biosorption different mechanisms could be responsible for dyes sorption, e.g., physicochemical adsorption, ion exchange, complexation, electrostatic interaction, and micro-precipitation (Asgher 2012). As biological materials for wastewaters decolorization, chitin, chitosan, peat, yeasts, white rot fungi, algae, and dead or living biomass are applied. Chitin and chitosan are efficient sorbents for dyes wastewaters treatment; even the dye concentration is small (at ppb or ppm levels). The main natural sources of chitin and chitosan are fungi, insects, annelids, crustaceans, and mollusks, but chitin are usually isolated from exoskeleton of crustaceans (crab, crayfish, krill) widely available by-product of food processing, whereas chitosan is prepared during the N-deacetylation of chitin using a cheap chemical reagents. These materials are abundant, versatile, environmentally friendly, renewable, and biodegradable, and due to the way of their production, they contribute to industrial solid wastes utilization. Moreover, they are hydrophilic in character of high reactivity possessing cationic charge in acidic pH. On the other hand, they possess some limitations such as variability in the polymer characteristics, nonporous structure, non-effectivity for cationic dyes (except after derivatization), and strongly pH dependence. Additionally, they possess limited application in the column treatment due to hydrodynamic limitation and column fouling (Crini 2006; Crini and Badot 2011). Chitin contains 2-acetamido-2-deoxy-β-ᴅ-glucose through a β (1 → 4) linkage, whereas chitosan is a nitrogenous (amino-based) polysaccharide containing chitosan 2-amino-2-deoxy-β-ᴅ-glucopyranose and 2-acetamido-2-deoxy-β-ᴅ-glucopyranose. Chemical stability of chitosan, high reactivity and selectivity, and excellent chelation behavior make it competitive adsorbent to other biomaterials (Kyzas et al. 2017). Many studies proved that biosorbents of chitosan origin show high affinity for many classes of dyes.

Chiou et al. (2004) and Chiou and Li (2002) applied cross-linked chitosan for dyes: reactive blue 2, reactive red 2, reactive yellow 2, reactive yellow 86, reactive red 189, acid orange 12, acid red 14, acid orange 7, and direct red 81. The adsorption capacities were in the range from 1911 to 2498 (g/kg) and were much higher than those of commercial activated carbon (3.4–15.0 times) and chitin (2.7–27.4 times). Moreover the adsorption capacity of cross-linked chitosan is largely dependent of pH and biosorbent mass. Temperature and the cross-linking factor do not play an important role.

The variability of chitosan was proved by Wu et al. (2000). Reactive red 222 removal efficiency using chitosan in form of flakes and bead obtained from fishery wastes were paralleled. The uptake of reactive red 222 by chitosan (in form of beads) was higher than that on flake-type (1037 mg/g for chitosan, bead-type, from lobster; 1106 mg/g for chitosan, bead-type, from crab; 398 mg/g for chitosan, flake-type, from lobster; 293 mg/g for chitosan, flake-type, from crab). The reactive red 222 removal was faster for bead-type chitosan compared to flake-type chitosan.

Such acid dyes as green 25, orange 10, orange 12, red 18, and red 73 were removed by chitosan obtained from crab shell. The adsorption capacities were in the range from 645.1 mg/g to 973.3 mg/g (orange 12 (973.3 mg/g) > orange 10 (922.9 mg/g) > red 73 (728.2 mg/g) > red 18 (693.2 mg/g) > green 25 (645.1 mg/g)) (Wong et al. 2004).

Peat is a sedimentary rock consisting of organic matter in different stages of decomposition. Moss, woody, herbaceous, and sedimentary peat can be distinguish. It is abundant, cheap, and widely accessible sorbent, which has excellent adsorption properties. The main ingredients of raw peat are lignin, cellulose, humic, and fulvic acids. This material is polar due to the presence of alcohols, carboxylic acids, aldehydes, ketones, phenolic hydroxides, and ether functional groups capable for chemical binding; therefore they are useful for dyes and heavy metal ions removal (Crini 2006; Crini and Badot 2011). The removal efficiency of dyes is similar for acid and basic dyes whereas higher for dispersive ones, e.g., basic blue 9, acid blue 29, acid red 91, and disperse red 1 sorption onto peat (Konduru and Viraraghavan 1996). Similar observation was made by Ramakrishna and Viraraghavan (1997). Raw peat possesses low mechanical strength, poor chemical stability, high affinity for water, tendency to shrink, and/or swell; therefore its applicability may be limited; therefore they required the modification or activation step (Crini and Badot 2011). Results presented by Ho and McKay (1998b), Poots et al. (1976), and Sun and Yang (2003) show that peat modification gives better removal efficiency of dyes compared with raw peat. Ho and McKay (1998b) use peat for basic blue 69 and acid blue 25 retention. The maximum capacity was 195 mg/g for basic blue 69 and only 12.7 mg/g for acid blue 25 and was much lower than that obtained for modified peat. Sun and Yang (2003) applied functionalized peat (using sulfuric acid, polyvinylalcohol, formaldehyde) for basic violet 14 and basic green 4 removal and obtained sorption capacities equal to 400 and 350 mg/g, respectively.

In recent years, there has been an intensive research concerning application of biomass, fungi, algae, yeast, etc. for decolorization of dyes wastewaters. The use of dead biomass seems to be more reasonable than living biomass because dead biomass not only is insensitive to toxic dyes but also does not require maintaining sterile conditions and providing nutrients during the research (Kabbout and Taha 2014). The removal of dyes from aqueous solutions can be based on several mechanisms. Among them, chemisorption of dyes with functional groups of the cell wall can be distinguished, which may occur as a result of ion exchange, complexation, and chelation reactions. Moreover, physical adsorption is also possible (binding of dyes to the biosorbent occurs due to electrostatic interactions and van der Waals forces), oxidation, and reduction or micro-extraction reactions. The biosorption process may also take place according to the mixed mechanism. The type and charge of the adsorbate, composition of the external solution, as well as kind and origin of biomass affect the binding mechanism (Crini 2006; Fu and Viraraghavan 2001).

Many examples of above mentioned biosorbents application can be found in literature (Aksu 2005; Fu and Viraraghavan 2001; McMullan et al. 2001; Robinson et al. 2001; Stolz 2001). Aksu (2005) presented review papers examines fungi and living or dead cell applicability for dyes decolorization and discusses binding mechanisms and the effect of various parameters on this process. Moreover the elution and regeneration methods for fungal biomass were summarized. Other authors presented current treatment technologies for dye decolorization, microbial degradation of textile, and azo dyes (Aksu 2005; McMullan et al. 2001; Robinson et al. 2001; Stolz 2001). Crini (2006) collected and compare the sorption capacities of different biosorbents among other activated sludge biomass, yeasts, *Chlorella vulgaris*, *Rhizopus arrhizus*, *Spirodela polyrhiza* biomass, dead fungus *Aspergillus niger*, modified fungal biomass, and living biomass which was compered in Fig. 11.8.

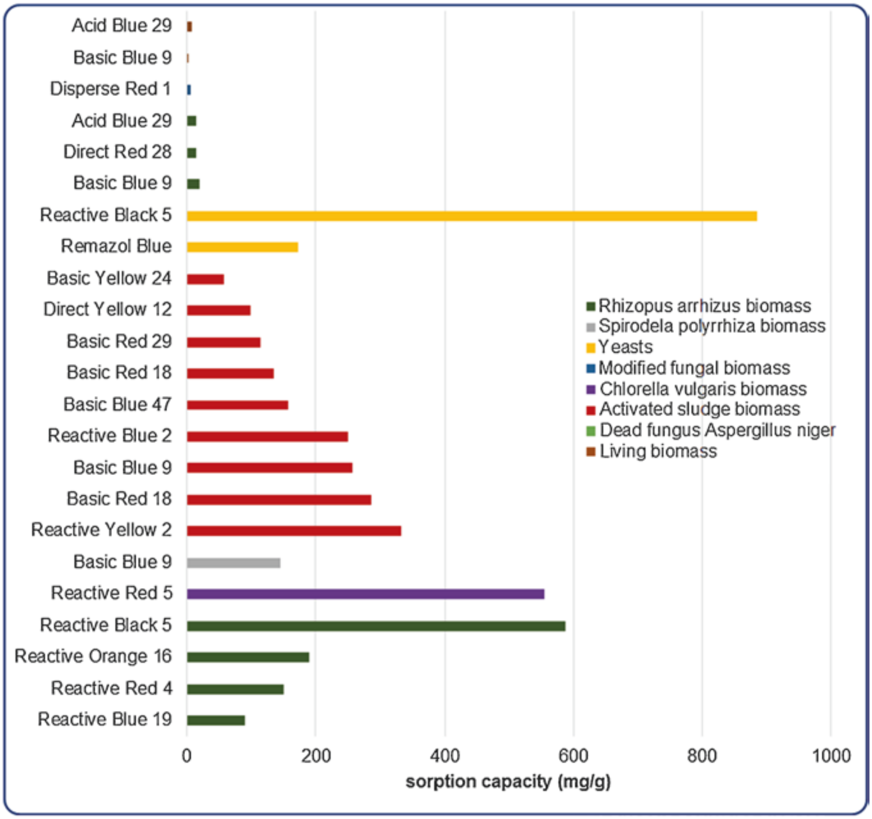


Fig. 11.8 Comparison of the sorption capacities of biosorbents for dyes removal

As can be seen at Fig. 11.8 the highest sorption ability for different dyes possesses yeast and fungi biomass. Remazol blue removal by yeasts was carried out by Aksu and Dönmez (2003) at optimum pH = 2. The yeast *C. lipolytica* exhibited the largest capacity for Remazol blue (250 mg/g).

On the one hand biosorption is efficient, but on the other hand the kinetics of dyes biosorption is usually slow and is limited by pH. The time required to reach equilibrium for micro-algae species during methylene blue sorption was in the range 60–80 min at 27 °C. Sorption of methylene blue was pH dependent. *Eucheuma spinosum* was found as the best biosorbent for methylene blue (solution of initial concentration below 1000 mg/L). Langmuir capacity was equal to 833.33 mg/g. *Aspergillus niger* gives 97% and 87% decolorization whereas *Aspergillus flavus* 78–83% decolorization after 48 h of phase contact time for static and shaking conditions, respectively. The time required for decolorization was in the range 24–120 h (Mokhtar et al. 2017). Moreover, the biosorption yield depends on biomass species, e.g., sorption of dyes on dried yeasts such as *Saccharomyces cerevisiae*, *Schizosaccharomyces pombe*, *Kluyveromyces marxianus*, *Candida* sp., *C. tropicalis*, *C. lipolytica*, *C. utilis*, *C. guilliermondii*, and *C. membranifaciens* (Mokhtar et al. 2017), removal of dyes by fungal species (Aksu and Dönmez 2003). Composition of cell walls, size of cell, functional groups present in the biomass and external factors like pH, salts, presence of other ions, temperature etc. are very important factors. Biomass have limited application for dyes removal using the column method but after biomass immobilization they could be applied (Crini and Badot 2011).

11.4.5 Nanomaterials

Nanotubes, nanofibers, nanorods, nanoparticles, fullerenes, and nanowires are typical nanomaterials (Camposeco et al. 2016; Gupta and Saleh 2013; Saravanan et al. 2014), and their sources and toxic properties were presented by Buzea et al. (2007). Carbon nanotubes discovered by Iijima (1991): single-walled and multi-walled could be applied for removal, degradation processes of dyes due to well-defined cylindrical hollow structure, high aspect ratios, large surface area, easily modified surfaces, and hydrophobic wall, but the single-walled carbon nanotubes show usually higher adsorption capacity than multi-walled carbon nanotubes (Gupta and Saleh 2013). Many examples of carbon nanotubes and fullerenes application for wastewaters treatment could be found in Gupta and Saleh (2013). Multi-walled carbon nanotubes were applied for rhodamine B degradation (Saleh and Gupta 2011), activated carbon nanotubes were applied for anionic and cationic dyes such as methyl orange (149 mg/g) and methylene blue (399 mg/g) (Ma et al. 2012) removal, and multi-walled carbon nanotubes functionalized by carboxylic acid for malachite green retention (142.85 mg/g) (Rajabi et al. 2016; Shirmardi et al. 2013), halloysite nanotubes for methylene blue removal (Kiani et al. 2011). The mechanisms of dye molecules binding on carbon nanotubes are very complicated, electrostatic attraction, precipitation, sorption, and chemical interaction between dyes and carbon nanotubes (Gupta and Saleh 2013). Kiani et al. (2011) indicated that the process of malachite green removal by halloysite nanotubes proceeds via physisorption (activation energy 18.28 kJ/mol). Nanoparticles smaller than 1 μm (Buzea et al. 2007) possess the unrepeatable features, e.g., catalytic potential, size, surface area, and number of active sites; therefore they could be an excellent adsorbents (Gupta and Saleh 2013).

Removal efficiency of dyes by nanomaterial depends on different experimental conditions, e.g., Rajabi et al. (2016) show that adsorption capacity of carboxylate group functionalized multi-walled carbon nanotubes for dye increases with time, pH, and temperature increase. Malachite green percentage removal by acid functionalized multi-walled carbon nanotubes increases with agitation time, pH, and dose increase but decrease with the initial malachite green increase (Shirmardi et al. 2013). The photocatalytic activities of TiO_2 nanotubes, nanofibers, and nanowires prepared by the hydrothermal treatment with NaOH depend on nanomaterials structure and pH of solution (medium) (Camposeco et al. 2016).

11.4.6 Composites, Nanocomposites, and Miscellaneous Adsorbents

Composites and nanocomposites are defined as inclusions in the matrix; they consist of two phases (dispersed and scattering), one of which is dispersed in another (matrix) thus creating a three-dimensional network. Other interesting materials are also starch and cyclodextrins. Starches consist of two polyglucans (highly branched amylopectin, nearly unbranched amylose), and they contain α-D-glucose units linked together. Starch is frequently used for food applications but due to its abundance, cost, availability in many countries, polyfunctionality, biodegradability, and adsorptive properties, there is a growing interest in its application for wastewater treatment. The main drawback of starch is its hydrophilic nature that seriously limits the development of new sorbents based on starch, but its chemical derivatization results in water-resistant sorbent production (Crini 2006; Raval et al. 2017). Some examples of above mentioned materials for different type of dyes removal are the following: methyl green and methylene blue removal by Fe/Ni/Zn/O/polyacrylamide nanocomposite (Kant et al. 2014); methyl green and methylene blue removal by polyaniline/ZnO nanocomposite (Eskizeybek et al. 2012); methyl green removal by magnetic *Pycnoporus sanguineus*-loaded alginate composite beads (Yang et al. 2014); different types of dye removal by cross-linked gels with starch derivatives, polymers prepared by reticulation of starch-enriched flour, as a cross-linking agent epichlorohydrin was applied in the presence of NH_4OH (Delval et al. 2001); dyes removal by β-cyclodextrin polymers (Crini 2003); and textile dyes removal by gels of β-cyclodextrin, hydroxypropyl β-cyclodextrin, poly(vinylalcohol) with epichlorohydrin (Shao et al. 1996), etc. More interesting examples of composites, nanocomposites, starch, and cyclodextrin derivates for malachite green and other textile dyes are collected in review papers (Crini 2006; Raval et al. 2017).

11.4.7 Ion-Exchange Resins

Ion-exchange resins (cation exchangers and anion exchangers) are popular materials for purification of industrial effluents. Ion exchangers reduce the bulk of toxic load and convert it into a form in which it is less toxic. Very important feature of ion-exchange reactions is separation and preconcentration of pollutants. Not only anionic but also cationic resins can be applied for anionic (acid, direct, reactive) and cationic type dyes (basic dyes), respectively. There are numerous literature reports on the use of the polystyrene, polyacrylic, and phenol-formaldehyde ion-exchange resins in the sorption of dyes from both aqueous solutions and wastewater (Wawrzkiewicz 2010, 2011a, b, 2012a, b, 2013, 2014). Among the commercially available anion exchangers and cation exchangers, the following resins Lewatit SP 112, Amberlite IRA 67, Amberlite FPA 51, Lewatit MP 62, Amberlyst A 23, Lewatit MP 64, Lewatit MP 68, Amberlite IRA 478RF, Amberlite IRA 910, Amberlite IRA

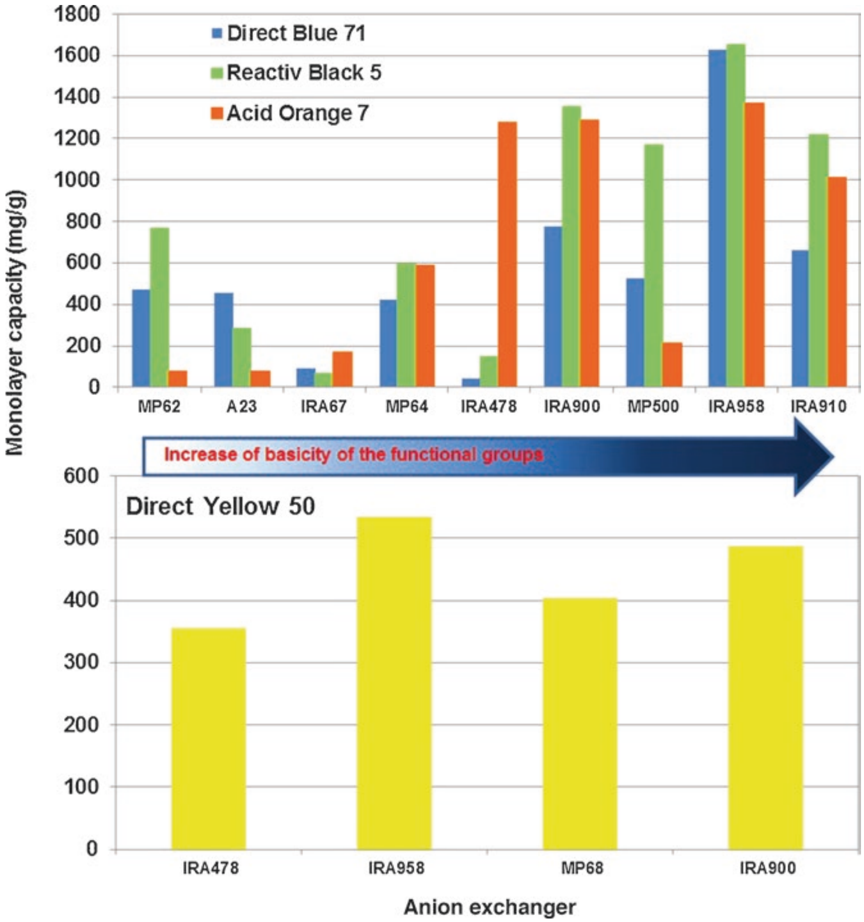


Fig. 11.9 Comparison of the sorption capacities of anion exchangers for acid, direct, and reactive dyes (where *MP62* Lewatit MP 62, *A23* Amberlyst A23, *IRA67* Amberlite IRA67, *MP64* Lewatit MP 64, *MP68* Lewatit MP 68, *IRA478* Amberlite IRA 478RF, *IRA910* Amberlite IRA 910, *IRA900* Amberlite IRA 900, *MP500* Lewatit MP 500, *IRA958* Amberlite IRA 958)

900, Purolite A 520 E, Lewatit MP 500, Lewatit M 500, Amberlite IRA 402, Lewatit M 600, Amberlite IRA 458, Amberlite IRA 958, and Purolite A 850 were used to remove basic (blue 3), acid (orange 7, tartrazine, sunset yellow, allura red), reactive (black 5, blue 21), and direct (yellow 50, blue 71, red 75) dyes from model and real effluents of the textile industry (Wawrzkiewicz and Hubicki 2015; Wawrzkiewicz et al. 2018, 2019; Wołowicz et al. 2018). Comparison of the anion exchange capacities for selected azo dyes such as acid orange 7, direct blue 71, and direct yellow 50 as well as reactive blue 5 determined by the static method is presented in Fig. 11.9 (Wawrzkiewicz and Hubicki 2015; Wawrzkiewicz et al. 2019). The vast majority of literature reports concern the use of anion exchangers to remove anionic dyes than cation exchangers for adsorption of basic dyes.

Summing up, the dyestuff sorption on the anionic and cationic resins depends on a few factors of which the most important are:

- Kind of the resin including its matrix composition and structure (macroporous, gel), kind of functional groups (weakly, intermediate, and strongly basic), sorption capacity, as well as kind of bead and form in which the anion exchanger is used.
- Sorption proceeds more quickly in the case of anion exchangers of more hydrophilic matrix (polyacrylic or phenol-formaldehyde) compared with their polystyrene counterparts; hydrophilic resins are more effective in organic substance sorption due to their greater flexibility of matrix, the presence of carbonyl group, and possibility of hydrogen bonds formation.
- The effect of functional groups basicity of macroporous anion exchangers on their affinity for the dyes of various kinds can be presented as follows: *strongly basic anion exchangers type 1 > strongly basic anion exchangers type 2 > weakly basic anion exchangers*.
- Dye sorption kinetics is affected by matrix structure of ion exchangers; in the case of dye sorption on the gel resins, the *sieve effect* consists in limited diffusion of large-size dye ions in the pores of the resin of microporous structure.
- The main binding mechanism of dyes is ion-exchange reaction; physical and hydrophobic π–π interactions (among benzene rings in dyestuff and resins matrix) play a more significant role in case of the polyacrylic anion exchangers such as Amberlite IRA 958, Amberlite IRA 458, and Amberlite IRA 67 in comparison to polystyrene ones; large sorption ability of anion exchangers resins toward dyes results from H-bond formation (nitrogen from quaternary ammonium and oxygen from carbonyl functional groups of anion exchangers interact with nitrogen from the -NH_2 group of dyes).
- A lack of evident impact of solution pH on dye uptake indicates that the process of their bonding on the resin proceeds not only by ion pair formation between the sulfonic groups of dyes and tertiary amine groups of the weakly basic anion exchangers or the quaternary ammonium functionalities of strong base anion exchange resins but also by the interactions of π–π type as well as hydrogen bonds.
- Kind of dye (composition and spatial structure, number and kind of chromophore, and auxochromium).
- Process conditions (kind of the dye-ion exchanger system, concentration of the dye, phase contact time, presence of auxiliaries in the system, e.g., electrolytes and surfactants, solution pH, temperature, rate of phases mixing or rate of flow in the column system, desorption, as well as way of its conducting (static or dynamic method) (Wawrzkiewicz and Hubicki 2015).

11.5 Conclusion

This review chapter provides information about dyes, its classification, various treatment methods, and adsorptive properties of a wide range of adsorbents such as commercial activated carbon, industrial solid materials, agricultural by-products, biosorbents, natural materials, ion exchangers, etc. As was provided, adsorption is very easy to operate, economic, selective, and highly effective. It is considered to be the most favored method for hazardous dye removal. Inexpensive and locally available raw materials, wastes, or treated ones are a cheaper alternative for expensive commercial activated carbon. Among huge amount of literature data and review papers concerning removal of various types of dyes, mentioned here, it is observed that adsorption efficiency, the mechanism of dyes binding, and kinetics depend on the properties of adsorbate, adsorbents, as well as experimental conditions (initial concentration of dye, pH of solutions, dose of adsorbent, phase contact time, temperature, etc.). Additionally as was observed, the pseudo first-order and the pseudo second-order kinetics as well as the Langmuir and Freundlich isotherm models are the most popular for evaluation of dye uptake by different adsorptive materials.

Although much has already been achieved in the field of dye removal from wastewater, further increased research is needed to better understanding of the mechanisms of dyes binding, to predict the sorptive properties of adsorbents in real wastewaters systems, and to use low-cost sorbents on macro industrial scale.

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Chapter 12
Application of Adsorption Methods for Boron Uptake

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Contents

Abstract Development of science and technology may cause increase in consumption of the products. Consumption is the main reason of the environmental pollution, which includes water, air, and soil pollution. Therefore, sustainability is the most important factor for our natural sources. Due to industrial applications, water sources are in great danger. There are many micro and macro pollutants in the water. For the removal of the pollutants, various methods have been applied such as physical, chemical, or biological treatment. However, mostly advanced treatment methods are used for the removal of pollutants such as adsorption, membrane operations, and solvent extraction. This chapter includes adsorption process for the removal of boron, which has noticeable effects on the environment. Boron, produced from natural sources, is released to the water during industrial activities. Its concentration in the water is the important parameter since it can negatively affect plants, animals, and humans. Therefore, various adsorbents were used for the removal of boron effectively.

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12.1 Introduction

The appearance of boron in salt form, not as a free element in nature, resembles a white rock. Boron is a mineral found naturally in soil, water, air, and rocks. Boron mineral concentration in the Earth's crust is around 10 mg L^{-1} (Bakirdere et al. 2010). Boron is an important element due to its harness, its resistance to high temperatures, and its ability to produce high amounts of energy when used as a fuel.

Boron and its compounds have a wide range of applications in industry. Boron is used for strengthening and insulation purposes in construction and cement industries; in detergent industries due to its bleaching and protective properties against bacteria; in cosmetics sectors due to its softness, stickiness, and durability properties; in agricultural sectors for increasing the yield purposes; and in various industrial areas such as ceramic sectors in terms of decreasing the cooking temperature of ceramics.

Boron compounds are found in surface water and groundwater. The concentration of boron in groundwater varies between 0.3 and 100 mg L^{-1}. In surface waters, it is in the range of 0.5–9.6 mg L^{-1} in seawater and 0.01–1.5 mg L^{-1} in freshwater (Ünlü et al. 2011). It has been defined as 0.3 mg L^{-1} for sensitive plants in irrigation waters, 1–2 mg L^{-1} for medium sensitive plants, and 2–4 mg L^{-1} for resistant plants. Boron is also a micronutrient for humans and animals, and the acceptable limit of use is 0.3 mg Boron kg^{-1} (Nable et al. 1997).

In order to eliminate the environmental effects of high boron concentration in water, it should be removed using appropriate methods. For this purpose, boron removal was tried with different methods. This review includes boron removal using adsorption method. Several adsorbents can be used for boron removal, including natural sources, metal oxides, and layered double hydroxides. A literature research was done to identify the kinds of adsorbent used in the studies and adsorption capacities.

12.2 Chemical Properties of Boron

Boron is a third group element of the periodic system, which has semiconductor properties. Boron has exists in the nature the mixture of two isotopes of mass number 10 (19.8%) and 11 (80.2%) (Power and Woods 1997). Boron can be found in nature in various allotropic forms. Crystalline boron is substantially lightweight, hard, scratch-resistant, and heat-stable. Boron is a good conductor at high temperatures. Chemical properties of boron element depend on its morphology and grain size. Micron-size amorphous boron reacts easily and sometimes violently, while boron crystal does not react easily. Boron reacts with water at high temperatures to form boric acid and some other products (Holleman and Wilberg 2001).

Boric acid is a weak Lewis acid, which has a pK_a value 9.24 at 25 °C (Delazare et al. 2014). The reaction, which is given below, is a function of the solution pH.

$B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+$

At pH above 9.24, borate ion ($B(OH)_4^-$) dominates in the solution, while below 9.24, boric acid ($B(OH)_3$) is prevalent. Besides, solution concentration also affects the formation of the species in the solution. At low concentrations, $B(OH)_3$ and $B(OH)_4^-$ species mainly exist, while at high concentrations, polynuclear ions or cyclic structures exist in the solution (Wang et al. 2014; Kabay et al. 2010; Zeebe et al. 2001; Power and Woods 1997).

Thermal waters and volcanic springs carry abundant boron. Generally, volcanic gases and sediments are rich in boron content. In such waters, boron can be detected between 4 and 36 mg L^{-1}. Rivers and volcanoes feed the marine waters in boron content. Clay minerals and biological activities may cause to participate of boron (Badruk 1998; Vengosh et al. 1999; Jyo et al. 2001).

12.3 Effects of Boron on Living Organisms

There is a narrow gap between boron toxicity and deficiency for plants. It is known that boron plays an important role on carbohydrate metabolism in plants, hormone movements, growth and nucleic acid synthesis, and membrane structure and functions (Howe 1998). Symptoms of boron deficiency are decreased root and leaf growth and low enzyme reaction, leading even to death (Wells and Whitton 1977). Sensitive plants can withstand at 0.3 mg L^{-1} boron concentrations, while susceptible plants can live in irrigation water at 4 mg L^{-1} boron concentration [Keren and Bingham 1985). Boron deficiency can be seen in plants due to easily adsorbed boron in heavy soils at high pH values (Howe 1998).

Boron plays an important role in calcium metabolism in human. Other effects of boron include the development of brain functions and psychomotor responses and improvement in women's estrogen uptake (Nielsen 1994). Besides, the literature has evidences that boron plays an important role in bone and joint health (Newnham 1994). Harchelroad and Peskind reported that after receiving 250 g of boric acid, a pregnant woman and her baby were unaffected (Harchelroad and Peskind 1993). A study in the literature showed that 98.7% of 600 mg boric acid was excreted from the body in 5 days (Jansen et al. 1984; Moore 1997).

12.4 Boron Sources and Industrial Applications

There are at least 200 types of boron mineral in the nature. Especially, borax, kernite, colemanite, and ulexite are the widely used boron minerals (Lyday 2000). Boron content in soils changes according to the type of soil and pH. Boron that is contained in the water comes from boron-containing soil and minerals (Parks and Edwards 2005; Gupta et al. 2008). Boron can also be found in the atmosphere due to volcanic activities and geothermal sources (Coughlin 1998). Oceans have 4.6 mg L^{-1} boron, and the atmosphere also contains boron due to the evaporation process of the water (Anderson and Kitto 1994). Raining may cause the increase of boron concentration in drinking water. These are the natural ways how boron may contain in drinking water.

Boron is used for laboratory glassware, aircraft glass, window glass, optical glass, plastics, and fiberglass in automobile and aircraft industries. Due to its lightweight, low price, and resistance to stress and to chemical effects, boron is used widely in industrial applications. It also gives hardness and durability to the materials used.

12.5 Adsorption

Adsorption is one of the efficient treatment methods for the purification of water. Adsorption is basically the interaction of adsorbate molecules (gas or liquid) with the adsorbent surface (solid). It is defined as the increase of the concentration on a substance surface (Thomas and Crittenden 1998). Electrostatic interaction between adsorbent and adsorbate molecules takes place via van der Waals interaction or chemical interaction. Using efficient and low-cost adsorbent is the key point of the adsorption process (Kong et al., 2017).

12.5.1 Clay Minerals

Clay minerals are the natural sources that can be used for adsorption process. Various types of clay minerals exist in the nature such as kaolinite group, smectite group, illite group, and chloride group.

Montmorillonite has 2:1 sheet structure, which means one octahedral sheet is placed between two tetrahedral sheets. Keren et al. (1981) studied the boron adsorption of montmorillonite clay. Montmorillonite clay was used in homoionic form. Sodium was used to change the surface charge from negative to positive form. Na-montmorillonite was an effective adsorbent at higher pH values. The maximum adsorption capacity was achieved at pH 9.3. This result was due to the ionic type of boron changing according to solution pH. Borate ion ($B(OH)_4^-$) dominates in the solution above pH 9.24. Electrostatic attractions were the key factor for the adsorption of boron on Na-montmorillonite surface (Keren et al. 1981). Boron adsorption on montmorillonite, illite, and kaolinite clays was investigated by Keren et al. (1981). Calcium (Ca) forms of the clays were used for the adsorption of boron. Maximum boron adsorption was achieved in alkaline conditions since the affinity of the clays for $B(OH)_4^-$ was much higher than $B(OH)_3$. Adsorption capacities were achieved as 2.94, 11.8, and 15.1 μmole g^{-1} for Ca-kaolinite, Ca-montmorillonite, and Ca-illite, respectively (Keren and Mezuman 1981).

Organic components were also used for the modification of the clay surface. Nonylammonium chloride was used to modify bentonite, sepiolite, and illite clays for boron adsorption. Hydrophilic surface was changed to hydrophobic form with the modification nonylammonium chloride. Freundlich and Dubinin-Radushkevich isotherm models were fitted the experimental data for boron adsorption. Modification of bentonite and illite with nonylammonium chloride increased the boron adsorption. It was concluded that the low-cost bentonite, which showed the highest adsorption capacity, could be used for industrial applications (Karahan et al. 2006).

Reinert et al. (2011) studied the boron removal using allophone, which is a natural mineral. Initial boron concentrations were between 1 and 100 mg L^{-1}. Natural clay mineral with aluminosilicate content was modified with N-methyl-D-glucamine structure, which is a boron-specific complex. As a result, 80% boron removal was obtained using modified allophone (Reinert et al. 2011).

12.5.2 Industrial Waste

Öztürk and Kavak (2005) used fly ash as adsorbent for removal of boron. There are metal oxides in fly ash structure. In the acidic medium, metal oxides are positively charged as they form complexes, and as a result, negatively charged borate ions were adsorbed to the fly ash surface by electrostatic interaction. Boron solution with initial concentration of 600 mg L^{-1} and fly ash as combustion process waste were used as adsorbent, and boron removal reached up to 90% from the solution (Öztürk and Kavak 2005).

Boron removal by using aluminum production process waste neutralized red sludge was studied by Çengeloğlu et al. (2007). Initial boron concentration was used between 2 and 1200 mg L^{-1}, and as a result of batch system studies, up to 90% boron removal was achieved. Since the neutral surface charge of neutralized red sludge is around pH 8 and is negatively charged at this pH value, the maximum adsorption was below pH 8 (Çengeloğlu et al. 2007).

Aluminum-based water treatment residuals include Al_2O_3, Fe_2O_3, and SiO_2 in its structure. It was used for removal of boron. van der Waals forces and electrostatic interactions were the major forces at different pH levels for boron removal. The maximum boron adsorption capacity was found as 0.98 mg g^{-1} at pH 8.3 (Irawan et al. 2011).

Iizuka et al. (2014) used waste concrete particles for boron removal. Efficient boron removal was not achieved at higher boron concentrations (100–300 mg L^{-1}); however, using 10 mg L^{-1} initial boron concentration, boron removal was increased and was attributed to ion-exchange mechanism (Iizuka et al. 2014).

Palm oil mill boiler (POMB) ash impregnated with various compounds, such as citric acid, tartaric acid, salicylic acid, etc., was investigated for boron removal. It was found that the impregnated type was effective on boron adsorption and boron removal was highly dependent on solution pH (Chieng and Chong 2013).

12.5.3 Oxides, Hydroxides, and Layered Double Hydroxides

Garcia-Soto and Camacho (2006) studied magnesium oxide precipitation/adsorption method on boron removal, and the initial boron solution concentration used was 500 mg L^{-1}. As a result of this study, 95% of boron was removed. Borate ion was adsorbed onto the magnesium oxide surface in aqueous solution. However, a metallic complex occurred between magnesium ions and borate ions in basic medium, which was performed the precipitation reaction (Garcia-Soto and Camacho 2006).

Öztürk and Kavak (2008) used cerium oxide as the adsorbent for boron removal. Statistical analysis was done to the experimental data by choosing the temperature, solution pH, and particle type as the parameters. All the parameters have positive effect on boron removal. However, temperature has the greatest effect on the removal of boron. Langmuir isotherm model was fitted well the experimental data (Öztürk and Kavak 2008).

Demetriou and Pashalidis (2012) studied boron removal from aqueous solution using iron oxide. Experimental data showed that the adsorption mechanism depends on the replacement of a water molecule by a boric acid molecule. Maximum adsorption capacity was achieved as 0.03 mol kg^{-1} according to Langmuir isotherm model (Demetriou and Pashalidis 2012).

Sub-micron calcium hydroxide particles were used for boron adsorption. Modified sub-micron calcium hydroxide particles improved adsorption efficiency compared with unmodified calcium hydroxide. The adsorption efficiency was increased from 67.2% to 76.2% at the same experimental conditions (Tsai and Lo 2015).

Prodromou (2004a, b) studied boron removal using amorphous aluminum hydroxides. Boron adsorption was affected by the type of acids exist in the soil. Boron adsorption increased according to the complexion reaction with the acids. Maximum boron adsorption occurred around 76%, and Freundlich isotherm model was the best isotherm model fitted the experimental data (Prodromou 2004a, b).

Freshly prepared magnesium hydroxide has the highest specific surface area. Therefore, Prodromou (2004a, b) used fresh magnesium hydroxide to adsorb boron from the aqueous solution. Complexation reaction occurs between magnesium hydroxide and boron. It was found that the adsorption mechanism was occurred according to both Langmuir and Freundlich isotherm models (Prodromou 2004a, b).

Mg-Al(NO_3) layered double hydroxide was used to investigate the boron removal from wastewater. The maximum adsorption occurred at alkaline pH level (9.0–9.2). A combination of electrostatic attractions and ion-exchange processes was the major forces for the adsorption of boron (Kentjono et al. 2010).

Mg-Al(NO_3) and Mg-Al(Cl) layered double hydroxides were synthesized by Kameda et al. (2015) for the removal of boron. Ion-exchange mechanism was the driving force for boron adsorption, which occurred between NO_3^- or Cl^- ions and $B(OH)_4^-$ ions. Langmuir isotherm model was best fitted the experimental data, and the maximum adsorption capacity was found at 3.6 and 3.8 mmol g^{-1} for Mg-Al(NO_3) and Mg-Al(Cl), respectively (Kameda et al. 2015).

Zn_2Al-Cl layered double hydroxide was synthesized by Koilraj and Srinivasan (2011). Maximum boron adsorption was achieved at 31 mg g^{-1} after calcination of layered double hydroxides. Boron adsorption occurred according to Langmuir isotherm model, and boron removal was constant between pH 3 and 7 (Koilraj and Srinivasan 2011).

Mg-Al layered double hydroxide was calcined at 450 °C and used for boron removal. Initial boron concentration was 5 mg L^{-1}, which is the boron content in seawater. Adsorption capacity of layered double hydroxides was found as 33 mg g^{-1} (Liu et al. 2014).

Qiu et al. (2014) synthesized hydrotalcite intercalated with d-gluconate for boron adsorption. Adsorption capacity of layered double hydroxides was found as 1.27 mmol g^{-1} according to Langmuir isotherm model (Qiu et al. 2014).

12.6 Conclusion

Boron is an essential element for plants, animals, and humans. However, there is a narrow gap between boron deficiency and toxicity. Therefore, boron removal from water is an important issue. There are numerous materials that can be used for boron removal. Natural materials, such as clay minerals, can be used for boron removal. However, most of them should be modified with a modification agent or synthesized its homoionic form to change the surface charge of the clay. On the other hand, low-cost industrial wastes also can be used at high boron concentrations with a high adsorption capacity. Complexation reactions are the major mechanism for boron adsorption. Layered double hydroxides (LDH) are another type of adsorbents that can be used for boron removal. However, they have low adsorption capacities and can be used for low boron concentrations. LDH synthesis is a new research area and can be improved in the future studies.

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Chapter 13
Waste Fruit Cortexes for the Removal of Heavy Metals from Water

Shangeetha Ganesan

Contents

Abstract In the recent years, contaminants of emerging concerns took the scientific community by a storm with one of the main issues being water security. Wastewater from the industries has been found to contaminate our water sources with heavy metals. Waste fruit cortexes made up of cellulose, hemicellulose, pectin, and lignin contain numerous hydroxyl and carboxyl bonds that are mandatory in the removal of heavy metals in water. This chapter highlights the various types of fruit cortexes that are available as a biosorbent for heavy metal removal from water.

Some of the commonly studied fruits were banana, orange, and mango, among which the various citrus peels showed highest adsorption capacity for most metals. Complexation and ion exchange are the commonly suggested mechanism for biosorption of heavy metals from water. Other than that, various factors were found to affect the uptake of metallic ions by waste fruit cortexes. The best pH reported for

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maximum biosorption were between 2 and 6.0. At this pH, it was found that there is no interference for the adsorption of metallic cations by the fruit cortex. Lower initial metal ion concentration and higher biosorbent dosage help in achieving maximum adsorption capacity of waste fruit cortexes. Pseudo-second-order kinetics and intraparticle diffusion models explain the kinetics of the biosorption. Hence, the use of waste fruit cortexes is highly recommended as biosorbent in heavy metal removal from water sources.

Keywords Fruit cortexes · Heavy metals · Biosorption · Biosorbent · Wastewater · Water · Hydroxyl groups · Carboxyl groups · Complexation · Ion exchange · Pseudo-second-order model · Intraparticle diffusion · Langmuir isotherm

13.1 Introduction

Rapid technological advancements in the race to up keep with the industrial revolution 4.0 in the global level have shown to have impacted the environment in adverse manners. Countries around the world are clamoring to make their presence felt by swift development in terms of infrastructure, buildings, and technological modern gadgets. The vast science and technological development inevitably add to the pollution of the environment, an issue that seems to have taken a backseat for the longest of time.

There is no denying that as we prosper in producing new materials, the wastewater produced by the manufacturing companies is often left unregulated. The environmental protection laws are in place in most of the countries around the world. However, the implementation seems rather lax. The presence of heavy metal contaminants such as chromium (Cr), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), zinc (Zn), manganese (Mn), and nickel (Ni) has been found to be toxic to humans and the environment (Meena et al. 2008).

Most of the time, the heavy metals found in the groundwater can be sourced back to the origin, and without fail, it was found to be sourced from the major industry players. Table 13.1 shows the major sources of heavy metal contamination. Arsenic that is found in water can sometimes be traced to have come from natural and anthropogenic sources where long-term geochemical changes release mineral ores (Sari et al. 2011). However, problem arises when the source of contamination is human-induced which commonly are industrial effluents.

The source of contamination is very much related to the industries that are booming in the recent years due to global demand. When metal ions are found to be present in the groundwater system, they possess a detrimental effect to the environment. The inorganic species has been found to be persistent and nonbiodegradable pollutants that pose a danger to the humans consuming the water source (Abdel-Ghani and El-Chaghaby 2014).

In view of the potential dangers of the presence of heavy metals in environmental aqueous, numerous researches have been done to find potential ways to remove the heavy metal contaminants from the wastewater sources (Asubiojo and Ajelabi 2009; Brown et al. 2000b; Meena et al. 2008). The importance in finding the best way to

Table 13.1 Major sources of heavy metal contamination

Heavy metals	Major sources of contamination	References
Arsenic	Metallurgical, ceramic, pesticides, wood preservatives, and dye industries	Gérente et al. (2010)
Antimony	Lead-storage batteries, soldering, bearing and power transmission equipment, casting, pewter, enamel, paints, sheet and pipe metals, ammunition, flame retardants	Iqbal et al. (2013)
Chromium (IV) anions	Wastewater from dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather, and mining	Vinodhini and Das (2010)
Cobalt	Alloys (magnetic steels and stainless steels), electronics, porcelain, and radioisotope therapy	W. Guo et al. (2013)
Manganese	Fertilizers, petrochemicals, electroplating, tanneries, metal processing, and mining	Hasan et al. (2012)
Mercury	Chlor-alkali, paper and pulp, oil refinery, paint, fossil fuel burning, metallurgical processes, pharmaceutical and battery manufacturing	El-Shafey (2010)
Lead	Production of batteries, gasoline additives, pigments, alloys, and sheets	Tunali Akar et al. (2012)
Nickel	Mining and metallurgy of nickel, stainless steel, aircraft industries, nickel electroplating, battery and manufacturing, pigment and ceramic industries	Alomá et al. (2012)
Zinc	Metallurgical processes, galvanizing plants, stabilizers, thermoplastics, pigment formation, alloys and battery manufacturing, and discharges of municipal wastewater treatment plants	El-Shafey (2010)

remove the toxic contaminants came due to the potential adverse effects of the pollutants to humans consuming the polluted water sources.

Some of the well-documented studies on the effects of heavy metals on humans are skin inflammatory diseases, damage to the kidneys, gastrointestinal issues, and, in more severe cases, death (Table 13.2). The problem becomes even more apparent in developing countries that do not have proper water treatment resources and no access to clean water source (Joseph et al. 2019). According to the WHO, 844 million people lack even a basic drinking water service, and 159 million are dependent on surface water (WHO 2017).

Therefore, it is highly imperative now to take measure to reduce or eliminate heavy metal contamination in water sources due to effluents from the industry. Many different approaches have been reported in recent times to remove heavy metals from wastewater or industrial effluents such as activated carbon adsorption (J. Li et al. 2018; Renu et al. 2016), carbon nanotechnology (Peng et al. 2017; Sherlala et al. 2018; Xu et al. 2018), modified adsorbents (Sajid et al. 2018; Xu et al. 2018; Zare et al. 2018), electrocoagulation (Al-Qodah and Al-Shannag 2017; Bazrafshan et al. 2015), membrane filtration (Kim et al. 2018), and microbial remediation (Ayangbenro et al. 2017; Li and Tao 2015).

However, the cost of production of these adsorbents and the process itself have been found to be too high to cater to the developing countries. Some of the methods

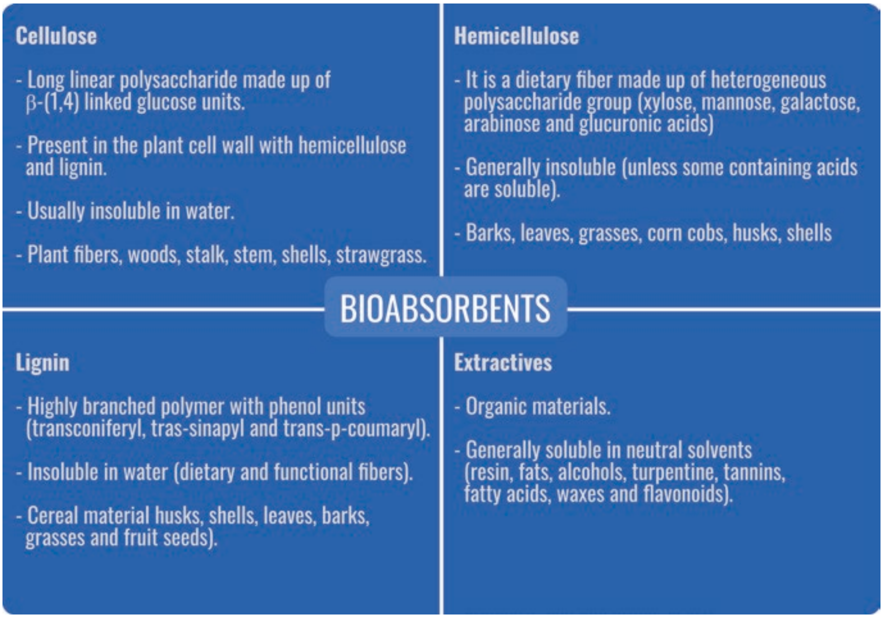
Table 13.2 Effects of heavy metals contaminant to humans and the maximum permissible limit

Heavy metal contaminant	Potential health effects to humans	Maximum permissible contaminant level (Cotruvo 2017)
Arsenic	Skin damage Circulatory system issues	0.010 mg L^{-1}
Cadmium	Kidney damage Carcinogenic	0.003 mg L^{-1}
Chromium	Allergic dermatitis Diarrhea, nausea, and vomiting	0.05 mg L^{-1}
Copper	Gastrointestinal issues Liver or kidney damage	2.0 mg L^{-1}
Lead	Kidney damage Reduced neural development	0.01 mg L^{-1}
Mercury	Kidney damage Nervous system damage	0.006 mg L^{-1}

Table 13.3 Advantages and disadvantages of the techniques for heavy metal removal

Advantages	Techniques of heavy metal removal	Disadvantages
Cost-effective, easy to operate, removes most metals	Chemical precipitation (Abaliwano et al. 2008)	Problem with disposal and sludge
Selective toward the metals adsorbed, material regeneration	Ion exchange (K. Rao et al. 2011)	Lower number of metals removed, incurs higher cost
Dewatering and sludge settling	Chemical coagulation (Abaliwano et al. 2008)	Expensive and consumes high amounts of chemicals
More than 95% removal for single metal, produces lesser solidified waste, lesser chemicals	Membrane process/ ultrafiltration (Fu and Wang 2011)	Interference from other metals, costly, slow
Cost effective, removes most metals	Natural zeolites (Fu and Wang 2011)	Inefficient
Very efficient (>99%), removes most metals	Activated carbon (Abaliwano et al. 2008)	Unable to be regenerated, performance is inconsistent
Isolation of pure metals and selective metals, no chemicals consumed	Electrochemical methods (K. Rao et al. 2011)	Costly in terms of running and capital

are also too tedious to be set up by small manufacturers. Table 13.3 compares the advantages and disadvantages of the reported methods for heavy metal removal. Hence, many industries shy away from implementing a proper wastewater treatment system. In lieu of the issues of cost-effectiveness and ease of use, researchers have started working toward the usage of agricultural waste materials as biosorbents for heavy metals from water source. Biosorbents can also be sourced from crustaceans (Vieira and Volesky 2000) as well as plant and algae based (Sud et al. 2008). The potential of these cheap, renewable materials is widely available to be explored. The usage of biosorbents also minimizes the potential of chemical and biological sludges, and at the same time, these biosorbents can be regenerated (Sud et al. 2008).



Cellulose

- Long linear polysaccharide made up of β-(1,4) linked glucose units.
- Present in the plant cell wall with hemicellulose and lignin.
- Usually insoluble in water.
- Plant fibers, woods, stalk, stem, shells, strawgrass.

Hemicellulose

- It is a dietary fiber made up of heterogeneous polysaccharide group (xylose, mannose, galactose, arabinose and glucuronic acids)
- Generally insoluble (unless some containing acids are soluble).
- Barks, leaves, grasses, corn cobs, husks, shells

BIOABSORBENTS

Lignin

- Highly branched polymer with phenol units (transconiferyl, tras-sinapyl and trans-p-coumaryl).
- Insoluble in water (dietary and functional fibers).
- Cereal material husks, shells, leaves, barks, grasses and fruit seeds).

Extractives

- Organic materials.
- Generally soluble in neutral solvents (resin, fats, alcohols, turpentine, tannins, fatty acids, waxes and flavonoids).

Fig. 13.1 The various components of a waste fruit cortexes that are found in a plant-based biosorbent with the corresponding characteristics. (Malik et al. 2017)

This chapter reviews extensively the different kinds of waste fruit cortexes that are available for the removal of heavy metals from water, the mechanisms involved, the kinetics and adsorption models, as well as the various factors that affect the adsorption of heavy metals. The thorough review serves to gather as much information as possible about the usage and research on potentials of waste fruit cortexes in removing heavy metals from water sources efficiently. As shown in Fig. 13.1, fruit cortex-based biosorbents are made up of various components such as cellulose, hemicellulose, lignin, and extractives.

13.2 Waste Fruit Cortexes as Biosorbents

The term biosorption refers to the ability of the biological materials through metabolically physicochemical pathways to uptake heavy metals from water sources. The heavy metal biosorbents can be sourced from algae, bacteria, fungi, yeasts, and some parts of higher plants. When heavy metal ions are present in low levels in wastewater, adsorption process can be used to remove the heavy metals from the wastewater. An adsorption process refers to a solid (adsorbent) that is capable of binding molecules by physical attractive forces, ion exchange, and chemical binding (Demirbas 2008).

The term biosorption refers to a system where the sorbate (an atom, molecule, or molecular ion) interacts with a biosorbent causing an increase of sorbate at the sorbate–biosorbent interface and effectively reducing the sorbate concentration in the original solution (Gadd 2009). Ease of availability in large quantities and regeneration makes the potential adsorbent more attractive to the industries. Hence, biosorbents have recently attracted the attention of researchers to work on the many types of biosorbents available in nature.

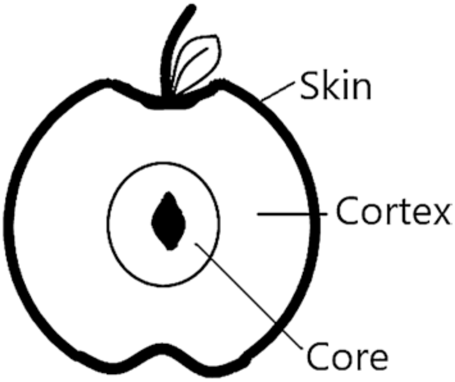
Some of the agricultural waste biosorbents reported are pomelo peel (Tasaso 2013), banana peel (Annadurai et al. 2002; Kelly-Vargas et al. 2012; Liu et al. 2012), (Alencar et al. 2012; Iqbal et al. 2013; Iqbal et al. 2009a, b), peat (Brown et al. 2000a Henryk et al. 2016; B. Sen Gupta et al. 2009), coconut fiber (Babel and Kurniawan 2004; Bhatnagar et al. 2010a, b; Guo et al. 2010), sunflower stalk (Benaïssa and Elouchdi 2007; Jain et al. 2013; Jalali and Aboulghazi 2013; Witek-Krowiak 2012), and kiwi (Al-Qahtani 2016). Many more waste fruit cortexes have been investigated and found to work as biosorbent for heavy metal in water.

The agricultural waste materials contain the basic components such as hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch that may contain functional groups suitable for adsorption of the heavy metals (Demirbas 2008; Hossain et al. 2012). The adsorbents can be used in the original or modified form. Cortexes of plants often refer to a plant bark/rind or the typical parenchymatous layer of tissue external to the vascular tissue and internal to the corky or epidermal tissues of a green plant. It can also be applied to the outer/investing layer of various algae, lichen, or fungi. Waste fruit peels can also work in other ways such as diffusion and ion transport, coprecipitation, ion exchange, and complexation to remove heavy metals from the medium of reaction (Papirio et al. 2017). Figure 13.2 clearly shows the part of the cortex in fruits that is available for heavy metal biosorption.

13.2.1 Banana Peel as Biosorbent

Banana peel is one of the extensively studied biosorbents due to its availability, ease of handling, and low cost. Banana plant (family of Musaceae) is commonly found around the globe as it is primarily planted for the fruit. However, in certain

Fig. 13.2 A representation of the cortex in an apple



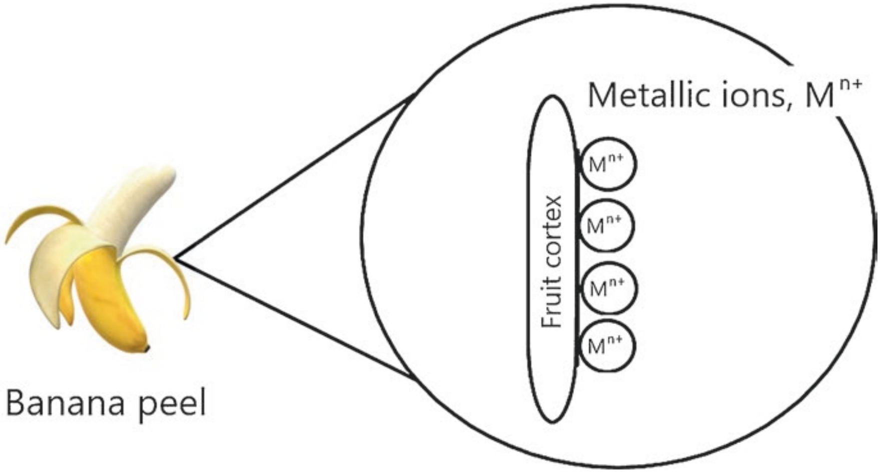


Fig. 13.3 Banana peel as an example of waste fruit cortex that can be used as biosorbent for heavy metals

Table 13.4 Various studies on the potential of banana peel as biosorbent

Previous studies on banana peel as biosorbent	Types of heavy metal adsorbed
Anwar et al. (2010)	Cd^{2+}, Pb^{2+}
Al-Qahtani (2016)	Cd^{2+}, Cr^{3+}, Zn^{2+}
Liu et al. (2012)	Cu^{2+}
Bediako et al. (2019)	Pb^{2+}, Pt^{2+}
Noeline et al. (2005)	Pb^{2+}
Ali et al. (2016)	Cr^{4+}

parts of the world, the whole banana tree is used for various applications, for example, the leaves are used as plates and food wrappers. Bananas are highly sought after as an energy food for the high sugar and potassium. In fact, bananas are one of the largest consumed fruits around the world and, hence, become one of the major agro-wastes (Anwar et al. 2010). An example of biosorption using banana peel is shown in Fig. 13.3.

In a study, Anwar et al. (2010) showed that banana peel has the potential to absorb 5.71 mg Cd^{2+}/g and 2.18 mg Pb^{2+}/g. In a separate study by Al-Qahtani (2016), it was reported that banana peel also gave the highest adsorption for Cd^{2+} compared to kiwi and tangerine. Banana peel was also reported to function most efficiently and optimally when it is dried and ground into a powder of <150 μm (Liu et al. 2012). In this study, it was also reported that the drying temperature and particle size of the banana peel powder affect the performance of the banana peel as a biosorbent. Various metallic cations that can be adsorbed by banana peel are listed in Table 13.4.

13.2.2 Citrus Peel as Biosorbent

As can be seen in Table 13.5, Feng et al. (2011) in their work used chemically modified orange peel for biosorption of heavy metals. Grafted copolymerization-modified orange peel and unmodified orange peel were used for the biosorption of Pb^{2+}, Cd^{2+}, and Ni^{2+}. The modified orange peel has increased biosorption capacities compared to the unmodified orange peel. Orange peel has a high potential to be used as a biosorbent as it has high content of cellulose, pectin (galacturonic acid), hemicellulose, and lignin.

Wide availability and low cost of the material make it a suitable candidate for biosorption of dissolved heavy metals. Al-Qahtani who worked on banana peels also compared the effectiveness of tangerine peel against banana peel. He found out that tangerine peel while does not perform as good as banana peel can be used as a biosorbent (Al-Qahtani 2016). The adsorption capacity of *Citrus sinensis* peel was compared to wood sawdust and was found that citrus peel is more efficient in Cu removal in drinking water (Khan et al. 2013).

Orange peel was also found to be a good biosorbent of Ni^{2+} and reported to be highly dependent on pH, adsorbent dosage, and initial metal concentration (Gönen and Selen 2012). Another group of researchers prepared modified orange peel biosorbents with the addition of Mg and K, respectively. They found out that the novel modified biosorbents were effective in removing Cu^{2+} (Liang et al. 2010a). The same group of researchers also successfully used sulfured orange peels for the removal of Pb^{2+} and Zn^{2+} (Liang et al. 2011). An interesting study was done to compare the adsorption capacities of banana, lemon, and orange peel. It was found that lemon and orange cortex showed better adsorption for Pb^{2+} and Cd^{2+}; meanwhile, banana cortex was found to be better performing for Cd^{2+} (Kelly-Vargas et al. 2012). Various metallic cations that can be adsorbed by citrus peel are listed in Table 13.6.

Table 13.5 Biosorption capacities of unmodified and modified orange peel. (Feng et al. 2011)

Maximum uptake capacity (mg/g of biosorbent)	Unmodified orange peel	Grafted copolymerization-modified orange peel
Pb^{2+}	113.4	476.1
Cd^{2+}	63.8	293.3
Ni^{2+}	9.9	162.6

Table 13.6 Various studies on the potential of citrus/orange peel as biosorbent

Previous studies on citrus peel as biosorbent	Types of heavy metal adsorbed
Liang et al. (2010b)	Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+}
Pérez Marín et al. (2009)	Cr^{3+}
Feng et al. (2009a, b)	Cu^{2+}
X. Y. Guo et al. (2011)	Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+}
Guiza (2017)	Cu^{2+}
X. Li et al. (2007b)	Cd^{2+}

13.2.3 Other Fruit Peels as Biosorbent

Over the years, many researchers have worked on various kinds of waste fruit cortexes as the cheapest and easily available source of biosorbent for heavy metal removal. Some extensive work was done on mango peel by a group of researchers from Pakistan. It was found that mango peel waste is able to remove Cd^{2+} and Pb^{2+} with a maximum absorption capacity of 68.92 and 99.05 mg/g (Iqbal et al. 2009b).

Another reported work shows that mango peel also has the capacity to remove Cu^{2+}, Ni^{2+}, and Zn^{2+} from constituted metal solutions and genuine electroplating industry wastewater (Iqbal et al. 2009a). The adsorption capacity of passion fruit shell as compared to *Citrus maxima* peel and sugarcane bagasse for the removal of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+} showed that the *Citrus maxima* peel and passion fruit shell gave the highest maximum adsorption capacity (Chao et al. 2014).

Pomelo peel, the white albedo, was separated from the peel, coarsely chopped, washed, and dried to be used as biosorbent for Cu^{2+} removal, and it showed that the maximum adsorption capacity is 19.7 mg g^{-1} (Tasaso 2013). A study on saponified muskmelon peel showed maximum adsorption capacity of 0.81 mol $k^{-1}g$ for Pb^{2+}. Muskmelon peels were found to contain pectic acid that is responsible for the uptake of lead ions (Huang and Zhu 2013).

Another type of fruit that is highly consumed around the world is grapefruit. Grapefruit peel activated with $ZnCl_2$ has been proven to remove lead ions (Pei and Liu 2011). The efficiency of grapefruit peel as an adsorbent was further investigated and shown to be able to remove U(IV) from aqueous solutions with an adsorption capacity of 140.79 mg g^{-1}. The biosorbent was also found to regenerate using 0.05 mol L^{-1} HCL solution at least three times with 80% recovery (Zou et al. 2012).

In a comparative study between citrus fruits, apples, and grapes, citrus fruits gave the best adsorption capacity for Cd^{2+} in conjunction with physical stability (Schiewer and Patil 2008). Al-Qahtani (2016) in his study compared kiwi, banana, and tangerine waste fruit cortexes for the removal of Cd^{2+}, Cr^{3+}, and Zn^{2+}. In terms of adsorption capacity, it was found that the adsorption capacities of banana differed from kiwi and tangerine waste fruit cortexes for the various heavy metals tested. For banana, it was reported to be $Cr^{+3} < Cd^{+2} < Zn^{+2}$, whereas it was $Cd^{+2} < Cr^{+3} < Zn^{+2}$ for kiwi and tangerine.

13.3 Heavy Metal Adsorption Mechanisms for Waste Fruit Cortexes

One of the most economical methods to treat wastewater for heavy metal content is through adsorption process. The process is simple and adaptable for small industries. Moreover, usage of biosorbent as the source of adsorbent greatly reduces the cost and increases the ease of operation, making the method attractive for small holders instead of dumping untreated wastewater unscrupulously. The metal biosorption process is a rather complex process. The understanding of the mechanism for the binding of metal to biomass involves identifying the functional groups present in the biomass.

Cell wall of the biomass or waste fruit cortex contains the necessary functional groups that are involved in heavy metal binding. The structure of plant cell wall is built by cellulose molecules that are arranged in microfibrils which are enclosed by hemicellulosic materials: xylans, mannans, glucomannas, galactans, arabinogalactans, lignin, pectin, and protein (Al-Asheh and Duvnjak 1997; Demirbas 2008; Nobel 2009). Cellulose that are mostly located in secondary cell wall behaves according to the degree of crystallinity, specific surface area, and degree of polymerization of the fibers (Lee et al. 1983).

The cellulose molecules are bundled together and are usually found in the form of microfibrils with crystalline and amorphous regions. The crystalline regions are more orderly while the amorphous regions are less ordered. The proportion of these two regions in cellulose varies on the type of sample (Demirbas 2008).

Due to the structure of plant cell wall, water permeates into the amorphous regions, hemicellulose, and lignin. The absorption of the water by plant cell wall is carried along the heavy metals bringing into contact with the functional groups present in the cortexes (Acemioglu and Alma 2001). The structure of the cell wall of plants plays an important factor in fruit cortexes in the adsorption of heavy metals. The structure of cellulose and pectin is shown in Fig. 13.4.

The polysaccharide-rich cell walls are mainly composed of cellulose and pectin compounds such as galacturonic acid polymers (Fry 2004). When these pectin-like compounds are ionized through alkaline treatment, negative charges are generated which binds metallic cations.

Pectin is an important element from waste fruit cortexes that is involved in the removal of heavy metals. A study was done to determine the role of pectin in biosorption by comparing the adsorption capacity of orange peels, depectinated orange peels, and pectic acid. Similar to cellulose, the two main functional groups that are responsible in the metal biding are the carboxyl and hydroxyl groups. The meta-binding ability of pectic acid was found to be the highest mean, while depectinated peels showed the lowest (Schiewer and Patil 2008).

Kiwi and tangerine peels were found to contain lesser amounts of starch, cellulose (Abdul Khalil et al. 2006), and pectin-type compounds (Yapo et al. 2007) compared to banana cortex. The differences in the cortexes of banana and citrus were apparent in the biosorption capacity of Cd and Cr. The higher amount of starch and cellulose in banana cortex helps in the binding of Cr and Cd compared to other metals (Al-Qahtani 2016).

The adsorption mechanism of heavy metals on the fruit cortexes is due to the presence of the carboxyl and hydroxyl groups on the pores' surfaces. The functional groups coordinate with metal ions to form metal complexes (Abdul Khalil et al. 2006). The role of the carboxyl and hydroxyl groups is depicted in Fig. 13.5. Alkalinization process creates active sites when it reacts with the cellulose- and pectin-like compounds in the fruit cortexes. The active sites will be negatively charged, hence accepting the metallic ions in the solution. The adsorption

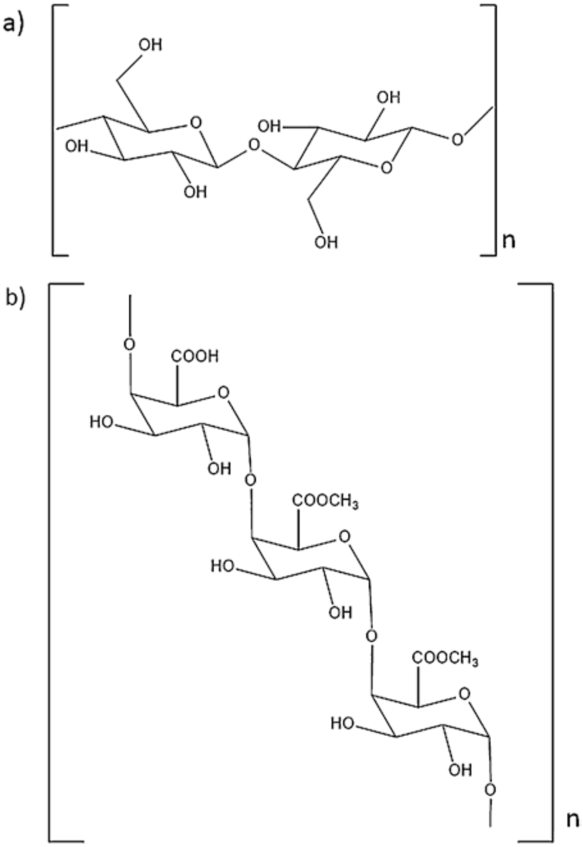


Fig. 13.4 The structure of (**a**) cellulose and (**b**) pectin bearing the hydroxyl and carboxyl groups required for the heavy metal removal in the waste fruit cortexes

mechanism is through complexation of the heavy metal by the treated fruit cortexes (Al-Qahtani 2016).

Predominantly, mango peel contains cellulose and pectin which are also rich in carboxylic acid (galacturonic acid in pectin) and hydroxyl (in cellulose). However, mango peel also contains hemicellulose, lipids, protein, polyphenols, and carotenoids (Ajila et al. 2007). The role of carboxyl and hydroxyl groups determined using FTIR showed that carboxyl and hydroxyl groups play the most important role in metallic ion binding in aqueous solution (Pehlivan et al. 2008; Shukla and Pai 2005; Xuan et al. 2006).

The presence of the carboxyl and hydroxyl groups is clearly visible on the Fourier transform-infrared spectroscopy spectrum of mango peel waste. A broad and intense peak at 3418 cm^{-1} indicating the presence of the stretching of O–H group is present as intermolecular and intramolecular hydrogen bonding of polymeric compounds, in this case, pectin, cellulose, and lignin (Iqbal et al. 2009b). Peak can be observed at 1733 cm^{-1} for the stretching vibration of C=O bond due to nonionic carboxyl groups that are commonly attributed to carboxylic acids or their esters (Li et al. 2007a).

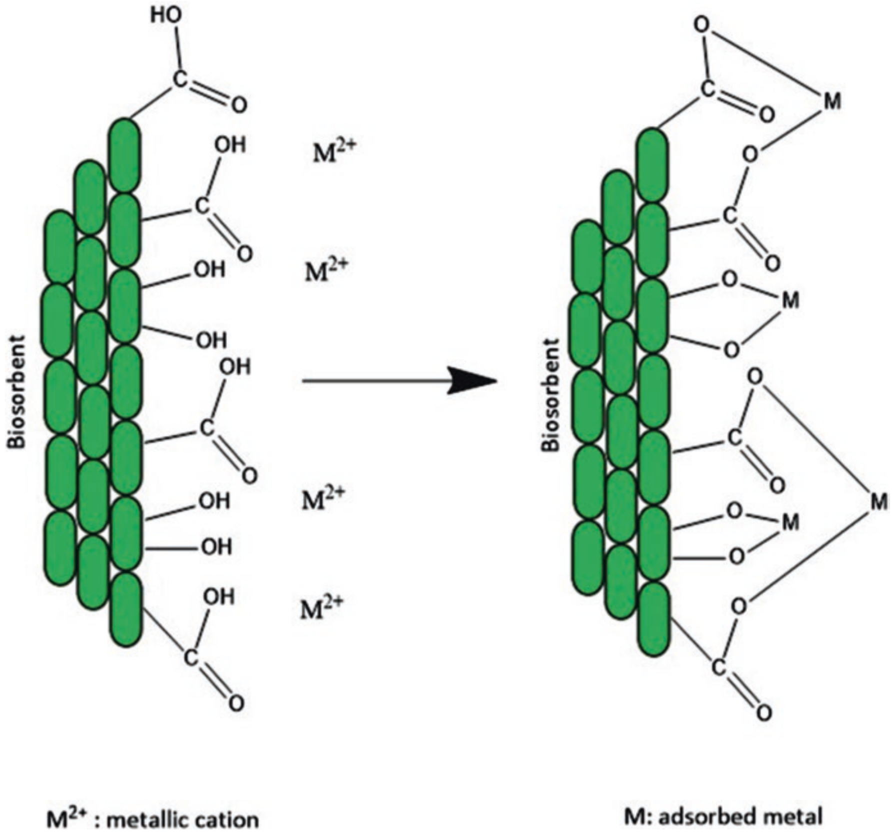


Fig. 13.5 Role of carboxyl and hydroxyl functional groups in biosorption of metallic cations

Various other peaks showing the abundance of the hydroxyl and carboxyl functional groups are listed in Table 13.7. This suggests that these groups may act as proton donors in the biopolymer. Deprotonation of these groups can lead to the uptake and coordination with the metal ions (Ashkenazy et al. 1997). The proof of the involvement of the hydroxyl and carboxyl groups in the metal ion uptake is apparent when the Fourier transform-infrared spectroscopy spectrum of Cd^{2+} and Pb^{2+} adsorbed mango peel shows the shifting of the associated peaks. The shifting of the peaks suggests the changes in counterions that are associated with carboxylate and hydroxylate anions (Ashkenazy et al. 1997).

The importance of these two functional groups can be tested by blocking the respective groups using two different methods. Blocking of the carboxyl group (Gardea-Torresdey et al. 1990):

$$\mathrm{RCOOH} + \mathrm{CH_3OH} \xrightarrow{\mathrm{H^+}} \mathrm{RCOOCH_3} + \mathrm{H_2O} \tag{13.1}$$

Table 13.7 Various peaks found in the Fourier transform-infrared spectroscopy spectrum of mango peel waste (Iqbal et al. 2009a, b)

Wavelength (cm^{-1})	Corresponding functional groups	References
3418	Intermolecular and intramolecular hydrogen bonding	Gnanasambandam and Proctor (2000)
2924	Symmetric or asymmetric C–H stretching vibrations of aliphatic acids	Li et al. (2007a)
2854	Symmetric stretching vibrations of CH_2 due to C–H bonds of aliphatic acids	Guibaud et al. (2003)
1733	Stretching vibration of C–O bond due to nonionic carboxyl groups (–COOH, $–COOCH_3$), carboxylic acids, and esters	Li et al. (2007a)
1619	Asymmetric stretching vibrations of ionic carboxylic groups (–COO−)	Iqbal et al. (2009b)
1446	Symmetric stretching vibrations of ionic carboxylic groups (–COO−)	Iqbal et al. (2009b)
1373	Symmetric stretching of –COO− of pectin	Farinella et al. (2007)
1228	Aliphatic acid group vibration	Guibaud et al. (2003)
1055	Stretching vibration of C OH of alcoholic groups and carboxylic acids	Guibaud et al. (2003)

In this method, biomass is suspended in anhydrous methanol and concentrated hydrochloric acid and agitated continuously for 6 h. After the biomass residue is separated by centrifugation and washed thoroughly, the residue is freeze-dried and stored for future use.

Blocking of hydroxyl group (Chen and Yang 2006):

$$2R-OH + HCHO \rightarrow (R-O)_2 CH_2 + H_2O \qquad (13.2)$$

As for this method, the biomass is suspended in HCHO and continuously agitated for 6 h before separation by centrifugation and washing and drying similarly to the method for carboxyl.

When carboxyl groups were blocked, the adsorption capacities of the biosorbent plummeted to 72.46% for Cd^{2+} and 76.26% for Pb^{2+}. However, when hydroxyl groups were blocked, a decrease of 26.64% for Cd^{2+} and 23.57% for Pb^{2+} were observed. The metals may have interacted with the vicinal hydroxyl groups that are present in pectins and cellulose (Li et al. 2007a). The data suggests the importance of the carboxyl and hydroxyl groups that are present on the waste fruit cortexes in the removal of heavy metals from water.

The findings were further reiterated by Zou et al. (2012) in their study involving grapefruit peel for the biosorption of uranium (VI). Similar hydroxyl and carbonyl peaks were found to be present in abundance in grapefruit cortex. The electrostatic attraction between the hydroxyl and carboxyl functional groups with UO_2^{2+} cation is responsible for the adsorption of uranium (IV) on grapefruit cortex (Zou et al. 2012).

The mechanism of biosorption appears to occur through a combination of mechanisms such as complexation, ion exchange, coordination, chelation, physical adsorption, and microprecipitation. However, complexation and ion exchange are the most commonly reported mechanisms for biosorption (Lü et al. 2010). Zou et al. (2012) in their study found that at pH above 5.0, deprotonation of carboxylic groups happens producing negatively charged carboxylate ligands (–COO–). The ligands then bind to the uranium (IV) molecules which are positively charged, hence, confirming the ion-exchange mechanism in the biosorption of the uranium (IV) ion by the cell wall of grapefruit waste.

13.4 Factors Affecting Metal Ion Biosorption

There are many factors that affect the biosorption process. Biosorbent dosage is important as it can decrease the ratio of biosorbed pollutant to weight of biosorbent and increase the efficiency of the removal of biosorbent when used optimally. Initial pollutant concentration has the potential to increase the amount of biosorbent used but if too much can decrease the efficiency of the biosorption. The overall pH of the solution can affect the biosorption of metallic cations in a positive way and the anionic metals in the negative way.

An increase in the temperature of the reaction can potentially increase the kinetic energy and surface activity of the biosorbent. However, too high temperature can destroy the active sites on the biosorbent. As the biosorption process requires agitation, the speed of agitation also can help to increase the adsorption rate as it can increase the mass transfer rate. However, too high speed can destroy the structure of the biosorbent.

Another important factor is the size of the biosorbent. Smaller biosorbent particles will have higher surface area helping in more effective biosorption. This is only true for batch processes as column process may be disrupted due to clogging. Other pollutant concentration in the solution may also affect the metal ion absorption as it can compete with the metallic cations for the binding sites on the biosorbent (Alfarra et al. 2014).

13.4.1 Effect of pH

The presence of heavy metals and its characteristics are heavily dependent on the pH of the water source. The pH of the water will determine the speciation of heavy metals in aqueous solution. Heavy metals normally exist in a more soluble, mobile, and cationic state at neutral to low pH. Complexes with hydroxides and other anions in the water will start forming if the pH rises. Apart from that, pH also influences the surface charge of the adsorbent, the ionization state of the adsorbent, as well as the concentration of ions on the functional groups of the adsorbent (Taşar et al. 2014).

The effects of pH value on the system's equilibrium are as follows (Romera et al. 2007):

$$B-H \leftrightarrow B^{-} + H^{+} \tag{13.3}$$

$$K_a = \left[B^{-}\right]\left[H^{+}\right]/\left[B-H\right] \tag{13.4}$$

$$pK_a = \log\left(\frac{\left[B-H\right]}{\left[B^{-}\right]}\right) \tag{13.5}$$

where *B* refers to the biomass and H to the hydrogen. When the pH value is lower than pK_a, this will cause the equilibrium in Eq. (13.3) to shift to the left. As consequence, the protons in the system will be consumed, increasing the pH in the process until pH is equal to pK_a. However, the reverse will happen if the pH of the medium is higher than pK_a.

Applying the theory to the adsorption of heavy metals by waste fruit cortexes, highly acidic medium ($pH \leq 4$) hinders the uptake of metallic cations present in the water. This can be overcome by increasing the pH of the medium. When the pH of the medium is low, the concentration of H^+ ions is very high and has higher mobility, hence competing with the metallic cations for adsorption site on the biosorbent.

The reverse is true when the concentration of H^+ ions is decreased (Feng et al. 2011). Looking at the effect of pH on the biosorbent surface, increasing the pH of the solution deprotonates the functional groups responsible for biosorption, in this case hydroxyl and carboxyl groups. Hence, the biosorbent is negatively charged, attracting the metallic cations from the medium. On the hind side, lowering the pH will cause the overall charges on the biosorbent surface to be positive, inhibiting binding of the metallic cations (Farooq et al. 2010). Table 13.8 shows the relationship between pH of the solution and metal ion species.

The pH of the point of zero charge (neutral biosorbent surface) also affects the biosorption process. If the pH of the medium is less than the pH of the point of zero charge of the waste fruit cortex, the functional groups will be protonated producing a positively charged polymatrix species (Farooq et al. 2010). Increasing the pH to be above the pH of the point of zero charge of the biomass will increase the adsorption of metallic cations although the surface of the adsorbent is negatively charged. However, when both the biosorbent and metallic cations are negatively charged, adsorption will be decreased (Ahmaruzzaman 2011).

Al-Qahtani (2016) in his work examined the relationship between heavy metal concentration and pH where the pH of the medium was varied from 2 to 10. He concluded that the metal removal was due to the immobilization of the metals in the rhizosphere, absorption, and partially precipitation. In this study, it was clearly shown that the highest metal removal capacity was at pH 6 for Cd, Cr, and Zn. One interesting trend was observed where the adsorption capacity was found to increase from pH 2 to pH 6 but gradually decreases from pH 6 to pH 10 which could be due to the saturation of the adsorption sites and solubility of the ions.

Table 13.8 Relationship between the pH of the solution and metal ion species

Metal ions	pH of the solution	Predominating metal species	References
Sb(III)	pH <3 pH 3–10 pH >10	$[SbO]^+$ and $[Sb(OH)_2]^+$ $HSbO_2$ and $Sb(OH)_3$ $[SbO_2]^-$	Iqbal et al. (2013)
Cu(II)	pH 3 pH 4–5 pH >6	Cu^{2+} $Cu(OH)^+$ $Cu(OH)_2$	R. A. K. Rao and Ikram (2011)
Cr ions	pH <3 pH 4 pH 7 pH >8	Cr^{3+} Cr^{3+} and $Cr(OH)^{2+}$ $Cr(OH)_3$ precipitate $Cr(OH)_4^-$	Blázquez et al. (2009)
Cd(II)	pH 3.5–5 pH >8	Cd^{2+} $Cd(OH)_2$ and $cd(OH)_3^-$	Lodeiro et al. (2006)
Pb(II)	pH 3.5–5 pH >8	Pb^{2+} $Pb(OH)_2$	Lodeiro et al. (2006)
Ni(II)	pH 2–3 pH 4.5–6	Ni^{2+} $Ni(OH)^+$ and $Ni(OH)_2$ (partial hydrolysis)	Onundi et al. (2010)
Se(IV)	pH <3.5 pH 3.5–9 pH >9	H_2SeO_3 $HSeO_3^-$ SeO_3^{2-}	Tuzen and Sari (2010)

Feng et al. (2011) also reported a similar result for both orange peel and modified orange peel, where the metallic ion adsorption increases as the pH increases from pH 2 to pH 5.5. They too stressed on the effect of pH on metal speciation where free Pb^{2+}, Cd^{2+}, and Ni^{2+} ions were most dominant at pH values below 6, 8, and 7, respectively. However, for pH values higher than 6, 8, and 7, lowly soluble hydroxyl species such as $Pb(OH)_2$, $Ni(OH)_2$, and $Cd(OH)_2$ may have been formed. The modified orange peel showed maximum biosorption at pH 5.5.

Biosorption of Cu^{2+} was low at strong acidic medium of pH 2 and increases as the pH is increased to pH 6.5. It was also found that at above pH 6.5, Cu(II) started precipitating in the form of $Cu(OH)_2$ rendering the biosorption process. Three main species of Cu(II) was found to be Cu^{2+}, $Cu(OH)^+$, and $Cu(OH)_2$. These species interact with the surface of the biosorbents through ion-exchange and hydrogen bonding mechanism (Habib et al. 2007). In this study, *Citrus sinensis* peel was found to contain carboxylic acid group that is responsible for the adsorption of copper (Khan et al. 2013). The deprotonation of carboxylic acid that will eventually lead to the uptake of metallic cations from the solution is depicted in Fig. 13.6.

13.4.2 Effect of Initial Metal Concentration

In order to test the effects of initial metal concentration on the adsorption capacity of the waste fruit cortexes, varying amount of Cd^{2+}, Cr^{3+}, and Zn^{2+} concentrations were prepared, and fixed amounts of waste fruit cortexes were added at a fixed pH

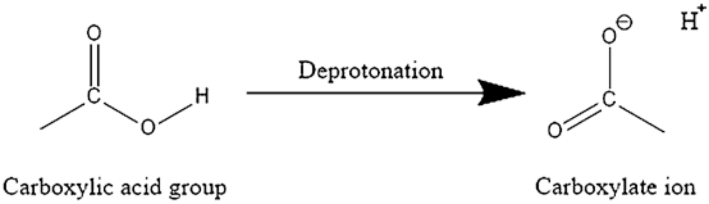


Fig. 13.6 Deprotonation of the carboxylic acid group results in the formation of the carboxylate ion that will bind with the metallic cations

and constant stirring speed and time. It found was that with the increase in initial concentration of the metallic ions decreases the removal by the waste fruit cortexes. The phenomenon is because the limited number of active sites on the adsorbents will be saturated above certain concentration (Al-Qahtani 2016). Therefore, the initial rate of external diffusion decreases as the intraparticles increase (Gode and Pehlivan 2005). The metallic ions adsorbed by waste fruit cortexes initially go through the boundary layer to diffuse into the porous structure of the biosorbent. Hence, a longer contact time will be required (Al-Qahtani 2016).

In an experiment conducted on different initial concentrations of Ni(II) ions, namely, 10, 25, 50, 75, 100, 125, 150, and 200 mg L^{-1}, it was found that lower initial concentration of ions has better surface mass transfer, hence more rapid uptakes. A simple, smooth, and continuous time variation curve was obtained for adsorption. This indicates a monolayer of coverage has formed on the adsorbent surface. The Ni orange peel system was found to have attained equilibrium in a short period of 14 min (Gönen and Selen 2012). Another study also showed that having a higher initial Cd^{2+} concentration gives a higher driving force for the collision between Cd^{2+} ions and active sites on the orange peel (V. K. Gupta and Nayak 2012).

13.4.3 *Effect of Bioadsorbent Dosage*

As discussed in the mechanism of adsorption, biomass provides the binding sites for the biosorption of the heavy metals. Therefore, the amount of biosorbent used becomes a crucial factor in determining the rate of the metal adsorption process. When the initial concentration of a heavy metal is fixed, increasing the adsorbent dosage means more surface area and active sites for the biosorption. The amount of metal ions that is adsorbed per unit adsorbent weight is high at low adsorbent dosage. Hence, when the biosorbent dosage is increased, the adsorption capacity decreases due to the lowering of the metal ions to binding site ratio as the metal ions are distributed all throughout the biosorbent surface as more binding sites will be available for heavy metal ions adsorption (Hossain et al. 2012).

The amount of solid waste fruit cortexes available as biosorbent can influence the rate of heavy metal removal from the solution. A study to investigate the effect of solid-to-liquid ratio on the biosorption capacity confirms that an increase in biosorbent concentration rapidly increases the adsorption rate. Sorption capacity of mango peel waste with varying mass for the sorption of Cd^{2+} and Pb^{2+} of constant initial concentration reveals a mere 0.5–2.5 g L-1 increase in biosorbent mass showed rapid intake of both the ions.

However, further increase in the mass of mango peel waste did not show any significant increase in the biosorption of the metals. Although, initially, more biosorbent means more active sites for heavy metal uptake, a saturation point will be reached where there are excess active sites for limited number of metal ions (Iqbal et al. 2009b). This was also shown in a study of the adsorption of Pb^{2+} by modified orange peels. The Pb^{2+} removal rate increases with the increase in the biosorbent until a saturation point and gave a maximum removal of 90% (Xuan et al. 2006).

13.5 Adsorption Models

The effect of time on adsorption capacity was studied to determine the adsorption kinetics to enhance the understanding of the dynamics of the metallic cations on the fruit cortexes. Al-Qahtani reported that the metal ion adsorption was rapid and can be achieved at full capacity within 60 min. A pseudo-second-order model was suggested for the kinetics data. The rate of reaction was found to be proportional to the square of the number of remaining free surface sites (Al-Qahtani 2016).

The equation for model (Ho and McKay 1999) is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{13.6}$$

where k_2 (g/(mg min)) is a pseudo-second-order rate constant, q_e is the adsorption capacity (mg/g), and t is the time taken for adsorption. It was found that $\frac{t}{q_t}$ and t are linear and $\frac{1}{q_e}$ is the slope intersecting at $\frac{1}{k_2 q_e^2}$. All linear graphs were obtained for kiwi, tangerine, and banana cortex as per a pseudo-second-order model, suggesting chemical adsorption as the mechanism (Feng et al. 2009a, b).

Adsorption kinetics for modified orange peel also showed a pseudo-second-order kinetic model suggesting that the rate-limiting step is the chemical sorption that involves the forces of the valence. The sharing/exchange of electrons between the metallic cations and the fruit cortexes gives the best correlation data for the heavy metal ions (Feng et al. 2011). *Citrus sinensis* peel also showed a pseudo-second-order adsorption kinetics with adsorption capacity higher than that of sawdust (Khan et al. 2013).

It is often important to study the adsorption kinetics to gain control of the efficiency of the adsorbent. This is because complex kinetics is involved in the adsorption of a solute. Heterogeneous reactive surface, physicochemical conditions, and state of the solid influence the adsorption rate significantly. For the study of orange peel for the adsorption of Ni(II) from wastewater, a pseudo-second-order model and intraparticle diffusion kinetic model were also employed for the kinetics study (Gönen and Selen 2012).

The adsorption of heavy metal by waste fruit cortexes such as lemon peel was also found to be exothermic. The biosorbent adsorption system does not follow a pseudo-first-order model but adheres to the pseudo-second-order model and the intraparticle diffusion model (Bhatnagar et al. 2010a). According to the intraparticle diffusion model (Weber and Morris 1963), there are two phases for the adsorption. The first phase is where the immediate utilization of the available active sites on the surface of the adsorbent takes place. The second phase is when the adsorbate diffuses slowly into the inner pores from the surface sites. Both phases are illustrated in Fig. 13.7. In this study, it can be deduced that the initial part of cobalt adsorption is controlled by surface diffusion during the initial intraparticle transport; meanwhile, pore diffusion controlled the later phase.

The curves plotted for the intraparticle diffusion model by Bhatnagar et al. (2010a, b) failed to pass through the origin, indicating that during the first and final stages of the adsorption, there was a difference in the rate of mass transfer (Panday et al. 1986). Another reason for the deviation is because pore diffusion is not the only rate-controlling step (Poots et al. 1978).

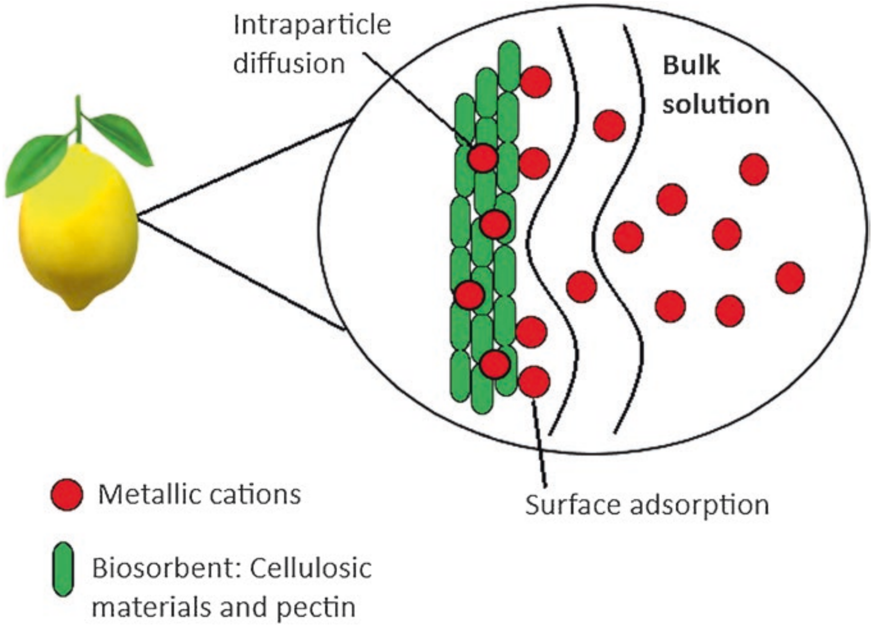


Fig. 13.7 Surface adsorption and intraparticle diffusion for the biosorption of heavy metals from water

13.6 Equilibrium Isotherms for Biosorption

The relationship between mass of heavy metals adsorbed and mass of biosorbent as well as the concentration of the heavy metals in the solution can be best described using biosorption isotherms. The surface properties and affinities of the biosorbent can be expressed with the parameters involved in the biosorption isotherms. The isotherm is also useful to compare the adsorptive capacities of the biosorbent for varying pollutants (Bulgariu and Bulgariu 2012; Tuzen and Sari 2010).

Several equilibrium isotherm models were used to study the biosorption process. If two parameters were involved, Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich were used. Meanwhile, if three parameters were involved in the isotherms, Sips and Redlich–Peterson were used.

13.6.1 *Langmuir Isotherm*

Most studies on waste fruit cortexes as the biosorbent for heavy metals from water reported the use of Langmuir isotherm. In a Langmuir isotherm model, it is assumed that the surface has homogeneous binding sites and the sorption energies are equivalent with no interaction between sorbed species (Vinod K. Gupta et al. 2010). This model also explains that no sorption will take place once the sorption sites are filled. The maximum adsorption capacity of the surface is reflected when the surface reaches a saturation point (Farhan et al. 2013). Irving Langmuir in 1916 developed an equation to explain this:

$$\frac{C_{\mathrm{eq}}}{Q_{\mathrm{eq}}} = \frac{1}{bQ_{\max}} + \frac{C_{\mathrm{eq}}}{Q_{\max}} \tag{13.7}$$

where $Q_{\max}$ (mg/g) is the maximum adsorption capacity to form a complete monolayer on surface bound at high C_{eq} (equilibrium concentration, mg/L) and b (1/mg) is the Langmuir constant in relation to energy of adsorption. A linear plot of $\frac{C_{\mathrm{eq}}}{Q_{\mathrm{eq}}}$ versus C_{eq} can be used to determine the $Q_{\max}$ and b (Abdel-Ghani et al. 2009; Langmuir 1918).

The favorability of an adsorption system can be determined from the isotherm shape. The Langmuir isotherm can be expressed as dimensionless separation parameter

$$R_L = \frac{1}{\left(1 + bC_0\right)} \tag{13.8}$$

unfavorable when $R_L > 1$; linear when $R_L = 1$; favorable when $0 < R_L < 1$; irreversible when $R_L = 0$.

In a study of the Langmuir isotherm for banana peels on the biosorption of Cd^{2+} and Pb^{2+}, a maximum capacity of 2.18 mg g^{-1} for Pb^{2+} and 5.71 mg g^{-1} for Cd^{2+} was obtained. The R^2 was also reported to be approaching 1 suggesting that the Langmuir isotherm can best explain the biosorption of Cd^{2+} and Pb^{2+} on banana peel (Anwar et al. 2010). In comparison, a study for biosorption of Cd^{2+} and Pb^{2+} using mango peel waste showed an adsorption capacity of 68.92 and 99.05 mg/g. The maximum adsorption capacity $Q_{\max}$ and concentration of metal ions at equilibrium C_{eq} were fit into a Langmuir isotherm model.

The correlation coefficient of for both Cd^{2+} and Pb^{2+} was found to be close to 1 confirming that the Langmuir isotherm is the best fit model for the mango peel waste adsorption of the metals (Iqbal et al. 2009b). The R^2 obtained for the Langmuir adsorption models of banana, kiwi, and tangerine waste fruit cortexes all showed close to 1 for Cd^{2+}, Cr^{3+}, and Zn^{2+}, confirming the favorable uptake of the heavy metals by waste fruit cortexes (Al-Qahtani 2016). Although some studies were done to fit the adsorption of the waste fruit cortexes into a Freundlich isotherm (Iqbal et al. 2009b), the best fit has always been reported for Langmuir isotherm.

13.7 Conclusions

As a conclusion, this chapter reviewed extensively on the usage of waste fruit cortexes in the removal of heavy metals from water. In a rapidly developing world, heavy metal contamination from the industries seems rather inevitable. The cost of removal or treating wastewater is high using common conventional methods; hence, small holders are taking the easy way out to release the untreated water into the environment. Heavy metals in water have been found to cause various health issues to humans such as skin and kidney damages, potentially carcinogenic, damage to the liver, and gastrointestinal issues.

In view of the detrimental effects of heavy metal contaminants and the high cost of conventional wastewater treatment methods, researchers embarked on investigating the usage of waste fruit cortexes for the removal of heavy metals from water. The removal is achieved due to the presence of the hydroxyl and carboxyl groups in the cellulose and pectin in the cortexes of the fruits. The functional groups take part in the complexation and ion-exchange mechanism to remove the heavy metals from water. Many different waste fruit cortexes were reviewed in this chapter. Over all, citrus fruits were found to have the highest maximum adsorption for the selected metals.

Various factors were investigated for the biosorption of heavy metals. A pH of 5–6.5 was found to be the most optimum for biosorption while an initial metal concentration should be low. A higher pH value will cause the release of H ions from the functional groups on the biosorbents, hence making way for the uptake of the metallic cations in the medium. Low initial metal concentration ensures that the active sites are not saturated for the uptake of the metal ions from the medium. A more robust surface mass transfer was achieved which resulted in more rapid uptakes. Another factor that is commonly studied was the biosorbent dosage. A right amount of biosorbent-to-liquid ratio can give the best results as too high dosage does not help if the number of metallic ions is low. Too low of a dosage means there will not be enough active sites to capture all the metallic ions.

Two adsorption models were suggested for the kinetics of adsorption of heavy metals by fruit cortexes. They were pseudo-second-order kinetic model and intraparticle diffusion model. It was found that through the intraparticle diffusion model, the metals must first attach to the active sites and then penetrate through to the inner pores of the surface sites. The relationship between the mass of biosorbent and mass of heavy metals can be explained using the Langmuir isotherm model as reported by majority of the researchers.

Based on the review of this chapter, waste fruit cortexes prove to be a low cost, easily available, efficient, and easy to handle biosorbent in the removal of heavy metals from water. By having a cheaper and easily handled method, it is much easier to convince the small and big manufacturing industries to take part in proper and safe wastewater treatment method for the safety and well-being of humans and environment.

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Chapter 14
Biomass-Based Absorbents for Heavy Metal Removal

Swarup Biswas and Soma Nag

Contents

Abstract With the increasing industrialization, the heavy metal contamination has become a serious environmental issue. Different activities, such as fertilizer, pharmaceutical, chemical, automobile, petroleum, and textile units, discharge a large amount of heavy metals laden effluent that contaminates the water streams. Traditional processes such as precipitation, ion exchange, membrane technology, and advance oxidation have been utilized for the remediation of heavy metal contamination. These processes could not be attractive for commercial applications

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because of their poor removal rate, problem of disposal, and high operating cost. Biosorption is now becoming a good alternative and environmentally friendly option. Biosorption of heavy metals is a metal uptake process by using ion exchange, precipitation, surface complexation, etc.. Various sources of waste biomaterials are utilized for the treatment of metal-contaminated wastewater stream. As natural biosorbents are not giving higher efficiency, modifications are done by physical and chemical activation of the biomaterials. Scientific developments were done for improving the efficiency, but limited research was conducted for the regeneration or reuse of the biosorbents. In recent years, researchers are paying attention on the reuse of the spent biosorbents by using eluent solutions such as acids, bases, chelating agents, etc. and getting the potential results. This makes the biosorption process more efficient and economic than the other conventional methods for the treatment of metal-tainted effluent. This chapter highlights the toxic metals and the various sources of biomaterials which are utilized for heavy metal removal.

Keywords Biosorption · Heavy metal ions · Wastewater · Agricultural biosorbents · Bacterial biomass · Fungal biomass · Algal biomass · Regeneration

14.1 Introduction

Heavy metal contamination with the surface and groundwater becomes a serious problem nowadays. The toxic metals which have higher specific gravity (>5) are known as heavy metals. The metals such as Hg, Pb, Cu, Co, Cd, As, Fe, Se, V, Ni, Cr, and Zn make various toxic effects to the human health. The toxic metals coming out from various industries like mining operations, refining process, fertilizer processing, tanneries, battery manufacturing, paper mill, and pesticides are contaminating water bodies (Celik and Demirbas 2005; Kjellstrom et al. 1977; Pastircakova 2004). To avoid such problems, various national and international regulatory bodies have fixed some standard limit for heavy metals before discharging [Table 14.1].

Table 14.1 Permissible discharge limits of hazardous heavy metals

	By Indian standards (mg/l)		By international organizations (μg/l)	
Metal contaminant	Into inland surface waters Indian standards: 2490(1974)	Into public sewers Indian standards: 3306(1974)	WHO	USEPA
Arsenic	0.20	0.20	10	50
Mercury	0.01	0.01	01	02
Cadmium	2.00	1.00	03	05
Lead	0.10	1.00	10	05
Chromium	0.10	2.00	50	100
Nickel	3.0	3.0	–	–
Zinc	5.00	15.00	–	–
Copper	3.00	3.00	–	1300

Conventional methods for heavy metal elimination from water stream are precipitation, advance oxidation, ion- exchange process, membrane separation, biosorption, etc. Among these processes, biosorption is an effective process due to its economical operation, abundant availability of biomaterials, easy operating process, and high competence of metal eradication. This section focuses on the effect of toxic metals, the metal removal options available in literature, and the adsorbents which are utilized for metal removal.

14.2 Sources of Heavy Metals and Their Hazardous Effect

Heavy metals such as Cr, Pb, Cu, Co, Hg, Cd, As, Fe, Se, V, Ni, and Zn have great hazardous effects on living beings. The metals are mainly discharged from various industries like mining, fertilizer, pesticides, and chemical manufacturing which are responsible directly or indirectly for the contamination of surface and groundwater. Major sources of discharging various hazardous heavy metals and their health effects are presented in Table 14.2.

14.3 Conventional Methods for Hazardous Heavy Metal Eradication

14.3.1 Chemical Precipitation

It has simple operating procedure, higher efficiency, and low operating cost, so it is considered as the good process for metal removal (Ku and Jung 2001). The coagulant is added to the metal-contaminated wastewater, and then the metal gets precipitated which is separated by using sedimentation or filtration process. Coagulants have long-chained polymers consisting of cationic and anionic charge which react with metal ion and bind the molecules together. There are mainly two types of chemical precipitation processes where one is hydroxide precipitation and the other is sulfide precipitation. Various chemical precipitation processes found in the literature are illustrated in Table 14.3.

14.3.2 Ion-Exchange Process

An ion-exchange process is an important treatment process which has great removal capacity, and it is used commercially for large-scale treatment processes (Kang et al. 2004). Several types of resins are utilized in treatment processes. In metal

Table 14.2 Common sources and health problems due to hazardous heavy metals

Metal	Common source of contamination	Health hazards
Pb	Industries such as fertilizer, petrochemical, automobile industries, and oil refineries	Lead is responsible for damaging the liver, kidney, neuron, brain, etc.
Cu	Pesticides, electroplating, and paper industry are main source of copper discharge in the water stream	Though copper is useful for human, excessive amount of copper in living beings may cause serious health problems
Cr	Chromium ion comes in wastewater from electroplating, leather, paper, chromate preparation, manufacturing of dye, petrochemical, etc.	Chromium causes diseases like cancer, lung problem, irritation of skin, etc.
Hg	Main sources of the contamination of the water are thermal power plants, pharmaceutical waste, power plants, and electronics material	Mercury makes problem in the heart, kidneys, brain, and lungs
As	Arsenic discharging sources are mining, thermal power plants, fuel, electronic material, mining industries, metallurgy, and pharmaceuticals industries	Arsenic causes serious health problems such as skin disease, respiratory problem, gastrological, and nervous systems
Ni	Nickel contaminates the water stream from industries such as electroplating, textiles, thermal power plants, ceramics, battery, etc.	Nickel has the cacogenic effect in the human body. It causes neurological, cardio, and pulmonary problems
Cd	Cadmium contaminates the water from waste batteries, electronics wastes, and paints industries	Cadmium may create different health problems such as lung disease, chest pain, bone defects, and high blood pressure
Zn	Electroplating industries are the major sources of zinc contamination in wastewater	Due to zinc contamination, health diseases like vomiting and damages of the kidney and liver may arise

Table 14.3 Chemical precipitation process

Heavy metals	Metal concentration (mg/L)	pH	Precipitant	Percent removal	References
Zn^{2+}	32	9–10	Calcium oxide	99–99.3	Ghosh et al. (2011)
Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}	100	7–11	Calcium oxide	99.37–99.6	Chen et al. (2009)
$Pb^{2+}Cu^{2+}$, Zn^{2+},	2.3 0, 018, 1.34	3.0	Hydrogen sulfide	92–100	Alvarez et al. (2007)
Cr^{3+}	5363	8.0	Calcium oxide and magnesium oxide	>99	Guo et al. (2006)
Hg^{2+}	65.6, 188	4.7, 6.4	1,3-benzenediamidoethanethiolate	>99.9	Blue et al. (2008)

Table 14.4 Metal eradication by ion-exchange process

Species	Conc. (mg/L)	pH	Adsorption capacity (meq/g)	Removal (%)	References
Pb^{2+}	2072	4.0	0.21–1	–	Inglezakis and Grigoropoulou (2003)
Pb^{2+}	1036	4.0	NA	55	Inglezakis et al. (2007)
Ni^{2+}	2900	NA	0.5–1.77	–	Rodriguez-Iznaga et al. (2002)
Ni^{2+}	25	7.0	0.11	93.6	Argun (2008)
Zn^{2+}	65.4–654	5.0	2.237 ± 0.15	100	Athanasiadis and Helmreich (2005)
Pb^{2+}	162.65–400	4.0	1.361, 1.372	–	Berber-Mendoza et al. (2006)

removal process, exchange between the cation of the resin and metal ion is the reason of removal. In literature, various ion-exchange processes are reported as described in Table 14.4. In this process, synthetic resins get the preference for the large-scale application because of their higher efficiency (Alyuz and Veli 2009). Solution pH, temperature, and the concentration of the metal ion play an important role for the removal of metal ion (Gode and Pehlivan 2006). Another important factor that affects ion-exchange process is ionic charge. The effect of ionic charge was evaluated by some researchers (Abo-Farha et al. 2009). They utilized Ce^{4+}, Fe^{3+}, and Pb^{2+}, and the adsorption sequence was found as $Ce^{4+} > Fe^{3+} > Pb^{2+}$. Similar type of results was also observed by Kang and his group (Kang et al. 2004) where they utilized Co^{2+}, Ni^{2+}, and Cr^{3+}. Utilization of the zeolites was also reported in literature which gave the efficient results (Motsi et al. 2009). Many researchers used iron oxide with clinoptilolite to improve the process (Doula 2009).

14.3.3 Membrane Filtration

Though membrane filtration is a costly process, it is very efficient for the remotion of heavy metals. Ultrafiltration technique is operated at low pressure while removing the contaminants from wastewater. It is somewhere inefficient for removing small particle as the pore size is large. In order to improve the efficiency of this process, two types of techniques are used. The first one is micellar-enhanced ultrafiltration, and the second one is polymer-enhanced ultrafiltration. In this process, various complex agents were utilized as reported in literature which includes polyacrylic acid, poly (acrylic acid) sodium, polyethyleneimine, poly-ammonium acrylate, and humic acid. It is an efficient process and also requires low energy. Reverse osmosis process is another important membrane separation process where semipermeable membranes are utilized. The process is very efficient and capable to remove the dissolved specie from aqueous solution. Drinking water manufacturing companies are using the reverse osmosis techniques commercially. The system requires high power as pump is utilized for the operation which makes the process uneconomical for wastewater treatment.

Nanofiltration is considered as one of the most efficient processes among the membrane filtration processes. It was found as the efficient process for removal of Cr (VI) (Muthukrishnan and Guha 2008), Ni(II) (Murthy and Chaudhari 2008), and Cu(II) (Csefalvay et al. 2009; Ahmad and Ooi 2010). The literature review suggests it was utilized for rejection of smaller particles of arsenic also (Nguyen et al. 2009; Figoli et al. 2010). The nanofiltration is nowadays a very effective method because of its higher efficiency and low energy requirement (Erikson 1988). Researchers utilized NF90 and N30F resins in this process for the treatment of arsenic-loaded water (Figoli et al. 2010). Others (Murthy and Chaudhari 2008) used composite polyamide membrane, and 98% Ni(II) was removed. Other group of researchers (Murthy and Chaudhari 2009) utilized nanofiltration for binary mixture of cadmium and nickel at a concentration of 5 mg/L, and the removal percentages were 98.94% and 82.69%, respectively. Nanofiltration and reverse osmosis were also effective for copper removal (Csefalvay et al. 2009). Treatment of metal-contaminated effluent coming out from metallurgical industry was done using this method by Liu and his group (Feini et al. 2008). The literature study suggests that for the recovery of the precious metal like silver, nanofiltration or reverse osmosis was utilized (Koseoglu and Kitis 2009).

14.3.4 Coagulation and Flocculation

It is another useful choice for heavy metal remediation. In this process, various coagulants such as ferrous sulfate and aluminum sulfate are utilized. Researchers used poly-aluminum chloride to remove the toxic heavy metals (El Samrani et al. 2008). In this process, doses of coagulants are optimized on the basis of the concentration of the impurities. Chang and Wang utilized polyethyleneimine for this purpose (Chang and Wang 2007). In flocculation process, the impurities are separated by filtration or flotation process. The recent research trend utilizes polyacrylamide and polyferric sulfate in flocculation process. Various flocculants were reported in literature where these were utilized for the removal of metal ion.

14.3.5 Flotation

Flotation is an important treatment method and is widely used in large-scale application. In this process, the metal is removed through bubble which is floated over the solution. For the flotation, sometimes air is introduced to the solution, and sometimes precipitation and flotation are used. Here, metals are attached with the microbubbles, and due to lower density, it floats. The floating bubbles bearing metal ion are separated as sludge (Lundh et al. 2000). The researchers were using the flotation

Table 14.5 Electrochemical method

Method	Metal ions	pH	Removal efficiency (%)	References
Electrochemical	Mn^{2+}	7.0	78.2	Shafaei et al. (2010)
	Ni^{2+}, Zn^{2+}	6.0	100	Kabdasli et al. (2009)
	As(III), As(V)	8.30	>99	Parga et al. (2005)
	Cr(VI)	1.84	100	Olmez (2009)
	Zn^{2+}	7.0	96	Casqueira et al. (2006)
	Ni^{2+}, Cu^{2+}	6	98–99	Khelifa et al. (2005)

process for the long time, and efficient results were observed (Tassel et al. 1997, 1998). Yuan and his team (Yuan et al. 2008) utilized bio-surfactant for the separation of Cd, Pd, and Cu where the removal percentages were 71.17%, 89.95%, and 81.13%. Medina et al. tested the process for removal of trivalent chromium where 96.2% removal was observed (Medina et al. 2005). Though the process is good, the process alone is not capable to give the higher removal efficiency in many times.

14.3.6 Electrochemical Treatment

Electrochemical treatment is another efficient treatment process which is widely used in recent research. The method is very useful to maintain the discharge limit of the metal ions as instructed by the various regulatory bodies (Wang et al. 2007). As electrocoagulation is the part of the electrochemical treatment process, the researchers utilized aluminum or iron electrodes in this treatment process (Chen 2004). In this process, hydrogen gas is generated which helps the impurities to float. Researchers (Heidmann and Calmano 2008) applied this process by using aluminum electrodes to remove the zinc, copper, nickel, and chromium. Zn and Ni were removed by utilizing electrochemical treatment, and 100% removal was found (Kabdasli et al. 2009). Nanseu-Njiki et al. utilized the electrochemical process for the removal of mercury where 99.9% removal was observed (Nanseu-Njiki et al. 2009). The applications of the EC process for the removal of various metal ions are shown in Table 14.5.

14.4 Biosorption

From economical point of view, adsorption is now becoming a sustainable option for the treatment of wastewater. A large number of adsorbents were utilized for treatment of metal-contaminated wastewater as reported in literature. Biosorption is an important process where the efficiencies are good and regeneration processes are also easier. Nonliving plant biomass such as wheat shell, cork biomass, food waste, coconut shell, different leafs, rice husk, sago waste, wood sawdust, rice straw, rubber wood, papaya wood, and many more were used as biosorbents. Biomasses such as bacteria, algae, and fungi play a vital role for the treatment of tainted water. Different chitosan-based materials also show remarkable efficiency for heavy metal remediation. Different categories of the biosorbents are utilized for finding an efficient and economical option of the remediation of heavy metals in literature.

14.4.1 Agricultural Biosorbents

Various low-cost adsorbents were tested to know their metal adsorption capacity [Table 14.6]. Many reviews were done where agricultural adsorbents were utilized for elimination of hazardous heavy metals. Sud et al. reported employment of agricultural waste materials for the remediation of metal ions (Sud et al. 2008). Rice bran was tested for the treatment of copper, zinc, lead, and cadmium, and the removal percentages were above 80% (Montanher et al. 2005). Rubber wood sawdust was applied for removal of hexavalent chromium and found an efficient removal of 60–70% (Karthikeyan et al. 2005).

14.4.2 Carbonaceous Biosorbents

Activated carbon is commercially used for drinking water production. It has high surface area which makes the adsorbent efficient for the removal of the contaminants. Many researchers utilized the activated carbon for the removal of metal ions and got the promising results (Kang et al. 2008). Various activation processes are available in the literature where waste materials were utilized for the preparation of the carbonaceous biosorbents (Dias et al. 2007). It was found that eucalyptus bark was utilized to remove the Cu and Pb (Kongsuwan et al. 2009). Carbon nanotube was utilized for the removal of Pb by researchers (Wang et al. 2007; Kabbashi et al. 2009). Others removed the Cd and Cr by carbon nanotube (Kuo and Lin 2009; Pillay et al. 2009).It was also used for the removal of Cu as reported by Li et al. (2010). Various activated carbons which were utilized to remove the heavy metal ions are illustrated in Table 14.7.

14.4.3 Bacterial Biomass Biosorbents

Bacterial biomass is now becoming an effective biosorbents for treatment of heavy metal contamination. In case of bacterial biomass, researchers used *Bacillus cereus* and *Escherichia coli* for the treatment of metal-contaminated wastewater (Pan et al. 2007). Metal biosorption capacity of various bacterial biomasses is presented in Table 14.8. *Pseudomonas aeruginosa*, *Bacillus* sp., *Pseudomonas putida*, and *Corynebacterium glutamicum* have been tested for lead ions where they display good adsorption

Table 14.6 Remediation by agricultural biosorbents

Raw agricultural waste	Metal	Removal	References
Oat biomass	Chromium	>80%	Gardea-Torresdey et al. (2000)
Beech sawdust		100%	Acar and Malkoc (2004)
Bagasse fly ash		96–98%	Gupta and Ali (2004)
Wheat bran		>82%	Farajzadeh and Monji (2004)
Coconut shell fibers		>80%	Mohan et al. (2006)
Eucalyptus bark		Almost 100%	Sarin and Pant (2006)
Neem leaf powder		>96%	Venkateswarlu et al. (2007)
Rubber wood sawdust		60–70%	Karthikeyan et al. (2005)
Modified bagasse fly ash		67%	Gupta et al. (1999)
Sugarcane bagasse		Up to 97%	Garg et al. (2007)
Raw rice bran		40–50%	Oliveira et al. (2005)
Oryza sativa husk	Lead	98%	Zulkali et al. (2006)
Agricultural by product *Humulus lupulus*		75%	Gardea-Torresdey et al. (2002)
Agro waste of black gram husk		Up to93%	Saeed et al. (2005a, b)
Febrifuga bark		100%	Bankar and Dara (1985)
Rice bran		>80.0%	Montanher et al. (2005)
Sawdust of *Pinus sylvestris*		96%,	Taty-Costode et al. (2003)
Maple sawdust		80–90%	Yu et al. (2001)
Water hyacinth		70–80%	Kamble and Patil (2001)
Waste tea leaves		92%,	Ahluwalia and Goyal (2005)
Peels of peas, fig leaves	Cadmium	70–80%	Benaissa (2006)
Wheat bran		87.15%	Singh et al. (2005)
Three kinds treated rice husk		80–97%	Kumar and Bandyopadhyay (2006)
Rice polish		>90%	Singh et al. (2005)
Base-treated juniper fiber		–	Min et al. (2004)
Husk of black gram		99%	Saeed and Iqbal (2003)
Straw, sawdust, dates nut		>70%	
Dried parthenium powder		>99%	Ajmal et al. (2006)
Bagasse fly ash		65%	Srivastava et al. (2007)
Bagasse		90%	Mohan and Singh (2002)
Bagasse fly ash		90.0%	Gupta et al. (2003)
Rice bran		>80.0%	Montanher et al. (2005)
Papaya wood		98, 95, 67%	Saeed et al. (2005a, b)
Rice straw, soybean hulls		Pb > Cd	Johns et al. (1998)
Poplar wood sawdust		Cu > Cd	Sciban et al. (2007)
Powder of green coconut shell		98%	Pino et al. (2006)
Bark of *Abies sachalinensis* and *Picea glehnii*		Up to 63%	Seki et al. (1997)
Cassia fistula biomass	Nickel	100%	Hanif et al. (2007)
Maple sawdust		75%	Shukla and Pai (2005a, b)
Tea waste		86%	Malkoc and Nuhoglu (2005)
Waste tea leaves		92%, 84%, 73%	Ahluwalia and Goyal (2005)

Table 14.7 Removal of heavy metal ion by carbonaceous adsorbents

Activated carbons	Metal ion	Results	References
Coconut char-based activated carbon	Pb^{+2}	100%	Gajghate et al. (1991)
Activated carbon from coir pith	Hg^{+2}	100%	Kadirvelu et al. (2001)
Activated carbon of peanut shells	Cu^{+2}	Up to 75%	Wilson et al. (2006)
Activated sulfurized carbon (bagasse pith)	Cd^{+2}	98.8%	Krishnan and Anirudhan (2003)
Carbonized corn pith	Cu^{+2}	90%	Basci et al. (2003)
Carbon nanotubes	Cd^{+2}	25.7 mg/g	Vukovi et al. (2010)
Carbon nanotube immobilized	Cu^{+2}	67.9 mg/g	Li et al. (2010)
Carbon nanotube	Pb^{+2}	102.04	Kabbashi et al. (2009)

Table 14.8 Removal of metal ions by bacterial biomass

Bacteria species	Metal ions	Adsorption capacity (mg/g)	References
Pseudomonas aeruginosa	Pb	79.5	Chang et al. (1997)
Pseudomonas putida	Pb	270.4	Uslu and Tanyol (2006)
Bacillus sp.	Pb	92.3	Tunali et al. (2006)
Pseudomonas putida	Pb	56.2	Pardo et al. (2003)
Corynebacterium glutamicum	Pb	567.7	Choi and Yun (2004)
Streptomyces rimosus 30	Zn		Mameri et al. (1999)
Thiobacillus ferrooxidans	Zn	82.6	Celaya et al. (2000)
Pseudomonas putida	Zn	17.7	Chen et al. (2005)
Pseudomonas putida	Zn	6.9	Pardo et al. (2003)
Thiobacillus ferrooxidans	Zn	172.4	Liu et al. (2004)
Pseudomonas putida	Cu	96.9	Uslu and Tanyol (2006)
Pseudomonas aeruginosa	Cu	23.1	Chang et al. (1997)
Sphaerotilus natans	Cu	60	Beolchini et al. (2006)
Bacillus subtilis	Cu	20.8	Nakajima et al. (2001)
Pseudomonas putida	Cu	6.6	Pardo et al. (2003)
Pseudomonas putida	Cd	8.0	Pardo et al. (2003)
Aeromonas caviae	Cr(IV)	284.4	Loukidou et al. (2004)
Bacillus coagulans	Cr(IV)	39.9	Srinath et al. (2002)
Pseudomonas aeruginosa	Cd	42.4	Chang et al. (1997)
Streptomyces pimprina	Cd	30.4	Puranik and Paknikar (1997)
Pseudomonas sp.	Cr(IV)	95.0	Ziagova et al. (2007)
Bacillus megaterium	Cr(IV)	30.7	Srinath et al. (2002)
Bacillus thuringiensis	Ni	45.9	Ozturk (2007)
Streptomyces rimosus	Fe(III)	122.0	Selatnia et al. (2004)

capacity. Other species of the bacteria such as *Pseudomonas putida*, *Thiobacillus*, *Pseudomonas*, and *Aeromonas caviae* were also tested by other researchers. In case of low metal ion concentration, the bacterial biomasses show the higher efficiency.

14.4.4 Fungal Biomass Biosorption

Biosorption by using fungal biomass is a noble and economical process for the treatment of metal-contaminated water source. Various studies were reported in literature as summarized in Table 14.9 where fungal biomass shows the higher metal

Table 14.9 Removal of metal ions by fungal biomass

Fungal biomass	Metal ions	Adsorption capacity (mg/g)	References
Penicillium chrysogenum	Cd	11	Niu et al. (1993)
Penicillium chrysogenum	Cd	56	Holan and Volesky (1995)
Penicillium chrysogenum	Cr(VI)	–	Park et al. (2005)
Penicillium chrysogenum (modified)	Cd	210.2	Deng and Ting (2005)
Penicillium chrysogenum	Cd	39	Fourest et al. (1994)
Penicillium canescens	Pb	213.2	Say et al. (2003)
Penicillium chrysogenum	Pb	116	Kapoor and Viraraghavan (1995)
Penicillium purpurogenum	Cd	110.4	Say et al. (2003)
Penicillium digitatum	Cd	3.5	Veglio and Beolchini (1997)
Penicillium chrysogenum	Pb	96	Skowronski et al. (2001)
Penicillium notatum	Cd	5.0	Kapoor and Viraraghavan (1995)
Aspergillus niger (live)	Pb	2.25	Kapoor et al. (1999)
Penicillium chrysogenum	Pb	116	Niu et al. (1993)
Penicillium chrysogenum (raw)	Cr(III)	18.6	Tan and Cheng (2003)
Aspergillus flavus	U, Th		Hafez et al. (1997)
Aspergillus niger (growing)	Cu	15.6	Dursun et al. (2003)
Aspergillus carbonarius	Cu, Cr		Alasheh and Duvnjak (1995)
Aspergillus oryzae	Cu, Cd, Zn		Vianna et al. (2000)
Aspergillus awamori	Cu		Tsekova et al. (2000)
Aspergillus niger	Cu(II)	9.53	Dursun et al. (2003)
Aspergillus fumigatus	Au, Ag, Cu		Gomes and Linardi (1996)
Aspergillus terreus (immobilized in polyurethane foam)	Fe	164.5	Dias et al. (2002)
Aspergillus terreus	Cu	224	Gulati et al. (2002)
Aspergillus niger	Ag	–	Akthar et al. (1995)

adsorption capacity. In these studies, many species of fungal biomasses, such as *Penicillium chrysogenum*, *Penicillium* spp., *Aspergillus niger* (live), *Penicillium chrysogenum*, and *Aspergillus terreus* (immobilized in polyurethane foam) were tested. Various fungal biomasses such as *Aspergillus niger* (Dursun 2006) and *Saccharomyces cerevisiae* (Cojocaru et al. 2009) were used for the removal of metal ion. Metabolic activities of fungi depend on the presence of metal ion. There are many instances where fungal biomass shows the higher metal binding efficiencies.

14.4.5 Algal Biomass Biosorbents

Many algae show potential capacity of metal ion adsorption. As it is available in large quantities in nature, it has been used as an economical biosorbent. The researchers used dried marine green algae for the elimination of copper and zinc (Ajjabi and Chouba 2009). According to Brinza et al. 2007, brown algae show the higher metal adsorption capacity than the other forms (Brinza et al. 2007). Various studies from literature are reported in Table 14.10. Adsorption of lead by algal biomass was reported by Deng et al. (2007).

14.4.6 Chitosan Composite Biosorbents

Chitosan is basically a biopolymer and capable to remove the metal ions effectively from the wastewater. For the increasing of the adsorption capacity, various modifications of the chitosan were done and reported in literature. Various chitosan composites which are reported in literature are shown in Table 14.11. Some researchers utilized the chitosan for the treatment of copper, chromium, lead, and

Table 14.10 Removal of metal ions by algal biomass

Algal biomass	Metal ions	Adsorption capacity (mg/g)	References
Aphanothece halophytica	Zn	133	Incharoensakdi and Kitjaharn (2002)
Cladophora crispata	Cr	3	Nourbakhsh et al. (1994)
Ascophyllum nodosum	Ni, Pb	30, 270–360	Holan and Volesky (1995)
Ascophyllum nodosum	Cd	215	Holan et al. (1993)
Chlorella vulgaris	Cr	3.5	Nourbakhsh et al. (1994)
Sargassum fluitans	Cu	51	Kratochvil et al. (1997)
Pachymeniopis sp.	Cr(VI)	225	Lee et al. (2000)
Sargassum natans	Cd	135	Holan et al. (1993)
Sargassum sp.	Cd	120	Cruz et al. (2004)
Fucus spiralis	Cd	64	Cordeo et al. (2004)

Table 14.11 Removal of metal ions by chitosan composite biosorbents

Adsorbent	Metal ions	Adsorption capacity (mg/g)	References
Magnetic chitosan	Cr^{+6}	69.40	Huang et al. (2009)
Chitosan/cellulose	Cu^{+2}	26.50	Sun et al. (2009)
Chitosan/perlite	Cu^{+2}	196.07	Kalyani et al. (2005)
Chitosan/alginate	Cu^{+2}	67.66	Ngah and Fatinathan (2008)
Chitosan/calcium alginate	Ni^{+2}	222.2	Vijaya et al. (2008)
Chitosan/clinoptilolite	Cu^{+2}	574.49	Dragan et al. (2010)
Chitosan/clinoptilolite	Cu^{+2}	719.39	Dinu and Dragan (2010)
Chitosan/clinoptilolite	Co^{+2}	467.90	Dinu and Dragan (2010)
Chitosan/cotton fibers	Cu^{+2}	24.78	Zhang et al. (2008)

zinc (Sun et al. 2009). The utilization of the mixture of sand and chitosan was found for the removal of copper (Kalyani et al. 2005). As the surface areas of the chitosan composites are large, the adsorbents are capable to give higher adsorption capacity.

14.5 Chemical Modification of the Biosorbents

Many instances are reported in literature where biosorption capacities of natural biosorbents were increased by various chemical treatments. As reported in the literature, modification of the adsorbents was done by utilizing acids such as nitric acid, hydrochloric acid, sulfuric acid, citric acid, etc. Chemical modifications of the adsorbents were also made by using calcium hydroxide, sodium hydroxide, sodium carbonate, etc. Some organics such as formaldehyde, ethylenediamine, etc. were involved in the modification of the adsorbents. Hydrogen peroxide was also used for modification of the raw adsorbents. Chemically modified adsorbents which were utilized to remove the metal ions are presented in Table 14.12. Hydrochloric acid was utilized for the modification of oak tree sawdust (Argun et al. 2007). Peanut husk was modified by using sulfuric acid and utilized for the treatment of copper, chromium, and lead (Li et al. 2007). Some researchers modified banana pith by the treatment with nitric acid (Low et al. 1995).

14.6 Responsible Functional Groups

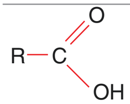
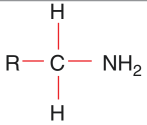
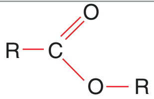
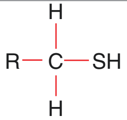
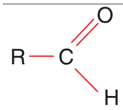
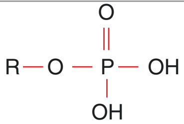
Biosorption of metal ion depends on the active groups. Various components such as cellulose, chitin, and glycol present in the biosorbents bind the metal ion. Some functional groups such as hydroxyl, amino, ester, sulfhydryl, carbonyl, and

Table 14.12 Removal of metal ions by chemically modified biosorbents

Adsorbent	Chemicals for modification	Metal ion	Adsorption capacity (mg/g)	References
Rice husk	Tartaric acid	Cu^{+2}	31.85	Wong et al. (2003)
Sawdust (cedrus deodar wood)	NaOH	Cd^{+2}	73.62	Memon et al. (2007)
Sawdust (poplar tree)	H_2SO_4	Cu^{+2}	13.95	Acar and Eren (2006)
Sawdust (oak tree)	HCl	Cu^{+2}	3.60	Argun et al. (2007)
Sawdust	Reactive Orange 13	Cu^{+2}	8.07	Shukla and Pai (2005a, b)
Sawdust (*Pinus sylvestris*)	Formaldehyde in sulfuric acid	Pb^{+2}	9.78	Taty-Costode et al. (2003)
Cassava tuber bark waste	Thioglycolic acid	Cd^{+2}	26.3	Horsfall Jr. et al. (2006)
Jute fibers	Reactive orange 13	Cu^{+2}	8.40	Shukla and Pai (2005a, b)
Banana pith	HNO_3	Cu^{+2}	13.46	Low et al. (1995)
Cork powder	$CaCl_2$	Cu^{+2}	15.6	Chubar et al. (2004)
Peanut husk	H_2SO_4	Pb^{+2}	29.14	Li et al. (2007)
Sugarbeet pulp	HCl	Cu^{+2}	0.15	Pehlivan et al. (2006)
Spent grain	HCl	Cd^{+2}	17.3	Low et al. (2000)
Bagasse fly ash	H_2O_2	Pb^{+2}	2.50	Gupta and Ali (2004)
Corncorb	HNO_3	Cd^{+2}	19.3	Leyva-Ramos et al. (2005)
Terminalia arjuna nuts	$ZnCl_2$	Cr^{+6}	28.43	Mohanty et al. (2005)
Sugarcane bagasse	$NaHCO_3$	Cu^{+2}	114	Junior et al. (2006)
Banana stem	Formaldehyde	Pb^{+2}	91.74	Noeline et al. (2005)
Alfalfa biomass	NaOH	Pb^{+2}	89.2	Tiemann et al. (2002)
Imperata cylindrica leaf powder	NaOH	Pb^{+2}	13.50	Hanafiah et al. (2006)

carboxyl group participate for the binding of metal ions as described in Table 14.13. For the determination of the metal uptake by the active sites of the biosorbent, various instruments such as Infrared spectroscopy, X-ray diffraction analysis, electron dispersive spectroscopy, nuclear magnetic resonance, etc. are utilized.

Table 14.13 Functional groups involved in biosorption (R stands for residue and others are elements)

Functional group	Name
R—O—H	Hydroxyl
	Carboxyl
 $R-\overset{H}{\underset{H}{C}}-NH_2$	Amino
	Ester
 $R-\overset{H}{\underset{H}{C}}-SH$	Sulfhydryl
	Carbonyl, terminal end
 $R-O-\overset{\overset{O}{\Vert}}{\underset{\underset{OH}{\vert}}{P}}-OH$	Phosphate

14.7 Regeneration of Biosorbents

Desorption of metal ions from adsorbent has an important significance for the reuse of the adsorbent. Regeneration study is required to check the economical feasibility of the biosorbent. Now, in recent trend, regeneration of the adsorbents is carried out by elution processes where acids, bases, and other chemicals are utilized. Elutent is an important factor in regeneration study, and the selection of the elutent is done based on its high efficiency, low cost, and environmentally friendly nature. Regeneration efficiencies of different biosorbents were investigated by various researchers as described in Table 14.14. Scientists (Bai and Abraham 2003) reported the regeneration of immobilized fungal biomass by using 0.01 N NaOH and Na_2CO_3 where 78% and 91.91 ± 3.9% regeneration were achieved. Others (Saeed et al. 2005a, b) utilized 0.1 N HCl for desorption of copper, cadmium, and zinc ions from the papaya wood and obtained the efficiency of 99.4%, 98.5%, and 99.3% after fifth cycle. Some researchers (Gupta and Nayak 2012) utilized nitric acid for the regeneration of orange peel powder with Fe_3O_4 and got the regeneration efficiency of 98.28% even after fifth cycle. Furthermore, it can be concluded that regeneration of the biosorbent makes bisorption process more effective and efficient.

Table 14.14 Regeneration efficiency of the different biosorbents

Adsorbent	Metal	Elutant	Regeneration efficiency	Number of cycles	References
Immobilized fungal biomass (*Rhizopus nigricans*)	Cr(VI)	0.01 N NaOH,	78%	25	Bai and Abraham (2003)
		Na_2CO_3	91.91 ± 3.9%		
Papaya wood	Cu(II)	0.1 N HCl	99.4%	5	Saeed et al. (2005a, b)
	Cd(II)		98.5%		
	Zn(II)		99.3%		
Coconut coir pith	As(V)	0.1 M HCl	(96.0%)	1	Anirudhan and Unnithan (2007)
			(95.7%)	2	
			(95.3%)	3	
			(93.8%)	4	
Marine algal biomass (*Cladophora fascicularis*)	Cd(II)	EDTA	83%		Deng et al. (2008)
Nonviable cyanobacterium (c) biomass	Cr(VI)	0.1 M HNO3 and EDTA	90%		Gupta and Rastogi (2008)
Orange peel powder with Fe3O4	Cd(II)	0.1 M HNO3	98.19%	1	Gupta and Nayak (2012)
			98.66%	2	
			98.58%	3	
			98.82%	4	
			98.28%	5	

14.8 Conclusion

To combat the environmental degradation in a sustainable way, many technologies have been developed. Among them, biosorption in considered as an efficient and economical process for its easy operation, local availability, and low cost. Some of the waste biomasses which are locally available in abundant quantities are utilized as biosorbents. Natural biosorbents such as activated carbon, wood sawdust, leaf powder, bacterial biomass, algal biomass, and fungal biomass were utilized for treatment of metal-tainted effluent. As most of the natural biosorbents have low adsorption capacity, researchers attempted to increase the adsorption capacity by a number of pretreatment techniques. These pretreatment includes physical and chemical activation where in physical treatment, the adsorbents are heated at high temperature with controlled rate of heating. In chemical treatment, various acids, bases, and other chemicals are utilized. Chemical modification increases the binding sites and modifies the functional groups of the adsorbent resulting enhancement of the adsorption capacity as well as their mechanical strength. Literature review suggests utilization of various biosorbents for the removal of heavy metals and their adsorption capacity were investigated at laboratory scale. The results are promising, but the real application of those bioadsorbent is very limited. So to increase the industrial applications of the biosorbents, more pilot-scale studies are required.

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Chapter 15
Remediation of Dyes from Industrial Wastewater Using Low-Cost Adsorbents

Moumita Sardar, Madhumita Manna, Manisha Maharana, and Sujit Sen

Contents

Abstract Due to the huge application of dye to color the product in many industries like pigments, leather, and textile, enormous amount of dyes are discharged through the effluent which is inherently dangerous to the surroundings as well as human health. Therefore, recently the dye elimination from industrial effluent has gained a massive attention. This book chapter presented the various developments on adsorption process for dye removal from industrial effluent. The chapter is furnished with the understanding of dyes with its classification and harmful effects, various treatment technologies, and adsorption of dyes using various low-cost adsorbents. Several traditional treatment methods such as physical, chemical, and biological are in use. Among all treatment technologies, adsorption occupies an eminent place because of its inexpensive method and effectiveness in dye removal.

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Although commercial activated carbon is most preferable as adsorbent in dye treatment, its application is restricted as it is very expensive.

So, the increasing demand for finding inexpensive and effective treatment method forces to develop and look for more efficient low-cost adsorbents in dye removal from industrial effluent. Therefore, different low-cost adsorbents like naturally obtained material, industrial and agricultural waste or by-product, as well as synthesized product from low cost material and its applications in water treatment have been compiled here. These adsorbents have been studied to remove various types of dyes ranging from 80 to 99.9%. In addition, the other conventional treatment methods for dye removal from various wastewaters are also described in brief.

Keywords Dye removal · Industrial effluent · Techniques · Low-cost adsorbent · Synthesized products

15.1 Introduction

Among the consequences of the expeditious growth of science and technology, environmental concerns have become the universal attention for last few years with the substantial pollution problems like global warming as well as water pollution (Makertihartha et al. 2017; Gupta and Suhas 2009). Due to the instantaneous enlargement of industrialization, huge amount of effluents are discharged from the individual industries which causes significant threats to environment for the adverse consequences of the pollutants (Ahmad et al. 2015). Among the numerous types of pollutants, one of the significant groups of pollutant is dye, which is more stable in water and problematic for biodegradation due to their synthetic origin and compound structure of molecules (Gupta and Suhas 2009). India has been discovered as explorer in the art of dyeing and considered as one the world's 12 megadiverse countries with more than 450 dye plants. The estimated worldwide annual production of dyes is over 7×10^5 tons with above 100,000 commercially available dyes among which approximately15% of dyes are lost during the making and handling operations and 20% of lost dyes come with industrial effluents (Hai et al. 2007; Rai et al. 2005; Kanawade and Gaikwad 2013; Demirbas 2009). Significant number of applications of dyes has been found in several industries including, textile, paper and pulp, tannery, plastic, paint, rubber, dyestuffs, and electroplating industries. Among them, the prime consumer of dyes is textile industry that is responsible for producing substantial volume and complexity of colored effluents (Ahmad et al. 2015; Crini 2006; Demirbas 2009). Dyes are also used in pharmaceutical, food, cosmetic, and petroleum industries as additives (Husain 2010).

Fundamentally, dyes are the organic compounds consisting with a compound aromatic structure of molecules for the radiant and firm color to the materials, which is problematic for biodegradation (Mondal 2008). Dyes are divided into two categories, (1) natural dyes and (2) synthetic dyes. Synthetic dyes are mainly employed in various fields of advanced technology in many industries. These are also used in tracing the ground water by the determining the surface area of sewage and activated sludge (Yagub et al. 2014). Dye is found very hazardous as it is very toxic, carcinogenic, and mutagenic, which increases the level of biochemical oxygen demand and chemical oxygen demand of aquatic sources and causes a critical warning for human health (Ruan et al. 2019; Fernández et al. 2010). Even 1.0 mg/L of dye concentration in drinking water could disseminate significant color and cautious for human consumption (Garg et al. 2004). Therefore, it is essential for dye removal from the effluent prior to their discharge to the environment. As the dyes are very harmful organic compounds to the surrounding and human health, the effective removal of dyes from the enormous amount of industrial colored wastewater become a great challenge to the chemical engineer and environmental scientists (Demirbas 2009; Mondal 2008).

To control the obstructive impacts of dye from the industrial effluent, several types of physical, chemical, and biological treatment methods such as coagulation and flocculation, biodegradation, oxidation, membrane filtration, and adsorption have been developed (Gimbert et al. 2008; Crini 2006; Ahmad et al. 2015). Many of these are very high budget and require significant start-up costs (Eletta et al. 2018). For the treatment of wide ranges of synthetic dyes like azoic, reactive, acidic, and basic dyes, alum coagulation method is not found so effective (Garg et al. 2004). Because of the low removal efficiency of reactive and anionic soluble dyes, aerobic biodegradation is also found very ineffective. So, the convectional biological treatment method are not so efficient in dye removing due to its low biodegradation, but it is efficient in basic dye removal (Saad et al. 2010; Garg et al. 2004). In the oxidation process ozone, hydrogen peroxide is often used for the removal of dyes and that could be a little bit expensive. Membrane filtration is found very effective method for the separation of dyes, but the barrier of this method is membrane fouling (Mondal 2008). Among all types of dye treatment processes adsorption has been found to be highly effective for dyes removal regarding its simplicity, cost, and ease of the separation process (Garg et al. 2004; Demirbas 2009). Due to the excellent adsorption capacity, activated carbon is highly preferable, but it is limited for its high cost, and also 10–15% loss of adsorbents are found in regeneration process by refractory technique (Garg et al. 2004; Ruan et al. 2019). Thus, there is a need for great efforts to exploit an innovative and cheap new promising low-cost adsorbent for dye removal.

Presently, the replacement of synthetic adsorbents with non-conventional and cost effective materials has become the hot topic in research and development (Eletta et al. 2018). Therefore, several researches are done on numerous approaches in developing the low-cost and potential adsorbents obtained from biosorbents, natural materials, agricultural waste, and industrial wastes for dye removal from industrial effluent that can be a feasible alternative to activated carbon (Demirbas 2009; Yagub et al. 2014; Gimbert et al. 2008). Various numbers of adsorbents have been reported as cheap adsorbents such as wheat straw, rice husk, banana and orange peels, spent tea leaves, mango peels, coconut shell, eucalyptus bark, chitosan, fly ash, silica, natural zeolites, and peat. For the removal of methyl red from the aqueous solution, sugarcane bagasse also can be used as successful adsorbent (Demirbas 2009). Waste from several industries such as sludge and slag from steel industry (inorganic), blast furnace dust, and a carbonaceous waste from a fertilizer industry (organic) can be also used as adsorbents in separating dye (Jain et al. 2003). However, new materials which are easily available, more economical and highly efficient are still under the development as the capacity of the above materials are not very large (Saad et al. 2010; Jain et al. 2003). The main objective of this book chapter is to cover the recent developments of various kind of non-conventional, sustainable low-cost adsorbent with their applications and also analyze the maximum adsorption capacity at various operation conditions.

15.2 Dyes

Colorant is the highly colored substance that is used for imparting color on various substrates. Colorants are subdivided into two groups such as dyes and pigments. Dyes are the colored substances having an affinity to give a permanent color when applied to fibers, made from more than one compounds obtained from distillation of coal tar (Rai et al. 2005). Dyes are soluble in a medium and mainly used as aqueous solution, but it requires a mordant for improving the fastness of dye on substrates. On the other hand, pigments are insoluble in the medium, and it has no affinity to the substrates (Moore et al. 2011). It has been found that India and the Middle East countries were carried out over 5000 year in variety of industries that consume huge amount of dyes (Parsa and Negahdar 2012; Sharma and Kaur 2018).

15.2.1 Definition of Dyes

Dyes are basically inorganic or organic compounds having a synthetic and compound unsaturated aromatic structures of molecules with accomplishing characteristics like color, intensity, fastness, and completely soluble in aqueous media (Gong et al. 2005; Sharma and Kaur 2018). Due to their chemical composition, synthetic dyes have the resistance for fading up in water, light, and variety of chemicals and the acidic properties build them more strong and stable to biodegrade when it mixed with water (Abid et al. 2012; Wang and Li 2007).

At present, more than 10,000 dyes are available commercially. Dyes comprise with two basic components such as, chromophore and auxochrome. Chromophores, i.e., electrons acceptor in dye molecules is basically an electron withdrawing group, responsible for creating color due to its capability for absorbing light near ultraviolet region. The chromogene is an aromatic compound containing benzene, anthracene, or naphthalene rings with binding chromophores containing double conjugated links with delocalized electrons that form a conjugated system. The most important groups of chromophores are the ethylene, azo, carbonyl, methine, carbon coupled with sulfur group, carbon with nitrogen group, nitro, nitroso, or chinoid groups (Rai et al. 2005). On the other hand, auxochrome, i.e., donor of electrons, which can not only supplement the chromophore but also intensify the casting of chromophore by modifying the overall strength of the electronic system and providing the solubility and the adhesion of the dye to the fiber by means of stable chemical bonds (Rai et al. 2005; Gupta and Suhas 2009). The most common auxochrome are carboxyl, sulfonate, amino, and hydroxyl group. The chemical bonds are organized by basic or acidic groups in nature (Rai et al. 2005).

15.2.2 Classification of Dyes

Dye can be arranged in a number of ways like basic chemistry, source of materials, industrial application, nuclear structure, nature of chromophores, Colour Index, and specific way of bonding (e.g., physical forces or robust bonds). Dyes are also arranged depending on their dissolution of particle charge in solution like cationic, anionic, and non-ionic. Dye can be classified based on their solubility. For example, soluble dyes include acid, basic, direct, mordant, metal complex, and reactive dyes; and insoluble dyes include sulfur, azoic, vat, and disperse dyes (Yagub et al. 2014). But the major classification of dyes is based on their sources, application methods, and their chemical structures which are given in Fig. 15.1.

Depending on their sources, there are two types of dyes:

(1) Natural dyes: There are three primary sources for natural dyes, minerals, plants, and animals. Natural dyes are mostly negative. Based on their source, natural dyes are classified as:

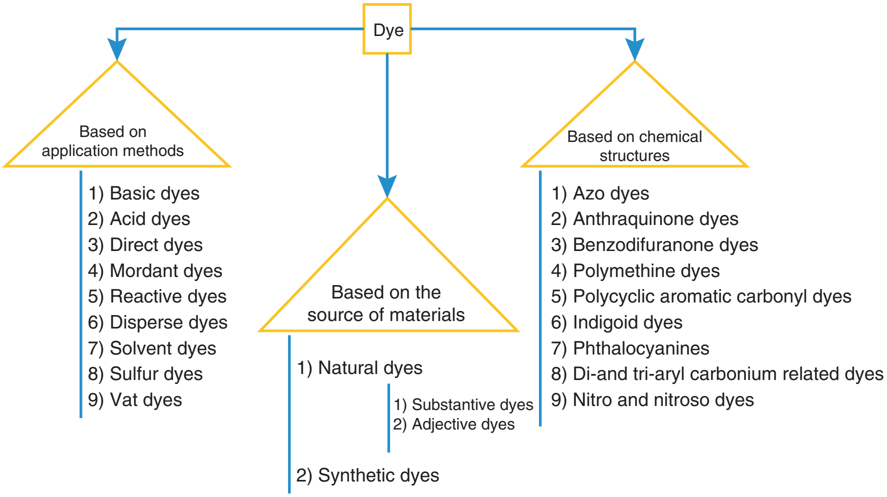

Fig. 15.1 Classification of dyes based on their sources, application methods, and their chemical structures. (Modified after [Sid and EL-Hawary 2019])

   (a) Substantive dyes: These types of dyes are chemically fixed to the fiber and do not require any chemicals are known as substantive dyes.
   (b) Adjective dyes: These types of natural dyes need mordant for making dyes colorfast are referred to as adjective dyes.

(2) Synthetic dyes: Synthetic dyes are mainly obtained from organic and inorganic compounds. These dyes are very popular as they are very cheap and easy to use including wide range of colors (Raval et al. 2017).

Generally, synthetic dyes are categorized into three groups, (1) anionic (acid, reactive, and direct dyes), (2) cationic (basic dyes), and (3) non-ionic (disperse dyes). Table 15.1 represents the classification of dyes based on their different applications.

15.2.3 Toxicity Effect of Dyes to the Environment and Human Health

Large-scale industrial application of synthetic dyestuffs causes intractable troubles in the environment. Due to the high intensity of colors in water, dyes are highly visible to human eye even in a very small concentration that is highly unacceptable on aesthetic grounds (Gupta and Suhas 2009). Apart from the aesthetic issues, the absorption of sunlight by the dyestuffs in the water can have serious environmental concern (Rai et al. 2005). The dyes are very toxic and carcinogenic because of the presence of aromatics, metals, and they block the light penetration and affect the biological metabolism process by upsetting the photosynthetic activity in aquatic life. In various types of microbiological and fish species, dyes are very toxic/teratogenic and mutagenic (Gong et al. 2005; Gupta and Suhas 2009). Additionally, it is also responsible for severe damages to human health including dysfunction of the liver, kidney, brain, and reproductive system. Reactive dyes are highly water-soluble and chemically stabled colored effluent which is a critical issue for the environment. Due to the presence of toxic amines in the water, azo dyes are extremely toxic. Anthraquinone dye is very stable and takes very long time for degradation (Yagub et al. 2014). Both the quantity and quality of effluent from various industries are a matter of concern for the public and governments (Parsa and Negahdar 2012). Since most of the dye compounds have been accounted as toxic, recalcitrant, carcinogenic, mutagenic, and chemically and photo-chemically stable, they are very threatening to human health as well as environment, and as the usage of synthetic dye is increasing so, it becomes a great challenge in the area of research for industrial effluent treatment (Sharma and Kaur 2018). Therefore, much more attention has been paid on effective, economical, and feasible specific methods and technologies

Table 15.1 Classification of dyes based on different application

Dye class	Properties	Application	Toxicity	Chemical class
Basic dyes	Water-soluble; cationic dye; applied in weakly acidic dyebaths	Acrylic fibers, wool, silk, paper, nylons, and polyesters materials	Vomiting, skin irritation, mutations, jaundice, cancer	Diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine, and acridine
Acid dyes	Water-soluble; anionic	Silk, nylon, wool	Carcinogenic (benign and malignant tumors)	Anthraquinone, azo, azine, triphenylmethane, xanthene, nitro and nitroso
Direct dyes	Water-soluble; anionic; applied directly without mordants (or metal-like chromium and copper)	Rayon, cotton, leather, and nylon	Bladder cancer	Oxazines, polyazo, and phthalocyanines
Reactive dyes	Water-soluble; anionic; largest dye class	Cotton, cellulose, nylon and wool	Allergic conjunctivitis; dermatitis	Phthalocyanine, anthraquinone, chlorotriazine, vinyl sulfone
Disperse dyes	Very low solubility in water	Cellulose, nylon, acrylic and cellulose acetate	Carcinogenic, skin irritation	Anthraquinone, azo, nitro, styryl and benzodifuranone
Sulfur dyes	Water-insoluble; colloidal; organic compounds containing sulfur and sodium sulfide	Rayon and cotton	Prone to allergies, tumors and cancers	Indeterminate structures
Vat dyes	Water-insoluble; colloidal; more complex; oldest dyes	Rayon and cotton	–	Indigoids and anthraquinone

Modified after Kaykhaii et al. (2018)

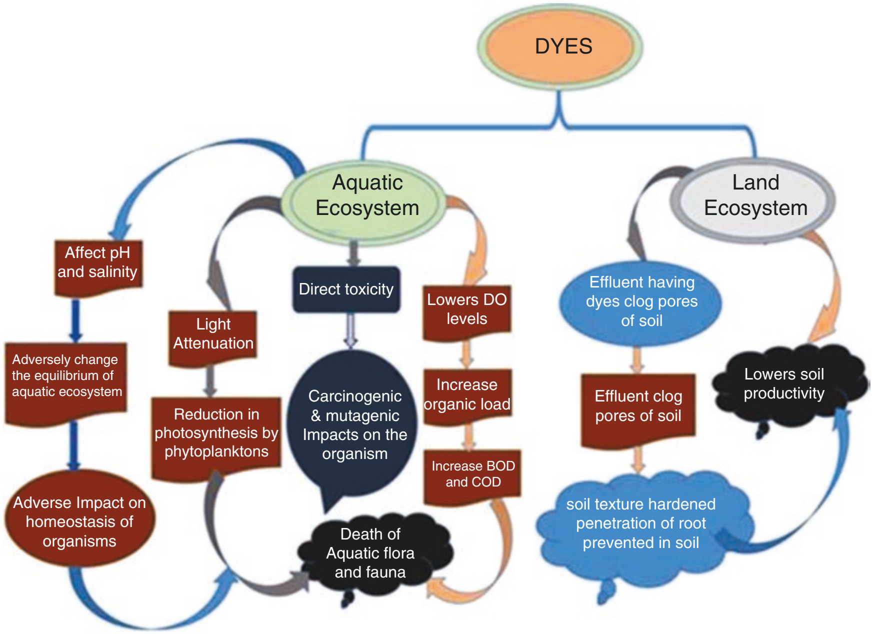

Fig. 15.2 Effects of dyes on aquatic and land ecosystems. In aquatic ecosystem, it lowers the dissolved oxygen level, effects on pH, salinity, and also on light attenuation. In land ecosystem, it clogs the pores of soil and lowers the productivity of soil. (Reprinted with permission of [Springer nature Inc.] from [Chakravarty et al. 2015])

to treat the various kinds of dyes as well as hazardous organic contaminants from wastewaters (Parsa and Negahdar 2012). The effects of dyes on aquatic ecosystem lowers the dissolved oxygen level, effects on pH, salinity, and also on light attenuation, and on land ecosystem, it clogs the pores of soil and lowers the productivity of soil, given in Fig.15.2.

15.3 Dye Removal Techniques

The conventional treatment process for dye removal can be divided as three categories:

1. Primary treatment process: The primary treatment process mainly involves the removal of suspended materials (e.g., pieces of fabrics, yarns, rags, and lint), grits, and oil by using bar screens and fine screens.
2. Secondary treatment process: The secondary treatment process involves the removal of color, oil, and the reduction of biological oxygen demand using microorganisms in aerobic or anaerobic condition.

3. Tertiary treatment process: The tertiary treatment process is the final removal stage of conventional treatment process to make the effluent suitable for intended reuse. In this process, all the pollutants such as suspendeded solids, organic matters, heavy metals, pathogens, which are difficult to remove in secondary treatment process, can be eliminated.

From the last few decades, different technologies have been developed to remove the different types of toxic dyes from the industrial effluents. Those are categorized in three groups: a) physical treatment, b) chemical treatment, and c) biological treatment.

(a) Physical Treatment

Different types of physical processes are applied for the treatment of dyes such as screening, coagulation, precipitation, adsorption, and membrane filtration. Among all, adsorption has been found the best process for the removal of dyes due to its simple design, easy operation, higher efficiency, low costs, and no effect by toxic substances. Membrane fouling and membrane replacement cost are the major restrictions for the membrane filtration (Ruan et al. 2019).

(b) Chemical Treatment

The chemical treatment methods include coagulation-flocculation, oxidation, ozonation, Fenton oxidation, photocatalytic oxidation, irradiation, ion exchange, and electrochemical treatment. These chemical methods are very efficient for dye removal but excessive chemical use causes the difficulty of sludge disposal, very high cost, and also electrical energy is required for these techniques (Ruan et al. 2019).

(c) Biological Method

The biological treatment methods include aerobic treatment, anaerobic treatment, and anaerobic-aerobic treatment where the organic pollutants are converted into harmless and stable substances. Aerobic treatment involves activated sludge, aerobic digestion, trickling filtration, lagoons, ponds, oxidation, and anaerobic treatment involves anaerobic digestion, lagoons, and septic tanks. The conventional treatment methods for dye removal based on physicochemical treatment and biological treatment from wastewater are given in Fig.15.3.

15.3.1 Physicochemical Treatment

Coagulation and flocculation process is an efficient, simple, and cost-effective process widely used for effluent treatment, drinking water treatment, and reduction of chemical oxygen demand (Ruan et al. 2019). The process is performed by destabilization of charged particles dispersed in water by reducing the charge of the surface and the formation of large particle by accumulation. Coagulants mainly used in this

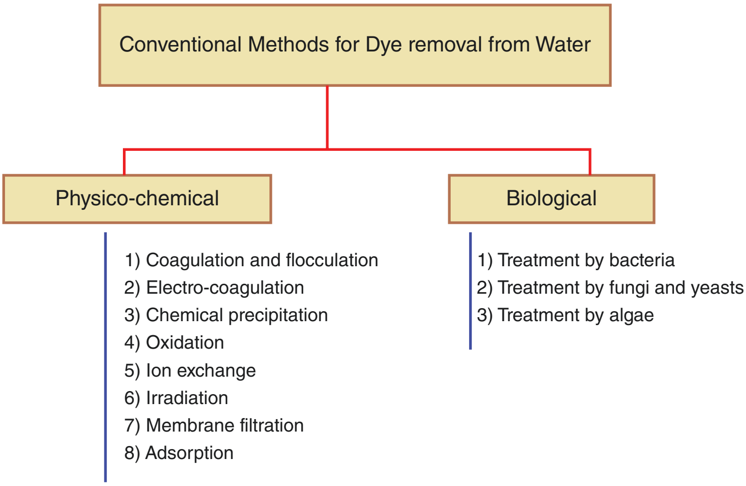

Fig. 15.3 Conventional treatment methods for dye removal from wastewater. The methods are based on physicochemical treatment and biological treatment

process are polymers, metallic salts, alum, clay, aluminum, ferric chloride, and calcium chloride. The major disadvantages in this process are process control, sludge handling, and non-ionic impurities in the effluent (Ruan et al. 2019; Ahmad et al. 2015). Jindal et al. (2016) found 75% removal of dye by using polyaluminium chloride coagulant and ferrous sulfate heptahydrate as flocculants (Jindal et al. 2016).

Electrocoagulation is an alternative and advanced electrochemical treatment. Here, the coagulants are produced inside the reactor by electrolytic oxidation of anode materials, such as aluminum, stainless steel, graphite, carbon, and iron without any addition of chemicals. That species neutralize the suspended particles and agglomerate to form larger particles for settle down. Electrocoagulation is very efficient for dye removal in high pH. But the major disadvantage is that the procedure is very costly for the use in industries (Aleboyeh et al. 2008).

Chemical precipitation is the simplest technique for the industrial effluent treatment in which different chemicals are used such as hydroxides, sulfides, and carbonates which react with dissolved molecules of dyes for the formation of insoluble particles to settle down. After that, to separate the sludge the effluent can be decanted (Ahmad et al. 2015).

Oxidation is an important wastewater treatment method using different oxidizing agents. Mainly two types of oxidations are done like the chemical oxidation process and ultraviolet-assisted advanced oxidation process using chlorine, ozone, hydrogen peroxide, or Fenton's reagent for the treatment of wastewater (Gupta and Suhas 2009). *Chemical oxidation* removes the dye from wastewater using chlorine, ozone, or hydrogen peroxide by formation of strong non-selective hydroxyl radicals, which break down the conjugated double bonds such as complex aromatic rings of dyes resulting in smaller molecules formation that are removed from industrial effluent. Chlorine is defined as a strong oxidizing agent used as sodium hypochlorite and calcium hypochlorite mainly used to remove efficiently direct, acid, reactive, and metal complex dyes, which are water-soluble, but water-insoluble dyes, such as vat, and disperse dye, are difficult to remove in this process (Gupta and Suhas 2009) *Advanced oxidation process* has become a popular oxidation technique for the removing dyes from industrial effluents. This is basically the process where above one simultaneous oxidation processes are involved because the single oxidation process is insufficient to remove the total dyes at a time (Holkar et al. 2016). Different types of advanced oxidation processes are developed using different combination of oxidation process such as combination of ozone, hydrogen peroxide, ultraviolet radiation, titanium dioxide, ultrasound, and electron-beam irradiation. Among all, ozone/hydrogen peroxide, hydrogen peroxide/ultraviolet, and ozone/ultraviolet are the promising methods to oxidize the dyes in effluent. The advanced oxidation process has the potential to remove the dyes, but it is quite expensive process in industry (Gupta and Suhas 2009; Holkar et al. 2016). *Hydrogen peroxide* is a strong oxidizing as well as powerful bleaching agent used for paper bleaching and making the peroxidase enzymes for dye decolorization (Gupta and Suhas 2009). Kim et al. (2004) studied 99% dye removal by using Fenton's oxidation process at optimum condition (Kim et al. 2004). *Ozone* has the powerful oxidizing property that can easily break down the aromatic ring in organic dyes with their cleavage of conjugated double bonds and decomposes the pollutants. Ozone may react with dye molecules directly or indirectly. Even at low pH, ozone efficiently reacts with the dye by direct reactions. The disadvantages are short half-life, i.e., 20 min, quite expensive, and produce toxic by-products (Ahmad et al. 2015). *Photo-chemical oxidation* treatment, the presence of hydrogen peroxide increases the efficiency of the treatment. The ultraviolet-assisted hydrogen peroxide breaks the dye molecules into smaller parts of organic particles or the ultimate products like carbon dioxide and water and the other inorganic oxides, etc. The efficiency depends on the pH, ultraviolet radiation, and the structure of dyes. *Electrochemical oxidation* has attracted great attention in the wastewater treatment under low temperature and moderate pH with complete decomposition of dyes. In this process the dye molecules decompose by non-soluble anodes such as conducting polymer and iron or by electro-coagulation using consumable materials either by direct or indirect oxidation process. The main disadvantages of this process are very costly (Gupta and Suhas 2009). Babu et al. (2011) studied that the methyl red azo dye removal by electro-oxidation process was 81% (Babu et al. 2011).

Ion exchange process is the most simple method in dye treatment from industrial effluent (Gupta and Suhas 2009). In this process, the dyes are removed by the strong interchange between the charged molecules of dyes and the ion exchange resins. Resins can be classified as four groups: anion exchange membrane, cation exchange membrane, cross-linkage membrane, and other ion exchange membrane (Ruan et al. 2019). Among all, cation exchangers and anion exchangers are mostly used for dye removal (Ahmad et al. 2015). Cation exchange membrane used the negative charged groups that helps to pass the cations but prevents anions to pass. The positively charged particles are used in anion exchange membrane that allows passing anions but also rejecting to pass the cations. The major drawbacks are the process is very expensive and also ineffective for disperse dye removal (Ruan et al. 2019).

Irradiation is very effective and simple technique for dye removal from wastewater by using radiations obtained from monochromatic ultraviolent lamp. This method requires a constant and sufficient supply of oxygen because of the requirement of huge quantity of dissolved oxygen to destroy the organic dye effectively by irradiation. This is a very cheap process and the dyes can be oxidized easily (Robinson et al. 2001).

Membrane filtration, an advanced technology used for color, salinity, and chemical oxygen demand removal from industrial effluent. Here, the wastewater passes through the membrane, and the large size solutes are trapped in the membrane pores. Based on the pore size, membrane filtration can be classified as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (Gupta and Suhas 2009; Ahmad et al. 2015). Among all microfiltration is less efficient for waste water treatment due to its large pore size. But ultrafiltration and nanofiltration are very effective for eliminating all kind of dye molecules (Gupta and Suhas 2009). On the other hand, reverse osmosis is also very efficient in desalting and removing wide range of dye wastes. The disadvantages are high cost, membrane fouling, and short membrane life, and it cannot be operated at above room temperature (Gupta and Suhas 2009; Holkar et al. 2016). Mo et al. (2008) studied the dye separation using nanofiltration polyamide membrane was almost 100% (Mo et al. 2008).

Adsorption is the most successful and established technology as it offers low cost, complete removal of dyes, and non-toxic by-product formation (Ruan et al. 2019). Depending on the attachment of adsorbate on the adsorbent surface, adsorption processes are categorized as physical sorption and chemical sorption. In physical adsorption, the adsorbate is attached on adsorbents by weak physical forces like van der Waals forces, polarity, hydrogen bonding, hydrophobicity, dipole interactions, static interactions, and π–π interactions. In chemical adsorption, adsorbates are attached on adsorbent surface by the chemically bound of electrons exchange. The adsorbents generally used in this process are activated carbon, low cost adsorbent, nanoparticle, and other types of adsorbent (Gupta and Suhas 2009; Robinson et al. 2001). Zhuang et al. (2009) studied high adsorption rates above 99.9% at low concentration dyes (Zhuang et al. 2009).

15.3.2 Biological Treatment

Biological treatment is one of the most familiar and widespread technology applied for dye treatment with low cost and eco-friendly nature as it requires no chemical addition and less amount of energy (Punzi et al. 2015; Ahmad et al. 2015). The principle of this treatment is that the biodegradable wastes are converted into more simple and harmless species by using different type of microorganisms. In this process the removal of dye is classified into three groups such as aerobic process (in presence of oxygen), anaerobic process (without oxygen), and coupled anaerobic–aerobic process (Rai et al. 2005; Gupta and Suhas 2009). In aerobic process the final products are water, biomass, and carbon dioxide, while in anaerobic process the products are methane, biomass, and carbon dioxide (Ahmad et al. 2015). Biological treatment offers considerable benefits such as (a) low cost, (b) eco-friendly, and (c) less and non-toxic sludge formation (Gupta and Suhas 2009; Holkar et al. 2016). According to the use of different kind of microorganism for the treatment of dyes, the treatment process is divided in to three groups such as treatment by bacteria, treatment by fungi/yeast, and treatment by algae. *Bacteria* are very popular microorganism for easy cultivation and rapid growing in dye treatment. In this process mainly the azo dyes are degraded under aerobic, anaerobic, or facultative anaerobic conditions (Ruan et al. 2019). Comparing with the anaerobic and facultative process, aerobic processes are responsible for the production of sludge (Holkar et al. 2016). In this process, bacteria degrades the azo dyes by reducing the azo bonds with the help of azo-reductase enzymes at anaerobic environment (Ruan et al. 2019; Holkar et al. 2016). Holkar et al. (2014) studied the anthraquinone-based reactive blue 19 degradation up to 90% in 1 day, and Wang et al. 2009 found anthraquinone-based reactive black 5 up to 92% degradation under anaerobic condition within 120 h (Holkar et al. 2014; Wang et al. 2009). Babu et al. (2011) experimented the removal of methyl red azo dye by biological treatment using bacteria with 95% removal (Babu et al. 2011). *Fungi and yeasts* can be an attractive alternative for dyes removal**,** due to their sustainability at any adverse condition and rapid bacterial growth even at very low pH. The intra- and extracellular enzymes of fungi and yeast help in metabolic activity to adjust in any environmental situation. These enzymes degrade various types of dyes from the wastewater. These enzymes are manganese peroxidase, lignin peroxidase, and laccase. White-rot fungal is the most popular fungi used for azo dye degradation. White-rot fungi have four popular genera such as *Bjerkandera*, *Trametes*, *Phanerochaete*, and *Pleurotus*. But, the major limitations by fungi treatments are high hydraulic retention time for dye removal and the fungi preservation in bioreactor (Ruan et al. 2019; Holkar et al. 2016). There is not so much research works on dye removal by yeast treatment but in some cases, it is found very effective. Yang et al. (2003) found the complete removal of reactive black 5 by using two fungi, *Penicillium geastrivorus* and *Umbelopsis isabelline*, within 16–48 h (Yang et al. 2003). Kwasniewska (1985) experimented that for the removal of crystal violet, *Rhodotorula rubra* is found very useful (Kwasniewska 1985). *Algae* are very successful application for the treatment of dye presence in wastewater. There are three different mechanisms for the dye degradation by algae. Those are (1) dye consumption for algae growth, (2) conversion of dyes to various intermediates or water and carbon dioxide, and (3) adsorption of chromophores on algae. They are capable of both biodegradation as well as biosorption of dyes. Meng et al. (2014) found that the azo-based acid red 27 dye removal by *Shewanella algae* with high sodium chloride concentration and different humic acids or quinones results in less toxic aromatic amines (Meng et al. 2014). Khataee et al. (2013) studied the degradation of azo-based color index basic red 46 by using Enteromorpha species algae that eliminate azo dyes significantly. For biosorption, algal waste also

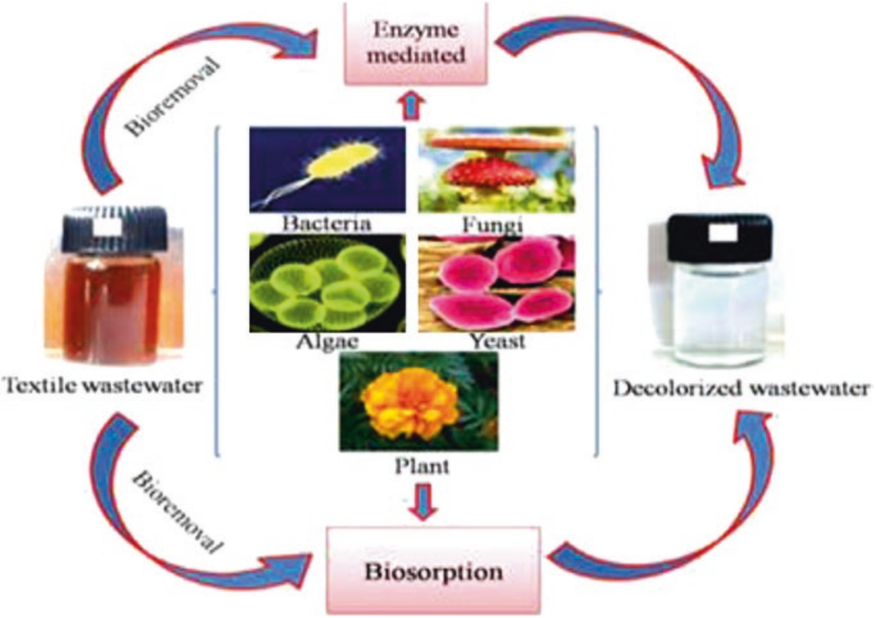

Fig. 15.4 Biological methods for the treatment of textile wastewater using bacteria, algae, fungi, and yeast by biosorption and biodegradation. (Reprinted with permission of [Springer nature Inc.] from [Singh et al. 2019])

can be an alternative for activated carbon (Khataee et al. 2013). The biological methods for the treatment of textile wastewater using bacteria, algae, fungi, and yeast by biosorption and biodegradation are given in Fig. 15.4.

15.4 Dye Removal by Using Low-Cost Adsorbent

Adsorption is very successful in removing cationic, acid, mordant dyes, and lesser extent of direct, dispersed, reactive, and vat dyes (Robinson et al. 2001). But the treatment cost can be a little bit high due to the high cost of the adsorbents. Hence, various researches have been done to find out effective alternative cheap adsorbents for removing wide variety of dyes. A low-cost adsorbent must be plentiful in nature and waste or by-product from industries or agricultures which cost is less and can be applied as adsorbents after some minimal treatment. A low-cost adsorbent should be (i) effective to remove the pollutants, (ii) high rate and capacity of adsorption, and (iii) high selectivity at different concentration (De Gisi et al. 2016). The low-cost adsorbents can be classified into four categories such as (1) natural materials (2), industrial and agricultural waste materials or by-products, (3) synthesized products, and (4) biosorbents.

15.4.1 Natural Materials

Natural materials are used as cheap adsorbents due to their abundant existence in nature. The materials used as low-cost adsorbents are:

Natural coal can easily eliminate rhodamine B and methylene blue (basic dyes) and sandola rhodine (acidic dye). Prior to the use as adsorbent, coal is prepared by sulfonating and heating in water bath (Mittal and Venkobachar 2014). Different types of coal are used as adsorbents such as lignite coal, bituminous coal, and char fines. Because of the existence of acidic groups such as carboxyl and hydroxyl in coal, it has chemisorption mechanism. As the coal is not a pure material, various sorption properties are also found due to its various surface properties. Its sorption properties are determined after some physicochemical pretreatment process (Karaca 2006).

Clay is naturally obtained adsorbent that has been widely used for dye removal. It is a mineral with the combination of silica and alumina with bound water. Due to their availability, low-cost, higher capacity of adsorption, and good mechanical and chemical strength, with good capacity of ion exchange, clay is very effective adsorbent for the treatment of wastewater. Clay particles have strong affinity to cations and anions because of its surface area consisting of exchangeable ions. Various kind of clay is used for dye removal present in aqueous medium such as kaolin clay, bentonite clay, and Algerian clay (Sharma and Kaur 2018; Raval et al. 2017). Nandi et al. (2009) used low cost kaolin clay for rhodamine-B, malachite green, and safranin-O dyes removal with 5%, 7%, and 2% (Nandi et al. 2009). Anirudhan and Ramachandran (2015) used bentonite clay as low-cost adsorbent and found the adsorption efficiency of methylene blue and rhodamine-B was 99.9% and 83%, respectively (Anirudhan and Ramachandran 2015).

Surfactant-modified clay is actually the naturally obtained montmorillonite clay modified with the cationic surfactant such as hexadecylpyridinium chloride and hexadecyltrimethyl ammonium bromide. This product can be used as adsorbent and efficiently remove dyes from industrial wastewater. It has been found that the removal efficiency of malachite green and methylene blue by using this product is 30% and 28% (Sharma and Kaur 2018).

Surfactant-modified alumina is also modified with sodium dodecyl sulfate for better efficiency in the treatment of wastewater. It effectively removes crystal violet dye with 99% efficiency (Adak et al. 2005).

Siliceous materials are actually sedimentary rocks which consist with silica as major constituent. Diatomite is one of the most convenient siliceous rocks in the form of diatoms, radiolarians, and different types of sponges. Silica, perlite, alunite, and glass fibers are the natural siliceous materials with low cost and easily available, mainly used as adsorbent in removing malachite green for the treatment of wastewater (Raval et al. 2017). Andrzejewska et al. (2007) studied by using aminosilane modified silica for removing anionic reactive color index reactive blue 19 dye with 90% removal efficiency (Andrzejewska et al. 2007).

Peat is naturally available porous and complex adsorbent mainly used for removing dye and organic pollutant. The removal efficiency of rhodamine-B dye by using this adsorbent has been reported 8.6% in studies (Sharma and Kaur 2018). Vijayaraghavan et al. (2016) used coco-peat for removing crystal violet and malachite green from aqueous medium. It was found that at pH 7 the dyes are effectively removed in 60 min (Vijayaraghavan et al. 2016).

Zeolites are highly porous crystalline hydrated aluminosilicates occupied by water, alkali, and alkaline earth cations. The structure of zeolite is described based on their geometry, size, and pore space connectivity. At present natural zeolite is used as adsorbent by many researchers for wastewater treatment because it comprises with the both sorption properties as well as combination of molecular sieve and ion exchange properties (Raval et al. 2017). Han et al. (2010) experimented on natural zeolite for the removal of malachite green from industrial effluent, and the regeneration was found 85.8% (Han et al. 2010). Syafalni et al. (2014) studied the adsorption capacity of natural zeolite, anionic-cationic surfactant-modified zeolite, and cationic surfactant-modified zeolite for dye treatment. They reported an efficient removal of dye such as 94% for natural zeolite, 94% for anionic-cationic surfactant-modified zeolite, and 90% for cationic surfactant-modified zeolite (Syafalni et al. 2014).

15.4.2 Industrial and Agricultural Wastes or By-Products

The utilization of industrial and agricultural wastes or by-products plays a significant role for wastewater treatment and in national economy. Although they have zero economic value and also have problem with disposal. In such case, wastes from agriculture and industrial section can be used as cheap adsorbent which is inexpensive and easily available in large quantities. Due to their physicochemical properties, they can be accounted as a very good adsorbent and has the potential for dye removal from industrial effluent. Those can replace the commercial activated carbon also. Industrial waste materials such as red mud, fly ash, metal hydroxide sludge are classified as low-cost adsorbents for remediation of pollutants such as dyes (Raval et al. 2017). Several agricultural wastes have been studied for dye removal at different operating conditions. Different kinds of agricultural waste-based adsorbents for removing water pollutants from industrial wastewater are given in Fig. 15.5. The agricultural wastes includes orange peel (Arami et al. 2005), coniferous pinus bark powder (Ahmad 2009)**,** wheat husk (Gupta et al. 2007a), activated palm ash (Hameed et al. 2007), cattail root (Hu et al. 2010), neem sawdust (Khattri and Singh 2009), peanut husk (Khaleque et al. 2018), Jujuba seeds (Reddy et al. 2012), and coir pith activated carbon (Santhy and Selvapathy 2006). Activated carbon also can be prepared from many others agricultural waste such as coconut tree sawdust, banana pith, silk cotton hull, maize cob, and sago waste for removing dye from industrial wastewater (Kavipriya et al. 2002). Different types of adsorbents using agricultural wastes have been discussed in Table 15.2.

Red mud is an aluminum industry waste used as adsorbent for dye removal (Sharma and Kaur 2018). At the time of alumina production, red mud is formed

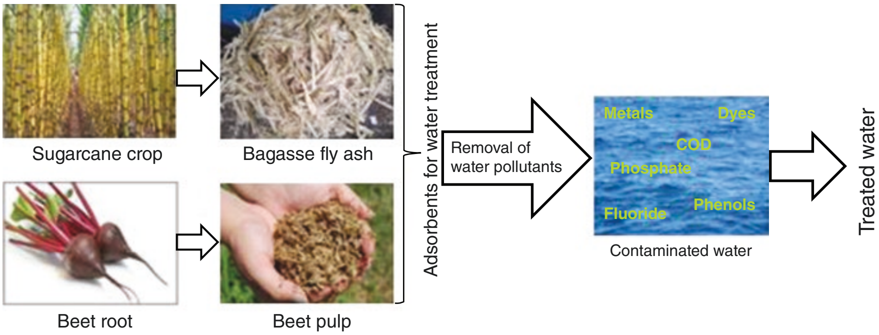

Fig. 15.5 Different kinds of agricultural waste-based adsorbents for removing water pollutants from industrial wastewater. (Reprinted with permission of [Journal of Molecular Liquids Inc.] from [Anastopoulos et al. 2017])

during caustic digestion of bauxite. Gupta et al. (2007a, b) successfully remove rhodamine B, methylene blue, and fast green with the percentage removal of 92.5, 75.0, and 94.0 from industrial effluent by using red mud at varying pH, initial adsorbate concentration, time, adsorbent dose, temperature, and adsorbent particle size (Gupta et al. 2007b). Bhatnagar et al. (2011) also found red mud as an effective adsorbent with significant potential of adsorption for dye removal (Bhatnagar et al. 2011).

Fly ash, the other industrial by-product, is very popular and effective technique used as adsorbent for dye removal. Bagasse fly ash from sugar industry is very cheap without containing any toxic metal (Sharma and Kaur 2018). Gupta et al. (2000) used adsorbent using bagasse fly ash for removing basic dyes such as methylene blue and rhodamine B. The adsorption capacity was very high and correlated with both Freundlich and Langmuir models (Gupta et al. 2000). Mohan et al. (2002) derived activated carbon by using fly ash from thermal power plant and used for dye removal from synthetic wastewater. The product successfully removed the crystal violet and rosaniline hydrochloride from the wastewater. The adsorption capacities was very good for both the dyes (Mohan et al. 2002).

Metal hydroxide sludge from different industries is used as cheap adsorbent for dye removal from industrial wastewater. Metal hydroxide sludge mainly contains the hydroxide ions of metals and its salts (Sharma and Kaur 2018). Netpradit et al. (2003) experimented on the capacity of adsorption for the removal of azo dyes from industrial wastewater. They experimented on anionic dyes and found the adsorption is more than 90% for greater charge value of dyes. Large amount and smaller size of particles results in faster the treatment process (Netpradit et al. 2003).

Saw dust is another by-product waste from timber industry which can be used for the dye removal as low-cost adsorbent. Garg et al. (2003) experimented on malachite green removal by using sawdust treated with formaldehyde and sulfuric acid. The product is very effective, and they also found that the adsorption efficiency is much higher in sulfuric acid-treated sawdust than formaldehyde-treated sawdust (Garg et al. 2003).

Table 15.2 Different types of adsorbents using agricultural wastes

Sl No	Adsorbent	Dye	Remarks	References
1	Coniferous pinus bark powder	Crystal violet (basic dye)	Adsorption capacity increases from 80% to 99.5% at pH 2–8.	Ahmad (2009)
2	Orange peel	Direct red 23 and direct red 80	Adsorption efficiency was 92% for direct red 23 and 91% for direct red 80 at 8 and 4 g/l concentration and maximum desorption at pH 2 was 97.7% for direct red 23 and 93% for direct red 80.	Arami et al. (2005)
3	Rice husk	Methylene blue and Congo red	Removal efficiency was 99.939% for methylene blue and 98.835% for Congo red dye.	Chowdhury et al. (2009)
4	Peanut hull particle	Methylene blue, brilliant cresyl blue, and neutral red	Removal efficiency increases for methylene blue from 34.75 to 89.51%, 36.82 to 96.62% for neutral red, and 79.14 to 96.47% for brilliant cresyl blue at 0.5–2.0 g/l dose.	Gong et al. (2005)
5	Activated palm ash	Acid green 25	Based on Langmuir model, the monolayer adsorption capacity around 123.4, 156.3, and 181.8 mg/g at temperature 30, 40, and 50 °C.	Hameed et al. (2007)
6	Cattail root	Congo red	The maximum adsorption capacities were 38.79, 34.59, and 30.61mgg^{-1} at temperature of 20, 30, and 40 °C.	Hu et al. (2010)
7	Peanut husk	Sunfix red (reactive dye)	At pH 7, the removal efficiency was 98% in 150 min.	Khaleque et al. (2018)
8	Neem sawdust	Malachite green	Abundantly available and also inexpensive. Its binding capacity for basic dye is also high. The maximum capacity for monolayer adsorption was 4.354mgg^{-1}	Khattri and Singh (2009)
9	Coir pith	Reactive dyes	Maximum amount of dye is removed at acidic pH. Highest was reactive orange followed by reactive red and reactive blue was lowest.	Santhy and Selvapathy (2006)
10	Jujuba seeds	Congo red	Maximum color removal at pH2. Fitted with the Langmuir model with maximum adsorption capacity of 55.56 mg g^{-1}	Somasekhara Reddy et al. (2012)

15.4.3 Biosorbents

Biosorption is defined as the adsorption process in which the concentration of biological materials, including bacterial, fungi, yeast, and biopolymers, is accumulated and used as inexpensive adsorbents that are used in removing dyes from industrial effluents. They are mainly used to remove basic dye malachite green from aqueous solution.

Biomass can be defined as the biological material that can be derived from both vegetables and animals as living or recently dead organisms. It can be used as adsorbent and efficiently removes the malachite green from wastewater. The advantages of this process are (1) high efficiency, (2) low cost, (3) easily available, (4) minimal biological and chemical sludge formation, (5) regeneration of biosorbent, and (6) no additional requirement of nutrient. Different types of living or dead biomass can be used as adsorbent such as white-rot fungi, submerged aquatic plant, brown marine algae, freshwater algae, and immobilized baker's yeast cells (Raval et al. 2017). Namasivayam et al. (2001) experimented on basic dye (e.g., methylene blue, rhodamine B) and acid dye (e.g., acid brilliant blue, acid violet) removal using coir pith biomass waste as adsorbent. The capacities of adsorption was 16.67, 1.65, and 203.25 mg g^{-1} for acid brilliant blue, acid violet, and rhodamine B dye, respectively (Namasivayam et al. 2001). Annadurai et al. (2003) studied the synthetic dye (Rhodamine 6G) removal present in industrial wastewater by using waste biological sludge. The waste biological sludge mainly contains protozoa and bacteria. The bacteria cell wall comprises with numerous organic compounds such as chitin, amino acids, lipids, acidic polysaccharides, and other cellular compounds that successfully adsorb the both dyes and heavy metal ions (Annadurai et al. 2003). Sirianuntapiboon and Srisornsak (2007) experimented on the removal of disperse dyes by using both the granular activated carbon and bio-sludge in which bio-sludge is found more effective in removing disperse dye as well as organic matter. The adsorption capacity is increased by 30% by using bio-sludge, and it can be washed with 0.1 N sodium hydroxide solution for reuse also (Sirianuntapiboon and Srisornsak 2007). Lata et al. (2008) also experimented on rhodamine-B dye removal by using the adsorbents prepared from parthenium biomass treated with formaldehyde and parthenium carbon treated with phosphoric acid. The result shows that the adsorption efficiency of parthenium biomass was 63.16%, and parthenium carbon was 85.95%. The removal of dye largely depends on the reaction time, adsorbent dose and the initial concentration of dye (Lata et al. 2008). Reusing the activated sludge waste is very interesting approach as resource utilization. But it suffers some drawbacks such as (1) emission of bad odor during storage and (2) changing the biomass quality continuously. However, sludge has some disadvantages like continuous the sludge change and of odor emission at the time of storage. They found the product is very efficient in removing rhodamine 6G dye successfully (Annadurai et al. 2003).

Biopolymers are the compounds with large molecular weight derived from living organisms. Among all, chitin and chitosan are two most popular polysaccharide, which are biocompatible, biodegradable, and easily available biopolymers with less chemical versatility. Generally, chitin is found in the exoskeletons of sea creatures such as prawns, lobster, shrimp, and crabs and also extracted from the fungi cell wall, whereas chitosan was produced by the boiling of chitin in potassium hydroxide. Both the chitin and chitosan are used as efficient adsorbents for metal as well as dye removal. But, because of the high affinity, chitosan has more potential to adsorb pollutant including dye and heavy metals (Vakili et al. 2014). These materials are used at the different shape, like bead types, flake types, fibers, or gels. Because of their robust crystal structure, it has been modified by using different cross-linking agents and surfactants to increase the adsorption efficiency and chemical versatility by controlling their undesirable characteristic (Raval et al. 2017). Rahman and Akter (2016) prepared the chitin from shrimp shell by using different chemical process involving demineralization, deproteinization, and decolorization for the treatment of dye. The result shows the removal the efficiency almost 96% at pH 5 in 60 min of contact time (Rahman and Akter 2016). However, the major drawbacks like low mechanical strength and solubility in acid and low surface area limited the performance in adsorption process (Vakili et al. 2014). Tang et al. 2014 used chitin hydrogel for removing malachite green effectively with maximum adsorption capacity 26.88 mg/g (Tang et al. 2014).

15.4.4 Synthesized Novel Products

Finally, this paragraph describes about the novel innovative materials, those are developed from various industrial and agricultural waste for the treatment of pollutant as low-cost adsorbents. Because of the high cost of commercial activated carbon, activated carbon can be developed from various agricultural wastes materials, such as coconut fibers, rice bran and husk, pecan nut shell, eucalyptus wood, waste coffee grounds, and fertilizer waste. Zeolite can be successfully synthesized by using fly ash, diatomite and kaolin. Diatomite and fly ash can be converted into zeolite P, while kaolin can be converted into a mixture of zeolites X and A (Hernandez-Ramirez and Holmes 2008). Rajeshwarisivaraj et al. (2001) synthesized activated carbon derived from cassava peel from food industry. The activated carbon using phosphoric acid activation was very efficient in removing almost 100% of all dye from industrial wastewater (Rajeshwarisivaraj et al. 2001). Kavipriya et al. (2002) prepared activated carbon from the agricultural solid wastes such as coconut tree sawdust, silk cotton hull, maize cob, sago waste, and banana pith for the removal of dye from industrial wastewater and found effective removal of methylene blue 93.35%, rhodamine-B 82.65%, and Congo red 76.55% in 24 h (Kavipriya et al. 2002). Singh et al. (2003) using coconut shell fibers also developed activated carbon for the removing methyl orange and methylene blue. The removal efficiency was 100% for both of the dyes at low concentration (Singh et al. 2003). Wang et al. (2005) used unburned carbon from fly ash as adsorbents for the removal of methylene blue from aqueous effluent. They studied that the unburned carbon has higher capacity of adsorption than natural zeolite and fly ash. The adsorption capacity of methylene blue for fly ash was 2.5×10^{-4} mol/g, whereas the adsorption capacity for natural zeolite and fly ash was 5×10^{-5} and 2×10^{-5} mol/g (Wang et al. 2005). Reddy et al. (2013) developed activated carbon from biowaste materials like rice husk and peanut shell using different physicochemical activation methods. It has been shown that developed activated carbon effectively removes methylene blue from aqueous solution. The hydrogen peroxide treated rice husk had the best adsorption capacity for the presence of acidic groups on surface (Reddy et al. 2013). Auta and Hameed (2014) synthesized modified ball clay with chitosan for methylene blue treatment. The composite material had higher adsorption capacity (above 50%) than modified ball clay after five regeneration cycles. Modified ball clay with chitosan has the potential for removing cationic dye (Auta and Hameed 2014). Hadi et al. (2015) reviewed that porous activated carbon can be prepared from sludge (carbon-rich material) by chemical activation using different activating agents (Hadi et al. 2015).

Li et al. (2016) prepared porous carbon by carbonization of pomelo peel followed by potassium hydroxide for removal of methyl orange. They found the adsorption capacity was 680.2 mg/g (Li et al. 2016). Fan et al. (2017) developed biochar from municipal sludge for removing methylene blue from industrial effluent. They found the methylene blue removal reaches 98% at optimum conditions (Fan et al. 2017). Conversion of sludge to activated carbon by different activation process for the remediation of water pollutant is given in Fig. 15.6. Sivalingam and Sen (2018) synthesized a microporous zeolite X as low-cost adsorbent from coal fly ash by modified hydrothermal method. The results showed the maximum adsorption were 99.62% for crystal violet by using microporous zeolite X whereas 82.42% by using coal fly ash and 96.23% by using commercial zeolite X (Sivalingam and Sen 2018). Mo et al. (2018) found polysaccharides, starch, and cyclodextrins together, reacting with hydroxyl groups, can be used for dye removal from aqueous solution. The cross-linked cyclodextrins polymer comprises with dual characteristic of hydrophilic and hydrophobic (Mo et al. 2018).

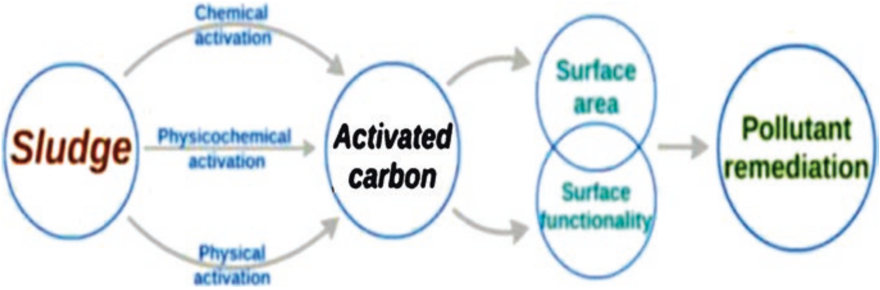

Fig. 15.6 Conversion of sludge to activated carbon by different activation process for the remediation of water pollutant. (Reprinted with permission of [Chemical Engineering Journal Inc.] from [Hadi et al. 2015])

15.5 Conclusion

In this book chapter, it has been revealed that the dye production and utilization has been largely expended in last few decades. So, the dye present in industrial wastewater is a serious threat to environment and human health. The dye can be removed by using various dye treatment processes such as physical, chemical, and biological treatment. Here, the chemical treatment is very expensive and the biological treatment is limited due to the large hydraulic retention time for complete removal of dyes. Adsorption could be the best choice for dye removal due to its low cost and high removal efficiency. But the major limitation in adsorption process is the use of high-cost adsorbent as activated carbon which limited its uses despite of their wide applicability and high adsorption efficiency. Their regeneration is also very costly with the loss of adsorbent as well as efficiency. Easily convenient, inexpensive, and effective materials could replace the commercially available high-cost activated carbon. Therefore, the book chapter has presented a wide variety of low-cost adsorbents for dye separation from industrial effluent. Those are obtained from various sources such as abundant natural resources, using various industrial and agricultural waste materials or by-products and biosorbents and also synthesizing new product using inexpensive materials for dye removal. The low-cost adsorbents have many advantages like they are obtained from the waste materials that have zero economic value and also disposal problem. The natural resources have been also used without or little pretreatment. The low-cost adsorbents are found very promising and also very effective in removing various types of dye. Certain low-cost synthesized adsorbents have excellent capability of dye removal than commercial activated carbon.

Still, the adsorption process is not enlarged fully at pilot as well as industrial scales. Therefore, much work is needed (a) for the prediction of the adsorption performance under some operating conditions, (b) for better perception on adsorption mechanism, (c) to develop more low-cost adsorbents with high efficiency, and (d) for the use of low-cost adsorbents in dye removal at pilot and industrial scales.

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Chapter 16
Hybrid Adsorbents for Dye Removal from Wastewater

Rozita M. Moattari and Toraj Mohammadi

Contents

Abstract The presence of dyes in effluents and wastewaters due to industrial activities has caused serious and critical problems for the public health and the environment. Various technologies have been introduced to remove dyes from wastewater. Among these technologies, the adsorption processes as a promising solution for the removal of dye from wastewater has attracted the attention of researchers and the industrial community. The performance of the adsorption process largely depends on the properties of the adsorbent used. Therefore, the development of novel adsorbents that can exhibit high adsorption capacity of the dye is an urgent need. In the

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meantime, the advent of hybrid adsorbents has raised hopes for a solution to the problem of the dye-containing effluents. This chapter first deals with dyeing materials, their types, sources of release, and their environmental effects and then focuses on different aspects of hybrid adsorbents such as synthesis methods and their applications in the removal of different types of dyes.

Keywords Dye · Adsorption · Hybrid · Removal · Wastewater treatment

16.1 Introduction

Water pollution is a serious public health and a worldwide environmental concern, and so much research has been conducted to find promising solutions (Anastopoulos et al. 2018). The most important causes of water pollution are mining activities, industrial waste, sewage and wastewater, fertilizers and pesticides, urban development, and radioactive wastes (Crini and Lichtfouse 2019). The environmental regulations on industrial wastewater, in particular in developed countries, become stricter and mandate wastewater treatment before being released into the environment (Crini and Lichtfouse 2019). Reducing the environmental impacts of effluents to acceptable levels is the first and foremost concern of the modern world that has increased the demand for pollutant removal technologies (Pereira and Alves 2012).

Dyes are one of the most important water pollutants in the effluent and wastewater of various industries (Angın et al. 2013). Dyes with a large coloring capacity play an important role in the leather, textile, plastic, food, paint, and paper industries. It is estimated that about 100,000 dyes and pigments are available today in the market and that around 7×10^5 tons of synthetic dyes are manufactured throughout the world each year for coloring purposes (Khan et al. 2016; Zubair et al. 2017a). The wastewater containing dyes poses serious environmental hazards (Iqbal 2016). Therefore, removing dyes from the wastewater is a vital step that needs to be addressed by the industrial communities. One of the most promising measures is the use of adsorption processes to remove dyes.

Due to their improved structural chemistry, hybrid adsorbents exhibit superior adsorption capacity over dyes. The development of nanostructured adsorbents due to their high specific surface area, availability of surface active sites, and high stability and regeneration capacities have led to significant advances in adsorption processes (Singh et al. 2018). Nevertheless, selecting the appropriate adsorbents and operating conditions is a thoughtful measure to achieve maximum adsorption efficiency. Researchers are still seeking new methods to produce new adsorbents with high adsorption capacities for an extent range of pollutants and excellent regeneration characteristics (Zafar et al. 2018). This chapter aims to explore different aspects of hybrid adsorbents in dye removal.

16.2 Dyes

16.2.1 Definition

Dyes are generally used as additives in the production of colored materials such as colored papers, colored fabrics, and so on. Due to their highly conjugated structures, the dyes can absorb the visible light. A dye consists of two main parts (for example, refer to Fig. 16.1) (Walger et al. 2018):

1. Chromophore (or core of the dye): A part of dye that colorizes the dye. But it cannot have color itself, or if it does, it has minor color.
2. Auxochrome: chemical groups (hydroxyl, amine, carboxyl or sulfonic) that are added to chromophore and provide multiple properties of the dye such as charge, solubility, etc. and change the color as well as the color intensity.

16.2.2 Types of Dyes

Dyes are fundamentally colored organic substances with very complex chemical structures (Yagub et al. 2014). Natural dyes are usually prepared on small scales from natural sources such as plants or insects (Kant 2011). However, the variety of natural dyes is limited, and also their color fades away when exposed to sunlight and rinsing (Solís et al. 2012). Synthetic dyes are produced on large scales as demand for dyes increases. A wide range of synthetic dyes for a great number of applications was invented by W.H. Perkins in 1856 (Kant 2011). The invention settled the problem of natural dyes, but there were new issues in which the dye-consuming industries released their effluent into the environment without decolorizing. This has had disastrous consequences because dye-contaminated water sources imposed a serious menace to ecosystem (Gholami-Borujeni et al. 2011). Although at first glance it seems that reusing natural dyes is a more appropriate option, it was realized that this

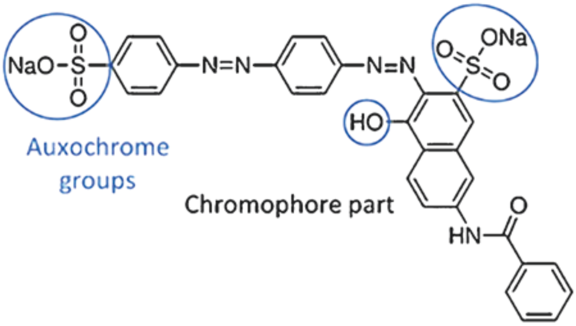


Fig. 16.1 A dye consists of two main parts, including chromophore and auxochrome groups. The figure shows these main parts in the chemical structure of direct red 81 dye (Walger et al. 2018)

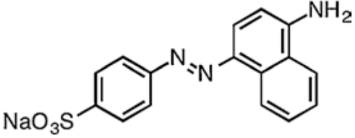
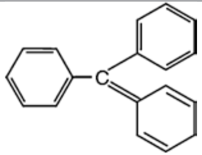
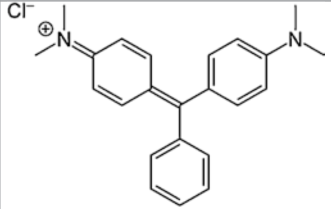
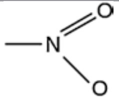
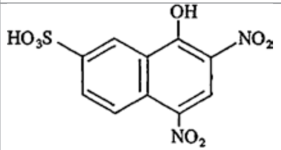
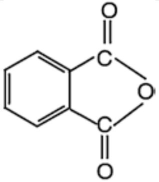
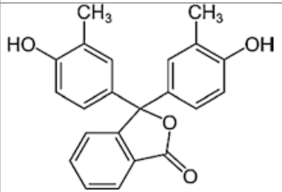
solution was as bad as using synthetic dyes. This is because of the fact that a mordant is needed to ensure natural dyes bond to fabrics. A mordant is a type of bonding agent that helps to bind natural dyes to the material. Mordants are much more dangerous and more toxic than synthetic dyes (Kant 2011). Today, synthetic dyes are staple materials which are used for colorizing cosmetics, textiles, printing, and plastics (Abdi et al. 2017; Ahmad et al. 2015). This is when the dyes are naturally rebellious materials and they are not easily degradable. Synthetic dyes have complex molecular structures owing to their auxochromes and chromophores (Chacko and Subramaniam 2011; Pan et al. 2017). Today, synthetic dyes are available in many different types. The synthetic dyes can be categorized based on their chemical structure as presented in Table 16.1.

Sometimes, dyes are classified by their application or even by their solubility, as tabulated in Table 16.2. Mordant, reactive, acidic, basic, and direct dyes are water-soluble dyes, while disperse, azo, and sulfur are examples of insoluble dyes (Rauf and Ashraf 2012). Among the various dyes, azo dyes have the highest production rate (~ 70%) and are the most widely used dyes throughout the world (Cotillas et al. 2018).

Another classification of dyes is presented in Table 16.3. Acidic dyes are commonly utilized for dyeing wool, silk, nylon, and modified acrylic. These dyes are also consumed in paper, cosmetics, inkjet printing, food, and leather industries. Xanthan, azine, triphenylmethane, anthraquinone, nitro, nitroso, and azo are the main classes of acidic dyes (Salleh et al. 2011). Acid red 57, acid blue 2, orange (I, II), and methyl orange are conventional acid dyes. Basic dyes are utilized in dyeing modified nylons, modified polyesters, and polyacrylonitrile as well as in pharmaceutical and paper industries. These are water-soluble cationic dyes and also consumed for wool, silk, and tannin mordant cotton (Salleh et al. 2011; Bouatay et al. 2016). Thiazine, cyanine, acridine, hemicyanine, oxazine, diazahemicyanine, malachite green, basic red 46, basic red 9, basic yellow 28, methylene blue, crystal violet, and basic brown are the main classes of basic dyes. Disperse dyes are utilized on nylon, cellulose acetate, cellulose fiber, and acrylic fibers. These are water-insoluble and nonionic dyes. The major classes are nitro, benzodifuranone, azo, anthraquinone, and styryl groups. Disperse blue, disperse yellow, disperse red, and disperse orange are some usual examples (Forgacs et al. 2004).

Direct dyes are commonly utilized in dyeing cotton, leather, rayon, and paper industries. If the dyeing process takes place in aqueous electrolytic solutions, direct dyes have affinity to cellulose fiber. Stilbenes, oxazine, and polyazo compounds are the major classes of direct dyes. Reactive dyes have found applications in dyeing wool, nylon, cotton, and cellulose fiber. The chromophores of the reactive dyes are azo, phthalocyanine, and triarylmethane (Chiou and Li 2003). Vat dyes are water insoluble and commonly consumed in dyeing rayon fibers, wool, and cotton (Karcher et al. 2001).

Table 16.1 The dye categories based on their chemical structure

Dye type	Chromophore	Example	Chemical structure
Azo	—N=N—	Direct brown 78	
Triphenylmethane		Malachite green	
Nitro		Naphthol yellow (II)	
Phthalein		o-Cresolphthalein	

(continued)

Table 16.1 (continued)

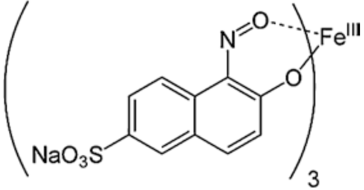
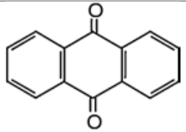
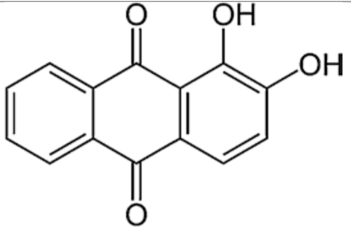
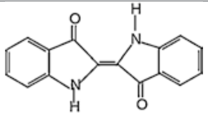
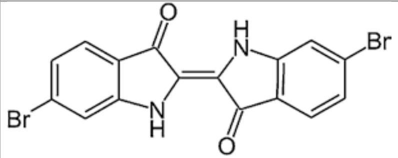
Dye type	Chromophore	Example	Chemical structure
Nitroso	$—N{=}O$	Naphthol green B	
Anthraquinone		Alizarin	
Indigo		Tyrian purple	

Table 16.2 Types and different uses of dyes

Type	Applications	Application method	Chemicals required	Example
Acid (water soluble)	Cosmetics, food, leather, modified acrylics, nylon, paper, printing ink, silk and wool	In dye baths with neutral to acidic conditions	Azo (including premetallized), anthraquinone, azine, nitro, nitroso, triphenylmethane, and xanthene	Acid yellow 36
Azo	Acetate, cellulose, cotton, rayon, and polyester	Coupling component used to impregnate fiber and a solution of stabilized diazonium salt is used for treatment	Azo	Bluish red azo dye
Basic (cationic dye) (water soluble)	Inks, medicine, modified nylon, modified polyester, paper, polyacrylonitrile, polyester, silk, tannin mordant cotton and wool	In dye baths with acidic conditions	Acridine, anthraquinone, azine, azo, cyanine, diazahemicyanine, diphenylmethane, hemicyanine, thiazine, triarylmethane, oxazine, and xanthene	Methylene blue
Direct (water soluble)	Cotton, leather, nylon, rayon, silk, and paper	In dye baths with neutral or slightly alkaline conditions with additional electrolyte	Azo, phthalocyanine, polyazo, stilbene, and oxazine	Direct orange 26
Disperse (water insoluble)	Acetate, acrylic fibers, cellulose, cellulose acetate, nylon, polyamide, polyester, polyester–cotton, and plastic	Padded on cloth and either baked or thermo-fixed at high-pressure and high-temperature or low-temperature carrier methods	Anthraquinone, azo, benzodifuranone, nitro, and styryl	Disperse blue 27, disperse red 4, disperse yellow 3
Fluorescent brighteners	All fibers, oils, paints, plastics, and soaps as well as detergents	Mass dispersion, solution, or suspension	Coumarin, naphthylamides, pyrazolos, and stilbene	4,4′-Bis (ethoxycarbonylvinyl) stilbene

(continued)

Table 16.2 (continued)

Type	Applications	Application method	Chemicals required	Example
Food, drug, and cosmetics	Food, drug, and cosmetics	Mixing	Anthraquinone, azo, carotenoid, and triarylmethane	Food yellow 4 and tartrazine
Mordant	Anodized aluminum, natural fibers, leather, and wool	Along with chromium salts	Anthraquinone and azo	Mordant red 11
Oxidation bases	Cotton, fur, and hair	The substrate is oxidized with aromatic amines and phenols	Aniline black and indeterminate structures	Direct blue
Reactive (water soluble)	Cellulosic, cotton, nylon, silk, and wool	Reaction between functional group on fiber and reactive site on dye. Covalently bonding under the influence of heat and an alkaline pH	Anthraquinone, azo, basic, oxazine, formazan, triphenylmethane, and phthalocyanine	Reactive blue 5
Solvent (water insoluble)	Fats, gasoline, inks, lacquers, lubricants, oils, plastics, stains, varnishes, and waxes	Substrate dissolution	Anthraquinone, azo, phthalocyanine, and triphenylmethane	Solvent red 26, Solvent blue 35
Sulfur	Cotton, leather, paper, polyamide fibers, rayon, silk, and wood	Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber	Indeterminate structures	Sulfur black 1
Vat (water insoluble)	Cotton, cellulosic fibers, polyester–cotton, rayon, and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogen sulfite and then exhausted on fiber and reoxidized	Anthraquinone (including polycyclic quinines) and indigoids	Vat blue 4 (indanthrene)

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Table 16.3 Classification of textile dyes

Dyes	Examples	Textile industrial products	Health effects
Acid dyes	Acid blue 25, acid red 57, methyl orange, Congo red	Polyamide, fibers, polyurethane, modified acrylics, nylon	Skin and mucous membrane irritation and burns
Basic dyes	Basic red 46, malachite green, basic yellow 28, methylene blue, basic brown, basic red 9	Silk, mordant acrylic, polyester, modified polyesters, modified nylons, paper	Carcinogens, allergic skin reactions, allergic dermatitis, skin irritation, mutations, cancer
Direct dyes	Direct orange 34, direct black, direct violet, direct blue	Leather, cotton, rayon, paper	Bladder cancer carcinogen
Disperse dyes	Disperse yellow, disperse blue, disperse orange, disperse red	Polyacrylonitrile, polyamide, nylon, acrylic fibers, cellulose	DNA damage, induction of bladder cancer in humans, splenic sarcomas
Reactive dyes	Reactive yellow 2, reactive red, Remazol, reactive black 5	Nylon, wool, cellulose, cotton	Allergic respiratory problem
Vat dyes	Vat green 6, vat blue, indigo	Wool, rayon fibers, flax wool cotton	Severe burns, skin and mucous membrane irritation

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16.3 Sources of Dyes

Natural dyes come from natural sources and are widely classified as animal, plant, microbial, and mineral based on their origin. However, plants are the main sources of natural dyes (Saxena and Raja 2014). Many industries such as paper, textiles, plastics, rubber, cosmetics, leather, pharmaceuticals, agricultural research, photoelectrochemical cells, pulp, hair colorings, tannery, food, and bleaching increasingly use synthetic dyes because of their low cost of synthesis, ease of use, stability, and variety compared to natural dyes. In addition, synthetic dyes have been used to control the effectiveness of wastewater treatment, to determine the specific surface area of activated sludge for groundwater tracking (Jafarinejad 2017a, b; Legrouri et al. 2017; Majolagbe et al. 2017). Approximately 700,000 tons of different coloring types are produced from about 100,000 commercially available dyes annually (Abdi et al. 2017; Holkar et al. 2016) which are used in various industries (Banerjee et al. 2017). Commercially, there are more than 10,000 dyes available, and their biodegradability is difficult due to their synthetic origin and complex aromatic molecular structure and. The textile industry releases significant amounts of dyes. About 15–20% of the color is discharged into the wastewater, during the coloring process (Duran-Jimenez et al. 2014). Due to the inadequacy of the coloring process, approximately 100 tons of dye is released to water during the process (Yagub et al. 2014). The textile and related industries generate a lot of dye waste that is

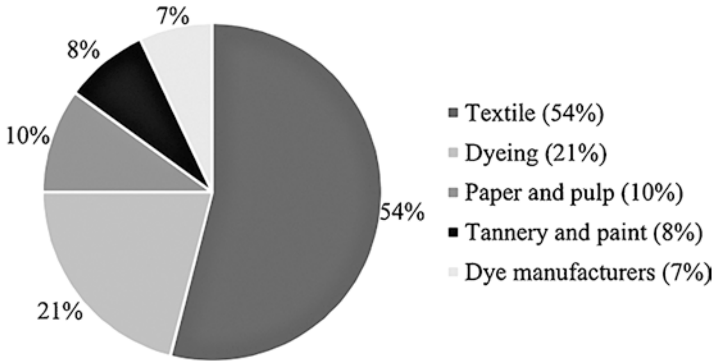

Fig. 16.2 The figure depicts the major industries responsible for contamination of the environment with dyes. As shown, the textile and dyeing industries are responsible for about 75% of the environmental contamination with dyes. (Reprinted with permission of Elsevier from Katheresan et al. 2018)

discharged into the environment (Hassanzadeh-Tabrizi et al. 2016). Figure 16.2 depicts the five main industries responsible for the dye-polluted environment. The textile industry with a 54% portion releases the highest quantity of dye effluent and accounts for more than half of the total dye effluent throughout the world. Dyeing (21%), pulp and paper (10%), paint and tannery (8%), and dye production (7%) industries generate large amounts of dye effluent from various related processes (De Gisi et al. 2016; Mojsov et al. 2016).

The exact amount of dye-polluted wastewater discharged by any industry is unknown, but it can be said to be large enough to constitute an important environmental issue. Of the other dye-consuming industries, it is said that the textile industry consumes the largest amount of dyeing material around 10,000 tons per year worldwide (Solís et al. 2012). The textile industry produces large amounts of dye effluent due to the industry's heavy need for water (Adegoke and Bello 2015; Salleh et al. 2011). The percentage of dye mixture discharged at the end of each textile process is illustrated in Fig. 16.3.

Exact information on the amount of dyes excreted in the environment is also not available. As a rough estimation, it is assumed that 1–10% loss in use and 1–2% loss in production are reasonable. A loss of around 4% can be considered for reactive dyes. Since the dyes are produced in large quantities and have a variety of applications, they can cause significant environmental contamination and critical public health problems. However, the great importance of protecting the environment has led to the development of environmentally friendly technologies, reduced freshwater consumption, and less wastewater generation. Dissemination of sizeable quantity of synthetic dyes to the environment raises legislation problems, public concern, and a thoughtful challenge for environmental researchers (Forgacs et al. 2004; Anjaneyulu et al. 2005; Arora 2014).

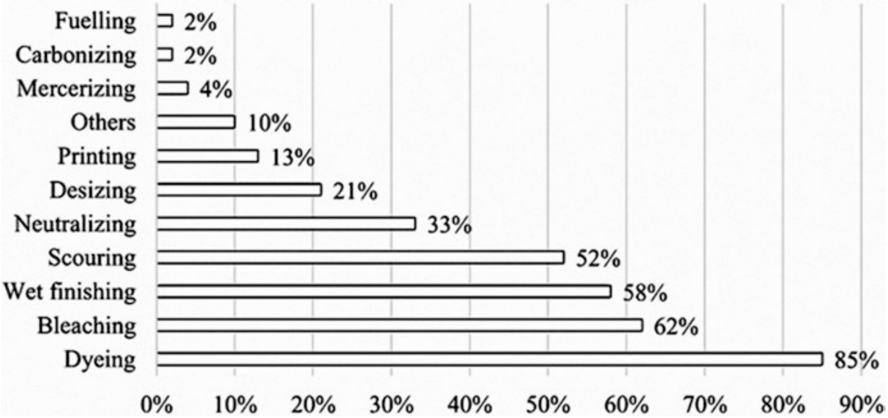

Fig. 16.3 Due to intense water consumption, the textile industry generates huge amounts of dye effluent. Different processes in textile industry have different contributions to dye release. (Reprinted with permission of Elsevier from Katheresan et al. 2018)

16.4 Environmental and Health Effect

The rapid growth of dye production and dye-consuming industries has contaminated water streams (Chiou et al. 2013). Without appropriate treatment, the discharge of wastewater containing dyes can cause many environmental problems (Khatri et al. 2015; Ngulube et al. 2017; Umpierres et al. 2017). As presented in Fig. 16.4, the textile effluent may have direct and/or indirect adverse effects on the environment. Due to the environmental and ecological impacts, dye-contaminated wastewater must be treated appropriately before discharge (Hassan et al. 2019).

Unfortunately, many dyes are stable in the environment due to high resistance against water, temperature, light, chemicals, and some other environmental factors, which make them highly toxic and carcinogenic and therefore very deleterious to ecosystem (Couto 2009). This is particularly crucial because many chemicals can be harmful to genetic material without being immediately expressed. It has been reported that nitro and azo compounds in aquatic sediments should be reduced or else they may cause potentially carcinogenic amines. Many dyes are composed of known carcinogens such as benzidine, so they pose a serious menace. Also, many dyes may convert into toxic compounds inside the bodies of living things. The carcinogenicity of azo dyes, as an important part of textile dyes, is well-known. Some azo dyes are found to be associated with bladder cancer in humans, hepatocarcinoma, splenic sarcomas, and nuclear abnormalities in laboratory animals (Percy et al. 1989). From a health and environmental point of view, removing these synthetic dyes is of serious concern. Due to their commercial significance, the influence and toxicity of dyes (Tsuda et al. 2001) which are released into the environment have been widely investigated. Many dyes are difficult to remove because of their stable molecular structure.

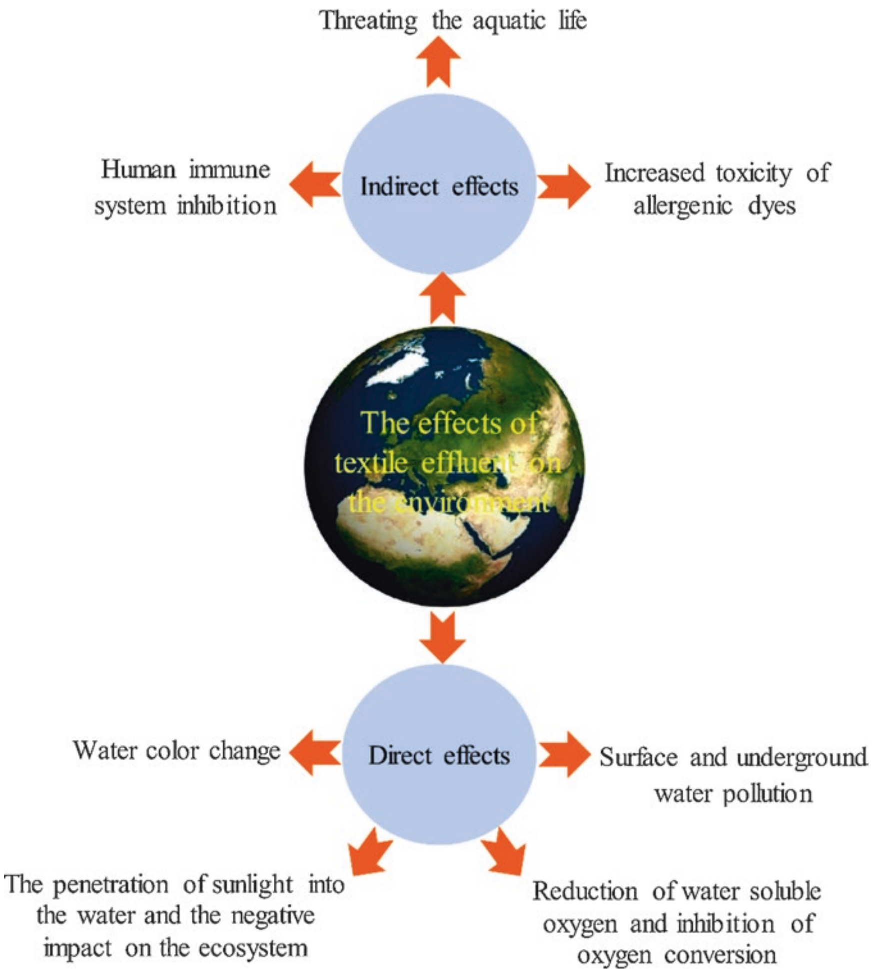

Fig. 16.4 Textile dyes can have direct and indirect adverse effects on the environment. Such negative effects can seriously threaten human life and ecosystem through various routes

The durable color and toxic, nonbiodegradable, and inhibitory nature of the used dye baths have significant harmful effects on soil and water. Moreover, some of the dyes or their metabolites are toxic or carcinogenic and mutagenic (Errais et al. 2011). The release of these dyes in contaminated wastewater not only affects aesthetics but also reduces the transmission of light in water and also decreases photosynthesis, which results in the ruin of the water ecosystem. Significant amounts of dyes can damage the human body (e.g., reproductive system, central nervous system, brain, kidney, and liver) as well as horrific consequences such as mutagenic, teratogenic, carcinogenic, etc. (Kösters et al. 2018; Salleh et al. 2011; Jiang et al. 2017). Therefore, one of the most critical environmental concerns today is the removing of dyes from wastewater due to their specific toxicity even at low concentrations (Jiang et al. 2017). The presence of dyes in water streams and bodies can prevent adequate chemical oxygenation (Ngulube et al. 2017; Umpierres et al. 2017). These dangerous dyes are absorbed into living organisms through the lungs, skin, and digestive tract (Humans et al. 2010) and cause serious diseases due to their mutagenic and carcinogenic nature (Akarslan and Demiralay 2015). Most dyes discharged from the textile industry are of azo type that are easily converted into aromatic amines by skin bacteria (Brüschweiler and Merlot 2017). Other widely consumed industrial dyes include indigo, phthalocyanine derivatives, and sulfur anthraquinone (Tan et al. 2016; Zare et al. 2015). These dyes are chemically stable and highly water soluble. Hence it is difficult to degrade them.

Apart from their structure, all synthetic dyes have one common drawback which is their dangerous nature (Montoya-Suarez et al. 2015). Therefore, efforts are needed to find solutions that can perpetually remove one or more types of dyes (Mojsov et al. 2016; Wang et al. 2011). Around 15% of dyes from industries directly pollute drinking water (Mittal et al. 2010; Bradder et al. 2010). Table 16.4 summarizes the existing literature on the various types of toxic dyes, their origin, and health/environmental impacts.

Table 16.4 Different types of dyes, their sources, and environmental/health effects

Dye type	Exposure route to humans	Health/environmental impact
Acid red 27	Food and textile industries. Color photography	Carcinogenic and affects the marine life. Toxic to flora and fauna
Acid black (210)	Cotton, leather, and woolen dyeing	Affects the skin and eyes
Acid yellow (42)	Dyeing of wool, silk, leather, and polyamide fibers	Harmful to the environment
Eriochrome black T	Carpet and textile industries	Degrades the water quality. Causes eye and skin allergies
Crystal violet	Paper and textile industries. Temporary hair colorant	Pollutes the groundwater in Basel. Causes vomiting, jaundice, quadriplegia, and tissue necrosis
Methylene blue	Dyeing cotton, wood, and silk	Causes eye burns or sometimes permanent injury to the eyes. Causes nausea, vomiting, and mental confusion
Malachite green	Textile industry (as dyeing silk, wool, paper, cotton). Food additive paints and printing inks	Disturbs the immune and reproductive system. Damages the spleen, liver, heart, kidney lungs, and eyes
Azo dyes	Food industry (chili powders, eggs, garlic curry sauce, and palm oils)	Cause of liver and urinary bladder tumors in mammals. Mutagenic and carcinogenic to humans
Methyl orange	Food, plastic, textile, and cosmetic industries	Mutagenic and carcinogenic to living organisms. Hazardous source of water pollution
Indigo carmine	Textile, food, and cosmetics industries for dyeing clothes (blue jeans)	Causes skin and eye irritations. Creates permanent injury to cornea and conjunctiva
Congo red	Leather, paper, and textile industries	Causes mutation of DNA and ecosystem. Causes neurodegenerative disease
Reactive blue (19)	Textile and garment industries	Degrades the water solubility/quality. Highly stable with bright color

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16.5 Dye Removal Methods

Various removal techniques including electrocatalytic degradation, chemical oxidation, membrane separation, reverse osmosis, electro-Fenton process (Rosales et al. 2012), photocatalysis (Li et al. 2017a), adsorption, coagulation/flocculation, and microbial degradation have been investigated for dye removal in wastewater (Chinoune et al. 2016; Blanco et al. 2017). These methods have their own benefits and disadvantages such as low dye removal capacity, slow dye removal kinetics, and poor reusability. Of all the methods mentioned, adsorption is one of the most promising techniques due to its low cost, simple operation, and high efficiency especially for low concentration solutions (Salama 2018; Oussalah et al. 2019). One of the benefits of adsorption process is that the adsorbents can be regenerated and reused, and this makes the process cheaper. Table 16.5 presents a summary of the benefits and disadvantages of these methods.

In recent decades, the adsorption process has emerged as one of the most popular methods of removing different types of dyes. This process is controlled by various parameters such as adsorbent dose, initial adsorbate concentration, pH, adsorbent particle size, contact time, temperature, etc. This process is operational in most physical, chemical, natural, and biological systems. The adsorption process is

Table 16.5 Various separation methods and their benefits and disadvantages

Separation techniques	Advantages	Disadvantages
Chemical methods		
Ozonation	No sludge generation	Operational cost is very high, half-life is short (20 min)
Photocatalyst	Operational cost is low and economically feasible	Some photocatalyst degrades into toxic by-products
Fenton reagent	Low-priced reagent and efficient procedure	Disposal issues and sludge production
Biological methods		
Anaerobic degradation	By-products can be used as energy resources	Under aerobic conditions requires more treatment and yield of methane and hydrogen sulfide
Aerobic degradation	Operational cost is low and effective in removal of azo dyes	Provides suitable environment for growth of microorganisms and very slow process
Physicochemical methods		
Adsorption/ sorption	High adsorption capacity for all dyes.	Low surface area for some adsorbents, high cost of adsorbents
Ion exchange	No loss of sorbents	For disperse dyes not effective
Electrokinetic coagulation	Economically feasible	Needs further treatments by flocculation and filtration and production of sludge
Membrane filtration	Effective for all dyes with high-quality effluents	Suitable for treating low volume and production of sludge

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extensively used in industrial applications and for water and wastewater treatment. In the past few years, natural and synthetic adsorbents such as activated carbon, zeolites, polymers, clays, graphene, carbon nanotubes, and synthetic materials have been used to remove a wide range of dyes from aquatic environments (Salama 2017, 2019; Salama and Hesemann 2018).

16.6 Adsorption

The adsorption is a popular process especially in removal of pollutants from wastewater owning to its simplicity, facile operation design using a variety of adsorbents, high efficacy of purification process, no sedimentation, and smaller investment (lower operating costs), in particular when the adsorbent is cheap and available (Siahkamari et al. 2017; Yang et al. 2017b; Li et al. 2017b). The adsorption involves an interfacial mass transfer process. Different modes of such mass transfer can occur between the fluid and solid phases such as liquid–liquid, gas–liquid, gas–solid, or liquid–solid. The properties of the adsorptive and adsorbent depend on their composition. The nature of the adsorption can be physical or chemical. The former is known as physisorption. In this case, the forces of attraction are the weak forces of van der Waals, and the results of the process are reversible. In addition, adsorption occurs at or below the critical temperature of the adsorbed material. The latter is known as chemisorption, during which the forces of attraction between the molecules of the adsorbed material and the solid surface are due to chemical bonding. Completely different from the physisorption, the chemisorption takes place only in a monolayer, and in addition, the chemically adsorbed material on the solid surface is difficult to remove due to the stronger forces. In appropriate conditions, both physisorption and chemisorption can happen simultaneously or intermittently. Physisorption is associated with reduced free energy and entropy of the adsorption system, and as a result, the process is exothermic (Saadi et al. 2013).

The adsorption process occurs in three stages (Tan and Hameed 2017):

Step (1) External diffusion, which involves the diffusion of adsorptive molecules within the fluid bulk to the outer surface of the adsorbent
Step (2) Intraparticle diffusion or intra-pore diffusion, in which the adsorptive molecules are transferred from the adsorbent surface into the pores
Step (3) The surface reaction in which the adsorptive molecules attach to the inner surface of the adsorbent pores

The first two steps of this process are the “transition steps” as shown in Fig. 16.5.

Each step imposes resistance to the uptake of the adsorptive molecules. The overall adsorption rate is calculated by the ultimate resistance obtained from the sum of the resistances of all three steps. Reducing the resistance of each step leads to the higher rate of adsorption. Usually the third step occurs faster than the first two ones because it creates less resistance. Each of the first two steps having the highest

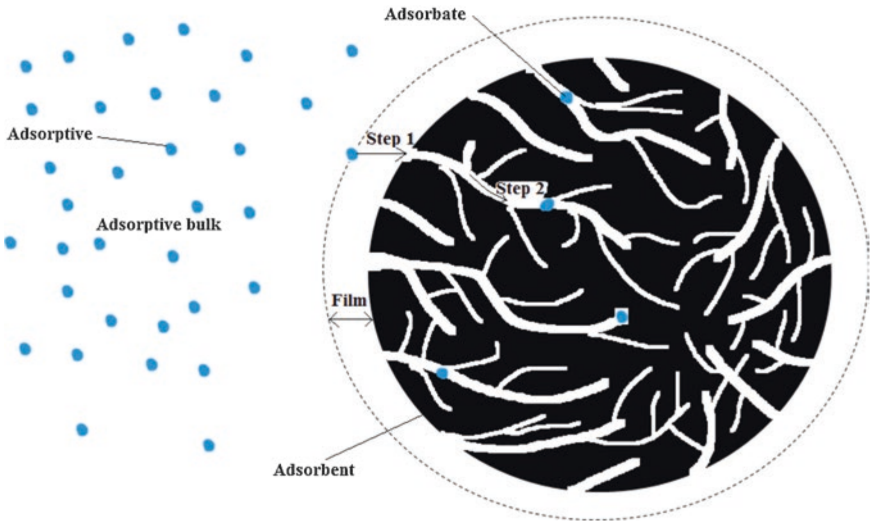
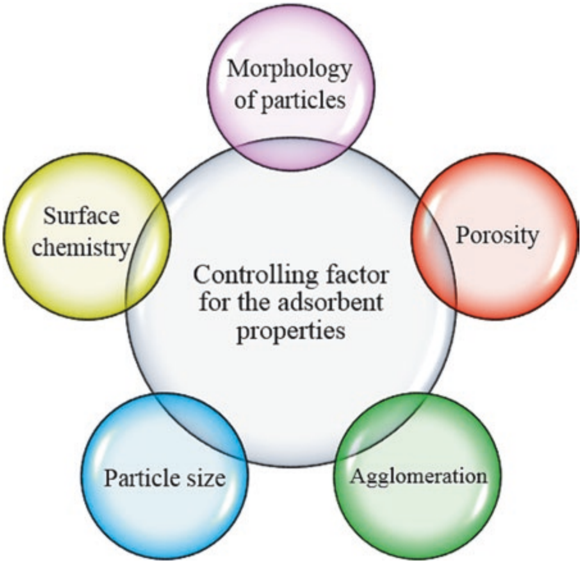


Fig. 16.5 Adsorption process takes place through some transition steps. These steps include external diffusion of adsorptive molecules within the fluid bulk to the outer surface of the adsorbent, intraparticle diffusion or intra-pore diffusion, and the surface reaction

Fig. 16.6 The adsorbent properties can be controlled by tuning the structural and surface factors. The figure shows the most important factors affecting the adsorbent properties



share of resistance controls the rate of adsorption. The resistance of the transition steps depends on several factors such as the type of adsorbent and adsorptive and operating conditions (Amanullah et al. 2000; Plazinski and Rudzinski 2009).

Various factors affect the adsorbent properties, the most important of which is shown in Fig. 16.6.

Fig. 16.7 The figure shows the most important factors affecting the adsorption efficiency. Optimization of these factors can be helpful in effectively removing dyes by the adsorption process

Particle size and agglomeration have direct effects on the specific surface area of the adsorbent. The agglomeration of particles can reduce the specific surface area of the adsorbent and therefore minimize the active sites. An appropriate surface chemistry can promote the adsorption mechanism. All these factors can be controlled through the adsorbent synthesis process.

Many factors are involved in adsorption efficiency such as adsorbent properties, contact time, temperature, pH of the wastewater, adsorbent dosage, and initial concentration of adsorptive (Fig. 16.7). Optimization of these factors can be helpful in effectively removing dyes by the adsorption process.

In the current decade, one of the major sources of environmental pollution is industrial wastewater. The textile and dyeing industries are one of the most important and basic industries and one of the indicators of development of any country. The cosmetics, paper making, and pharmaceuticals also produce colored wastewater. About 15% of all dye in dyeing processes comes into the wastewater and colored wastewater. Various methods have been studied by many researchers for the treatment of colored wastewater, such as ultrafiltration, reverse osmosis, ion exchange, and adsorption on various materials such as activated carbon, charcoal, and silica gel. There are many commercially available adsorbents, including activated carbon, bentonite, sepiolite, zeolite, and kaolin. Due to its large surface area and microporous nature, activated carbon exhibits good adsorption properties against nonpolar contaminants and acidic dyes. Bentonite, kaolin, and zeolite exhibit good adsorption capacity for Congo red, and sepiolite exhibits good adsorption capacity for azo dyes. On the other hand, activated alumina exhibits good adsorption capacity for malachite green (Raman and Kanmani 2016).

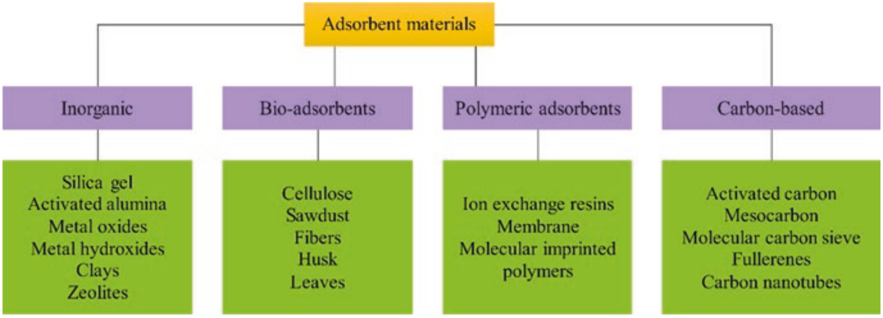


Fig. 16.8 The adsorbents can be divided into four categories according to their source of production. Each category exhibits a wide extent of adsorption efficiency

In general, the adsorbents should have the following characteristics (Mahfoudhi and Boufi 2017): (1) inexpensive, (2) good mechanical and structural properties to overcome the flow of water for a long period of time, (3) high surface area, (4) high adsorption capacities at high rates, and (5) easy recoverability and regeneration properties. As shown in Fig. 16.8, the adsorbents are divided into four general categories of carbon-based adsorbents, mineral adsorbents, polymeric adsorbents, and biosorbent adsorbents.

In order to improve the adsorption capacity and increase the separation rate, design and production of new adsorbents are still needed. Hybridizing materials is one of the promising techniques to achieve more efficient adsorbents.

16.7 Hybrid Adsorbents

Hybrid adsorbents are increasingly finding their place and importance in the adsorption applications and therefore the economics of adsorption-based separation processes. They cover prominent areas of science and are expected to expand some directions of modern technologies in the near future. This is evidenced by the significant growth in the number of scholarly works related to this field of research in recent years (see Fig. 16.9).

16.7.1 Concept

Hybrid structures are made of two or more distinct components. Hybrid structures can integrate the advantages of individual components and overcome their weaknesses. Hybridization can bring great features and new functions to the hybrid materials. These features and functions of the hybrid materials depend not only on their composition but also on their structure, the crystalline phase, the distribution of the individual components, and the interface between the individual components

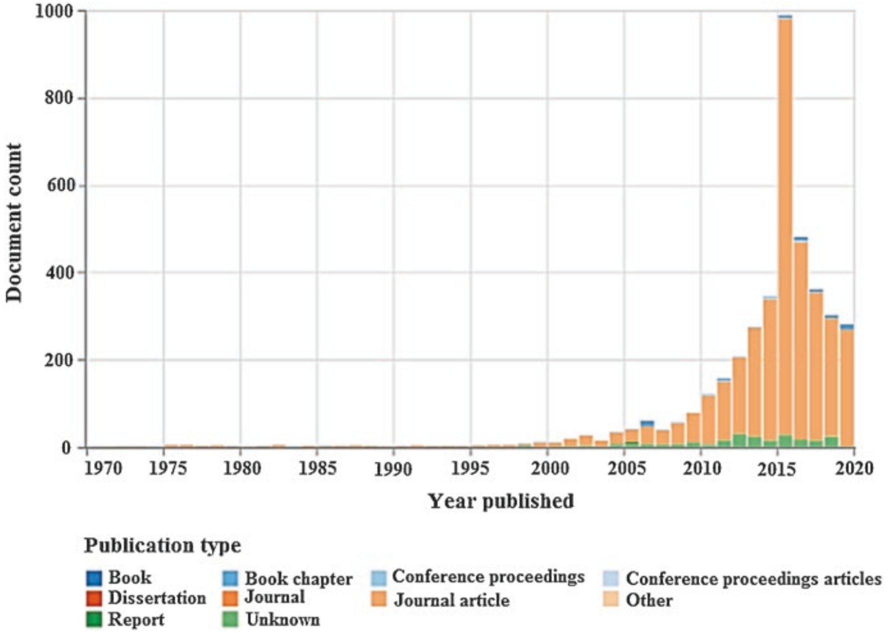


Fig. 16.9 The figure illustrates scholarly works in hybrid adsorbent research field. As shown, a significant growth in the number of scholarly works can be clearly observed in recent years. (Based on the data on Oct. 2019 from lens.org)

(Costi et al. 2010; Huang et al. 2014; Tan and Zhang 2015). Therefore, the proper design and controlled synthesis of hybrid structures are important not only for the development of advanced materials in specific applications but also for improving their performance and properties.

As shown in Fig. 16.10, different structural architectures such as core–shell structures, nanoparticle-incorporated structures, well-defined heterostructures, hierarchical heterostructures, and plate-like structures can be used to design hybrid materials. Such structures can sometimes be achieved under very controlled conditions. These architectures for hybrid materials can be synthesized through a variety of routes such as colloidal synthesis, chemical reduction, chemical vapor deposition, physical vapor deposition, electrochemical method, wet chemical synthesis routes, etc.

16.7.2 Synthesis

Sol–Gel Method

Hybrid adsorbents are synthesized in a variety of ways such as sol–gel method, hydrothermal method, microemulsion technique, coprecipitation, chemical vapor deposition, physical vapor deposition, laser ablation, combustion synthesis, etc.

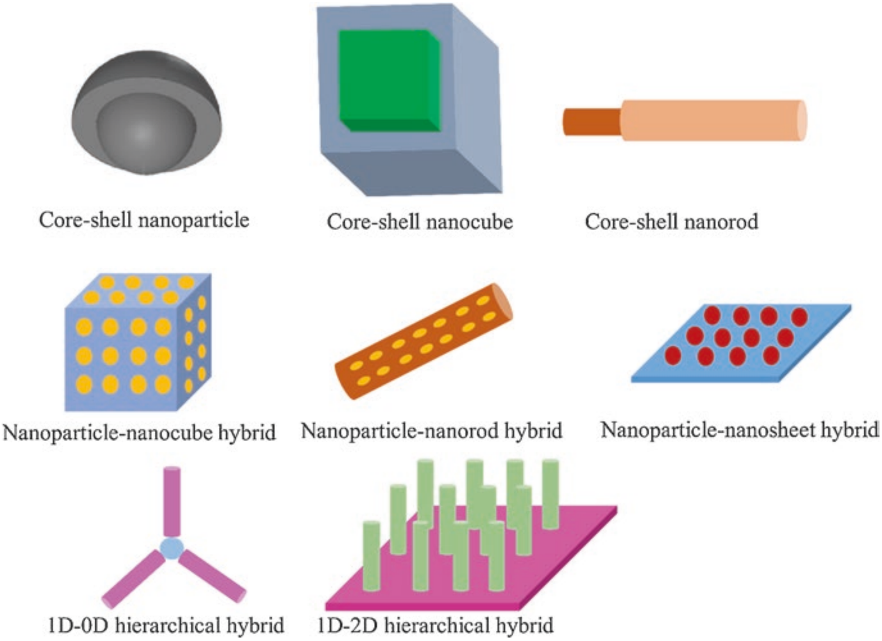


Fig. 16.10 The figure shows different architectures of hybrid nanostructures. The diversity of these structures can lead to the appearance of effective adsorbents for dye removal processes

The sol–gel method is performed in organic solvents and water, and the precursors used are usually metal halides and metal alkoxides. As shown in Fig. 16.11, the precursors undergo a series of hydrolysis and condensation reactions to form sol. Typical hydrolysis and condensation reactions mechanisms can be as follows:

Hydrolysis reactions (Gupta and Tripathi 2012):

$$M(OR)_n + H_2O \rightarrow M(OH)(OR)_{n-1} + ROH \tag{16.1}$$

$$M(OH)(OR)_{n-1} + H_2O \rightarrow M(OH)_2(OR)_{n-2} + ROH \tag{16.2}$$

Polycondensation reactions:

$$\text{-M-OH} + \text{HO-M-} \rightarrow \text{-M-O-M-} + H_2O \tag{16.3}$$

$$\text{-M-OR} + \text{HO-M-} \rightarrow \text{-M-O-M-} + ROH \tag{16.4}$$

in which M is the metal atom.

The formed sol is then transformed into wet gel through subsequent drying, aging and gelation, and chemical precipitation processes. Sol–gel method provides well-controlled synthesis route to prepare mixed metal oxides. As an example, to prepare TiO_2–MgO mixed oxide via sol–gel process, a given amount of titanium

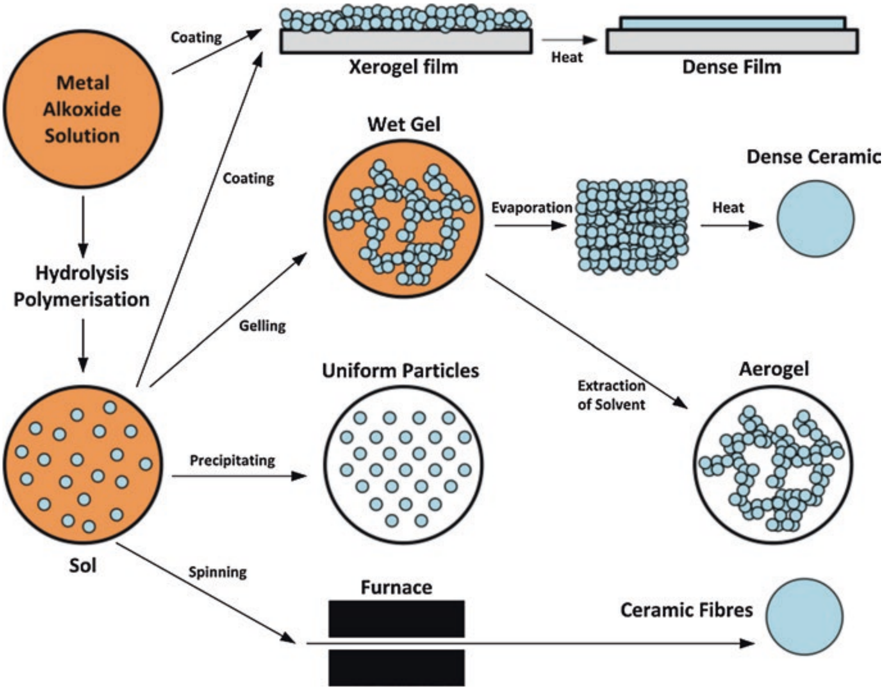


Fig. 16.11 The sol–gel method is performed in organic solvents and water, and the precursors used are usually metal halides and metal alkoxides. The sol–gel process can lead to the production of dense and porous materials. [Available on line: http://en.wikipedia.org/wiki/Sol-gel (Accessed on 20 September 2019)]

isopropoxide is dissolved in acetic acid to obtain a transparent sol after a few minutes. Then magnesium pre-prepared slurry is added to the formed sol under continuous stirring. After about 5 h, a sol is achieved. The sol is kept in an oven at 80 °C to be converted to the gel. The obtained gel is finally dried at 100 °C to produce a powder. For the dehyroxylation purpose, the prepared powder is calcined at temperatures> 500 °C to obtain TiO_2–MgO mixed metal oxide powder (Bayal and Jeevanandam 2014).

Hydrothermal Method

Hydrothermal method is an important approach for preparation of advanced materials. This method involves any heterogeneous chemical reaction in water medium above ambient temperature and the pressures higher than 1 bar in an appropriate autoclave. The hydrothermal synthesis encompasses the crystal growth, phase transformation of crystal, and phase equilibrium (Byrappa and Adschiri 2007). In a typical hydrothermal approach for the synthesis of core–shell Fe_3O_4@C, given amounts of hydrated ferric nitrate, $NH_4H_2PO_4$, hydrated sodium sulfate, and glucose are separately dissolved in distilled water and then mixed with each other for a few minutes. The resultant mixture is transferred into a steel autoclave. The reaction is performed at 180 °C for 48 h. Afterward, the obtained black product is left to cool to room temperature and then rinsed with a distilled water/ethanol mixture. The washed and dried product is finally calcined at 450 °C (Ji et al. 2018). The hydrothermal method is also very popular for the synthesis of inorganic–organic hybrid materials such as $Co(C_4H_4N_2)(VO_3)_2$ and $Co(C_{12}H_{12}N_2)(VO_3)_2$ (Li and Bai 2008), manganese tetraphosphonate (Stock et al. 2004), and metal diphosphonates (Stock and Bein 2002).

Coprecipitation Method

Coprecipitation is a wet chemical synthesis method, including the occurrence of nucleation, growth, and Ostwald ripening stages. The products are prepared from the solution phase under supersaturation conditions. Nucleation forms a huge number of small initial nuclei. The formed nuclei can grow through Ostwald ripening process. Such a process can result in the formation of aggregates, which consequently affect morphology and particle size (Athar 2015). As an example, to prepare iron–titanium mixed oxide, $FeSO_4 \cdot 7H_2O$ and $Ti(SO_4)_2 \cdot 4H2O$ are dissolved in water to prepare a mixed salt solution. Then 12.5% ammonia solution is added to the solution until the pH value of ~7.0. The resultant gel is aged for 48 h to obtain a suitable crystalline structure. After washing and drying, the gel is calcined in a furnace (Chen et al. 2012).

Coprecipitation technique can be applied to synthesize core–shell strictures. For this purpose, two or more water-soluble salts are first dissolved in water. Then, the pH value of the mixture is adjusted by adding a suitable precipitating agent. Figure 16.12 illustrates a schema of the formation of core–shell structure. The core phase is first dispersed in an aqueous salt medium as colloidal form. Achieving a desirable dispersion is very important in this stage. Then, the particles of shell are precipitated on the outer surface of core particles by the addition of a precipitant or acid/base with a proper concentration (Dembski et al. 2018).

Chemical Vapor Deposition

Chemical vapor deposition is an extensively used synthesis technique, during which a thin film is formed on the surface of a substrate. The film is deposited through a gas-phase chemical reaction. The chemical vapor deposition can be carried out in different media in cold-wall/hot-wall reactors. The pressure of the reactor may be controlled at sub-torr to above atmospheric pressure. The temperature is usually over the range of 200–1600 °C (Yan and Xu 2010; Warwick et al. 2011). Typically, chemical vapor deposition encompasses the chemical reaction of a metal-containing species on a substrate. An illustration of the typical main steps is shown in Fig. 16.13.

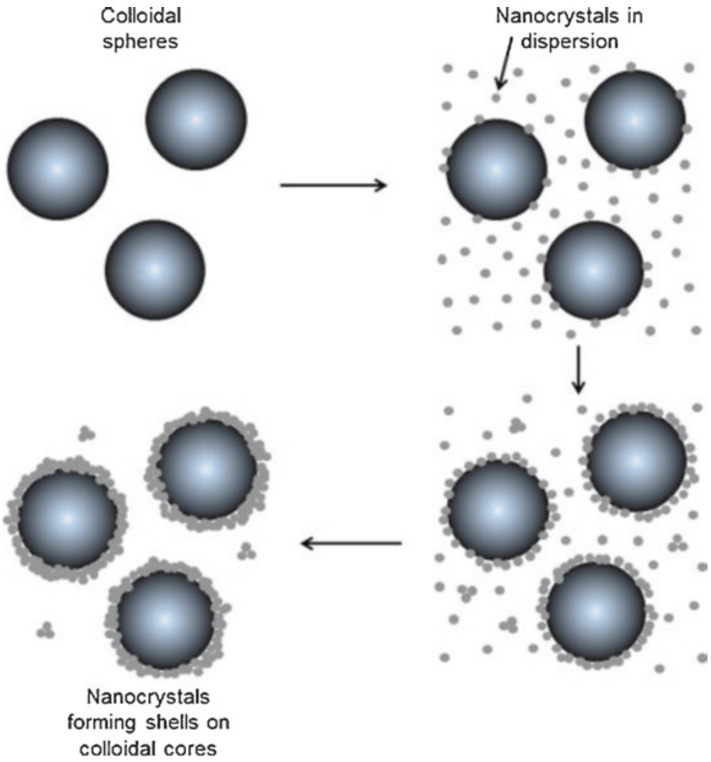


Fig. 16.12 The figure shows the formation of core–shell structure by coprecipitation method. The core is well dispersed in an aqueous salt medium as colloidal form. Then, the particles of shell are precipitated on the outer surface of core particles by the addition of a precipitant. (Reprinted with permission of Elsevier from Dembski et al. 2018)

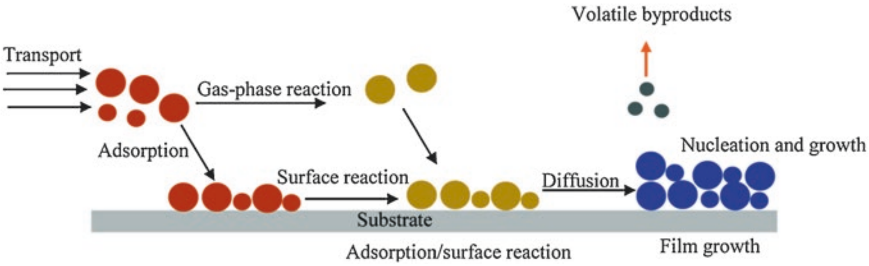


Fig. 16.13 The figure shows a typical chemical vapor deposition synthesis route. Chemical vapor deposition encompasses the adsorption and chemical reaction of a metal-containing species on a substrate

A metal-containing precursor is transported into the chemical vapor deposition chamber. The precursor is adsorbed on the surface of the substrate and then reacts. The metal or metal oxide species diffuses to form nuclei, followed by growth process. The chemical vapor deposition technique is relatively complex, and particular controls and calculations are required.

Physical Vapor Deposition

Physical vapor deposition method is an atomistic deposition synthesis route. During the physical vapor deposition process, solid or liquid precursors are vaporized in the form of molecules or atoms. The formed atoms/molecules are then transported through a low-pressure gas-phase or plasma medium to the substrate. The species are then condensed on the substrate. Typically, the physical vapor deposition method is applied to deposit films with nanometer thicknesses. The main categories of physical vapor deposition processing include sputtering deposition, thermal deposition, ion plating, arc vapor deposition, etc. (Mattox 2010).

Microemulsion

Microemulsions are stable colloidal dispersions which are formed through mixing oil and water phases in the presence of surfactant. Three types of microemulsions are possible: oil in water (O/W), water in oil (W/O), and bicontinuous. In the O/W microemulsion systems, the fraction of oil is low. On the contrary, in the W/O microemulsions systems, the amount of water is low. The size of droplet usually varies from 10 to 140 nm. Bicontinuous microemulsions may be formed if oil and water exist in equal amounts (Sakamoto et al. 2017). Figure 16.14 represents possible microemulsion-based routes for the synthesis of hybrid metals or metal oxides.

As schematically shown in Fig. 16.14a, the prepared reactants A and B are mixed with each other. During mixing, the droplets are interacted to form coalescences. The reactant B can be dispersed in the reactant A-containing microemulsion as a solid phase (Fig. 16.14b). Also, the microemulsion can undergo a thermal treatment to decompose to target product (Fig. 16.14c) (Khadzhiev et al. 2013). The microemulsion approach can be used for the synthesis of bimetallic compounds, mixed metal composite (Khalili and Hassanzadeh-Tabrizi 2017), polyamine chelating adsorbents (Meng et al. 2019), etc.

16.7.3 Application in Dye Removal

Different criteria such as chemical structure, structure architecture, number of phases used in the chemical structure, etc. can be considered for the classification of hybrid adsorbents. So there is no comprehensive classification of hybrid sorbents. The hybrid adsorbents discussed in this chapter are the ones most used in adsorbent of dyes.

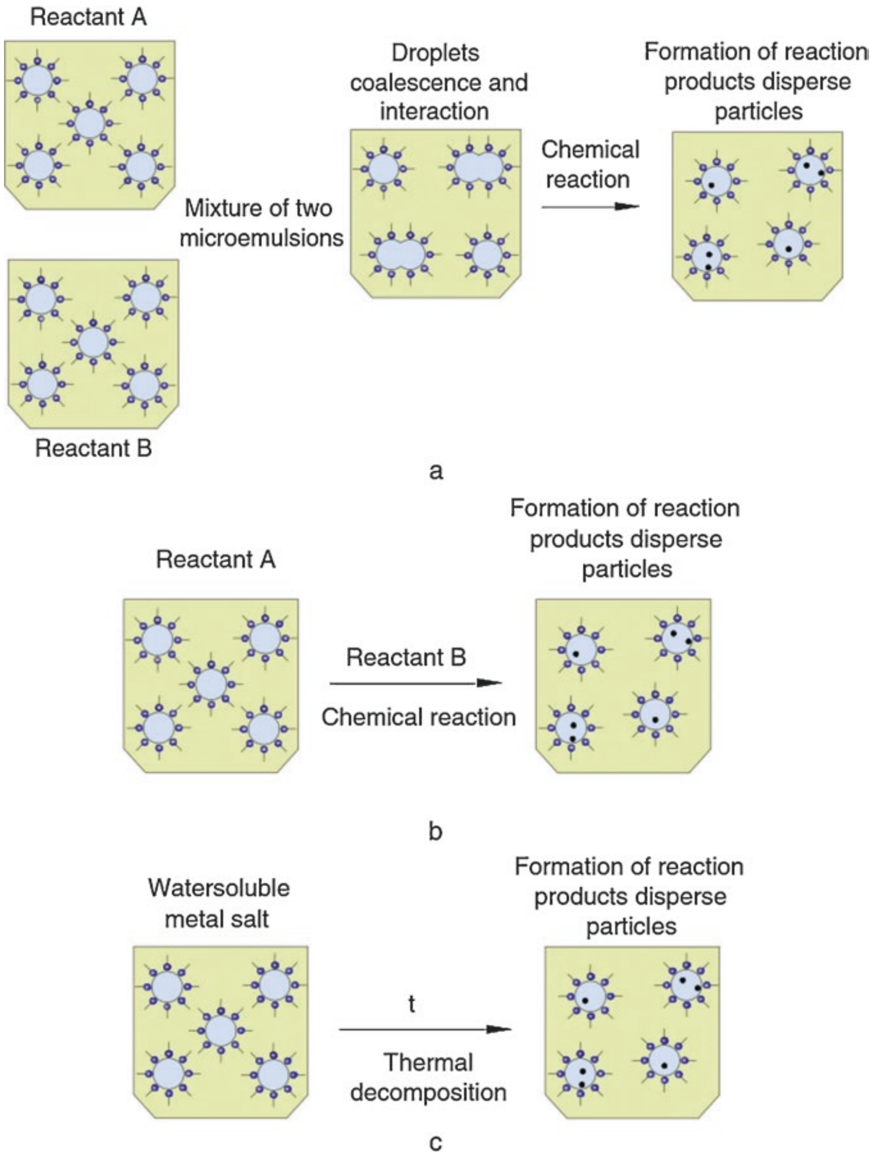


Fig. 16.14 Microemulsions are stable colloidal dispersions which are formed through mixing oil and water phases in the presence of surfactant. Microemulsion route can be used for synthesis of nanoparticles through (**a**, **b**) physical and chemical and (**c**) thermal treatment. (Reprinted with permission of Elsevier from Khadzhiev et al. 2013)

Bimetals

Bimetals have an undeniable role and a promising future in pollutant removal. Monometal and metal oxide have limitations such as slow contaminant removal efficiency and facile deactivation (Wang et al. 2015; Hong et al. 2010). Also, the removal process is easily influenced by pH. To tailor the monometal and metal oxide reactivity, the bimetallic particles were prepared by coating small quantities of noble metals (Pt, Ag, or Pd) or other metals (Cu, Mn, or Ni) onto a fresh metal surface. In the last few years, there has been a great deal of interest in the utilization of bimetallic particles for the disposal of pollutants (Fang et al. 2015; Zhao et al. 2015).

The application of bimetal nanoparticles in the removal of azo dyes and nitro compounds is well investigated (see Table 16.6). Xiong et al. (2015) compared the reactivity of zero-valent iron and Fe–Cu particles in degrading p-nitrophenol under different aeration conditions. It was found that dissolved oxygen can tailor the p-nitrophenol mineralization. Also, results showed that Cu can increase the zero-valent iron reactivity. p-Nitrophenol was decomposed into biodegradable and non-toxic intermediate compounds and eventually transformed into H_2O and CO_2. Kim et al. (Kim et al. 2014) used Pd–Pt bimetallic nanoparticles on functionalized multi-walled carbon nanotubes for the reduction of olefins and nitro compounds. The findings revealed that the prepared Pd–Pt bimetallic nanoparticles exhibited significant activity for effective reduction of nitro compounds.

Table 16.6 Removal of azo dyes and nitro compounds using bimetals

Bimetals	Azo/nitro dye	Removal efficiency (%)	Reference
Bi/Fe nanoparticles	Hexahydro-1,3,5-trinitro-1,3,5-triazine	100	Gong et al. (2015)
Fe–Cu	Hexahydro-1,3,5-trinitro-1,3,5-triazine	100	Koutsospyros et al. (2012)
	2,4-Dinitroanisole	100	Koutsospyros et al. (2012)
	Nitroguanidine	100	Koutsospyros et al. (2012)
	High melt explosive	100	Koutsospyros et al. (2012)
	Trinitrotoluene	100	Koutsospyros et al. (2012)
	Nitrotriazolone	100	Koutsospyros et al. (2012)
	Acid black 1	94	Yip et al. (2007)
	Methylene blue	98	Ma et al. (2004)
Pd/Fe	Para-nitrochlorobenzene	100	Xu et al. (2006)
Fe–Au nanoparticles	2-,4-Nitrophenols	100	Gupta et al. (2014)

The nanostructured bimetals were found to exhibit remarkable catalytic activity in reduction of dyes. Bokare et al. (2008) found that the Fe–Ni bimetallic nanoparticles could efficiently degrade azo dye orange G in aqueous environment. The results showed that the catalytic reduction of the azo dye leads to the formation of intermediate compounds of aniline and naphthol amine. Cai et al. (2014, 2015) synthesized two kinds of bimetal-supported catalysts of Fe–Co/GAC and Fe–Co/SBA-15 and then utilized them in degrading acid orange 7 and orange II.

Mixed Oxides

The mixed metal oxides play a key role in wide applications like photocatalysis and manufacture of absorbents (Ansari and Salavati-Niasari 2016; Mahdiani et al. 2017; Miller and Ko 1997). In recent years, the development of new metallic oxide-based hybrid materials has been rapidly attracting attention for use in several fields, including environmental applications. Hybrid materials have the advantages of their parent oxides, but they clearly exhibit the synergistic effect of all other oxides, leading to enhanced electronic (Guo et al. 2016) and physicochemical characteristics (Thanh et al. 2016). Metal-doped iron oxides for the synthesis of bimetal oxides have also been of interest to scientists. Bimetal oxides have been studied as adsorbents or catalysts to eliminate a wide range of pollutants (Wen et al. 2015a, b).

Recently, researchers have increased their endeavors in probing the utilization of metal oxide-based adsorbents to remove pollutants from wastewater. In this regard, mixed metal oxides, such as Sn–Fe oxide in removing fluoride (Biswas et al. 2009), Zn–Ni oxide in removing tartrazine and methyl orange (Klett et al. 2014), and Mn–Fe oxide in removing selenium (Szlachta and Chubar 2013), have been examined. The mixed oxides have favorable features such as small crystalline size and high surface area which will have a considerable effect on the adsorption process. Therefore, more attention has been paid to the development of new adsorbents with different properties. Phatai and Futalan (2016) studied the adsorption behavior of mesoporous Ce–Al oxides toward methyl violet dye. Banu and Santhi (2013) investigated Zn–Mn–Fe triple oxides to adsorb reactive yellow 15 from aqueous medium.

Dan Li et al. (2016) used ultrasonic spray pyrolysis process to prepare hierarchical core–shell ZnO/NiO. Yudin et al. (2016) synthesized NiO hollow nanostructure powder by ultrasonic spray pyrolysis technique. NiO/Ag_3VO_4 nanocomposite was prepared by sonication-assisted synthesis route to investigate the photocatalytic activity (Raja et al. 2018). Kara et al. prepared magnetite/nickel oxide mixed metal oxide nanoparticles and applied as a novel adsorbent to dispose of dye wastewater.

Among metal oxides, nanoparticles of Fe_2O_3, MnO_2, ZrO_2, CeO_2, and Al_2O_3 have widely been assessed for adsorption of dye from polluted water (Debnath et al. 2016; Asfaram et al. 2015). Sahoo et al. (2015) used Fe_3O_4–MnO_2 nanohybrid for the efficient removal of methylene blue and crystal violet dyes from contaminated water. Singh et al. (2018) prepared Fe–Mn–Zr triple metal oxide and used it for the adsorption of methyl orange and eosin yellow dyes from mixed dye solution. The results showed a removal efficiency of 99.26% and 99.55% for methyl orange and eosin yellow dyes, respectively, at optimal experimental conditions.

The application of Co and Ni binary oxide in removing methylene blue and Procion red has been reported (Khosravi and Eftekhar 2014). Also, Fe_2O_3–Al_2O_3 exhibited an appropriate adsorption capacity toward Congo red (Mahapatra et al. 2013). Wawrzkiewicz et al. (2017) proposed a novel mesoporous aluminosilicate adsorbent for the removal of acid orange 7, reactive black 5, and direct blue 71 dyes from the wastewaters.

The highly efficient adsorption of azo and nitro dyes has also been reported by using bimetal oxides. Hua et al. (2013) studied the catalytic performance of CuO/γ--Al_2O_3 for degradation of two dyes. Results revealed complete transformation of dye to H_2O and CO_2.

Chiou et al. (2013) prepared Ag–Fe oxide nanohybrid and used it for removing 4-nitrophenol. Safavi and Momeni (2012) assessed the catalytic activity of Pd/hydroxyapatite/Fe_3O_4 nanocatalyst in degrading the selected azo dyes.

Layered Double Hydroxides

It has been reported that layered double hydroxides are efficient adsorbents for the removal of anionic pollutants from wastewater (Extremera et al. 2012; Abdellaoui et al. 2017). The layered double hydroxides are popular adsorbents because of their high chemical stability, low cost, reusability, less toxicity, and easy preparation (Almoisheer et al. 2019). The layered double hydroxides are anionic clay with 2D nanostructures. The layered double hydroxides have a general chemical composition as $[M^{2+}_{(1-X)}M^{3+}_{(X)}(OH)_2]^{X+}(A^{n-})_{X/n}.mH_2O$, where M^{2+}, M^{3+}, and A^{n-} stand for bi- and trivalent cations, respectively (Fig. 16.15) (Scarpellini et al. 2014; Ai et al. 2011).

The layered double hydroxides have a hydrophilic nature due to the presence of the intercalated inorganic anions, but their surface may be hydrophobic by incorporating large organic anions into the interlayer space (Abdellaoui et al. 2019). The layered double hydroxide-based hybrids have found to be the promising materials in wastewater treatment (Daud et al. 2019). The facile modification of layered double hydroxides has made them efficient adsorbents for removing anionic dyes (Zubair et al. 2017a). Table 16.7 presents the recent findings on utilizing layered double hydroxide-based hybrids for removing a wide variety of dyes. As can clearly be seen from the data in Table 16.7, the layered double hydroxide-based hybrids exhibited excellent dye adsorption/removal performance. However, the adsorption process can be influenced by operating conditions (Stawiński et al. 2017; Zhang et al. 2017).

Anionic dyes can be adsorbed based on the strong electrostatic attraction due to the positively charged surface of layered double hydroxides and anionic dyes. The hybridization of layered double hydroxide by integrating nanomaterials such as nanoparticles (carbon nanotubes, iron), polymers, surfactants, and anions can remarkably enhance the adsorption efficiency. Despite good dye adsorption

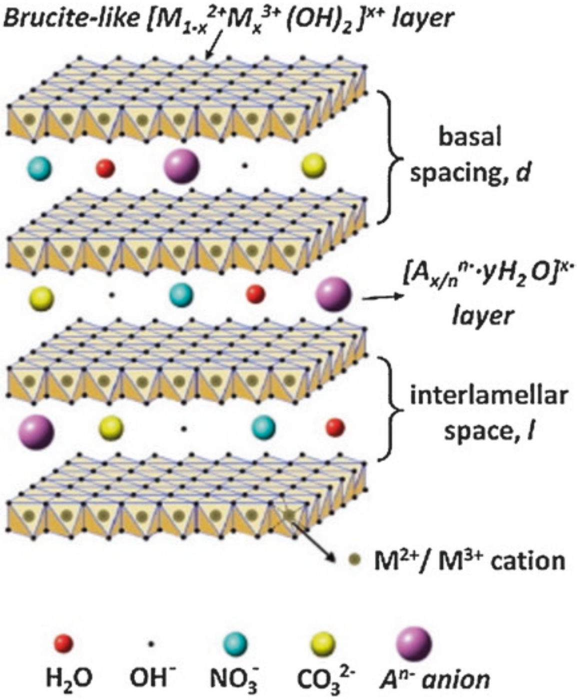


Fig. 16.15 The layered double hydroxides are anionic clay with 2D nanostructures. The figure shows typical structure of layered double hydroxides. (Reprinted with permission of Elsevier from Scarpellini et al. 2014)

capacity, two main challenges require further investigation: first, the mass production of layered double hydroxide-based hybrids requires appropriate continuous process to obtain high-quality product. Secondly, there are multi-pollutants in the real wastewater. Thus, it is essential to examine the adsorption/removal performance of these layered double hydroxide-based hybrids for real wastewaters (Daud et al. 2019).

Organic–Inorganic Adsorbents

Organic–inorganic materials are not clearly defined, since substances that contain both organic and inorganic compounds do not necessarily fall into the group. The requirement for a substance to be considered as an organic–inorganic compound is a molecular-level combination of the two fractions. Therefore, some hybrid materials such as commercial mineral-charged polymers and metal alkoxides should not be considered as organic–inorganic materials (Gómez-Romero and Sanchez 2006). An initial categorization of the most conventional types of organic–inorganic materials typically comprises (1) intercalation compounds (e.g., transition metal dichalcogenides), (2) organic derivatives of inorganic solids, and (3) sol–gel composites (e.g., organic-functionalized silica) (Aguado et al. 2009).

Table 16.7 Adsorption/removal performance of layered double hydroxides at different operating conditions

Adsorbate	LDH hybrids (adsorbent)	Surface area (m^2/g)	Initial concentration (mg L^{-1})	Dosage (g)	Adsorption conditions			Adsorption capacity (mg/g) or removal efficiency (%)	Ref.
					pH	T(°C)	t(min)		
Congo red	Calcined ZnAl–DH/Al[OH]$_3$	122	1000	1	4.5	25	360	1574.4/99	Guo et al. (2018)
	Zn/Cr–LDH	–	–	0.1	4	25	60	15.25/60	Rahayu et al. (2018)
	Fe_3O4@MgAl–LDH	57.2	100	0.02	–	25	30	404.6/99.8	Wu et al. (2017)
	Ni/Mg/Al–LDH	179	100	0.01	7	30	(0.9–2.2)	1250	Lei et al. (2017)
	NiAl–LDH	–	10	0.01	6	25	30	120.5/96.1	Bharali and Deka (2017a)
	ZnAl–LDH	104.0	100	0.01	–	25	6 h	1540/90	Huang et al. (2017)
	MgZnCr–TiO_2–(1:1:2–0.05) LDH	170.336	100	0.05	5.5	40	40	526.32/98	Ma et al. (2017)
	Fe_3O_4@MgAl–LDH MgAl–LDH Fe_3O_4	–	100	0.01	–	25	72 h	813 520.83 133.7	(Lu et al. 2017)
Reactive red	ZnAl–LDH	104.0	100	0.01	–	25	6 h	390/22	Huang et al. (2017)
	Mg–Fe–LDH Mg–Al–Fe–LDH Mg–Zn–Al–Fe–LDH	152.799 207.792 317.214	100	0.02	6.5	25	90	150.03/55 210.4/70 279.23/85	Samuei et al. (2017)

Methyl orange	Flower-like LDH	133	100	1	3	25	10	500.6	El Hassani et al. (2017)
	Starch/NiFe–LDH (2:1) Starch/NiFe–LDH (1:1) NiFe–LDH	–	20	0.01	3	25	180 180 60	387.59/90 358.42/99 246.91/78	Zubair et al. (2018)
	Calcined glycerol-modified nanocrystallined Mg/Al–LDH Uncalcined glycerol-modified nanocrystallined Mg/Al–LDH	170.3 71.4	600	6	4.5	25	20 30	1062.3 443.5	Yao et al. (2017)
	DPA/MgAl–LDH	140.65	20	0.01	3	25	4 h	242.98	Blaisi et al. (2018)
	Hierarchical SiO_2/LDH	–	0.092 M	0.3	4.5	25	10	166.1/92	Yang et al. (2017a)
	ZnAl–LDH	104.0	100	0.01	–	25	6 h	1153/70	Huang et al. (2017)
	LDH@Fe_3O_4/PVA magnetic	87	100	0.05	6	25	5 h	18.71/97	Mallakpour and Hatami (2019)
	Calcined ZnAl–DH/Al$[OH]_3$	122	500	1	4.5	25	360	1015.1/95	Guo et al. (2018)
	Chlorine interlayer microsheets ZnAl–LDH	122	50	0.4	6	25	12 h	359.71/100	Kumar et al. (2017)
	CuMgAl–LDH	131	20	0.005	7	25	180	79.2/98	Bharali and Deka (2017b)
	Mg3Al–LDH	–	50	0.05	7	25	60	45.93/99	Qiao et al. (2018)
	FH–CpAl–LDH	318.13	100	0.05	4	25	1440	2189.23	Gao et al. (2018)
Acid red	2-Hydroxyethyl ammonium acetate/MgAl–LDH	96.7	180	0.5	6	25	500	313.6/95.8	Bu et al. (2016)
	Fe_3O_4/MgAl–LDH	133	40	0.03	2	25	30	92	Shan et al. (2014)

(continued)

Table 16.7 (continued)

Adsorbate	LDH hybrids (adsorbent)	Surface area (m²/g)	Initial concentration (mg L⁻¹)	Dosage (g)	Adsorption conditions			Adsorption capacity (mg/g) or removal efficiency (%)	Ref.
					pH	T(°C)	t(min)		
Methylene blue	CuFe–LDH (3:1)	–	20	0.2	5.6	25	18	–/100	Ma et al. (2018)
Eriochrome black T	DPA/MgAl–LDH	140.65	20	0.01	2	25	4 h	425.16	Blaisi et al. (2018)
	MgAl–, CoAl–, and NiFe–calcined LDH	69.5	20	0.01	2	25	60 30 60	419.87/93.13 540.91/96.54 132.49/91.50	Zubair et al. (2017b)
	Bentonite–CoAl–LDH CoAl–LDH	119.14 44.20	20	0.05	2	25	120	675.67/92.03 361.06/86.46	Mu'azu et al. (2018)
Acid blue 74	Mesoporous Mg/Fe–LDH	85.6	13.98–55.92	0.1	9.5	25	30	62.8/95	Ahmed and Mohamed (2017)
Safranin T dye	Ppy NF/Zn–Fe LDH	23.27	5	0.05	5	25	360	–/99.99	Mohamed et al. (2018)
RR-120 (anionic reactive textile dyes)	MgAl–LDH	159	500	0.05	5	25	120	800/80 910/93	Mohamed et al. (2018)
Direct red 23	CoFe–LDHs	108.9	20	0.5	6	25	30	–/95.6	Chen et al. (2017)
Cationic dyes Anionic dyes	Hydrotalcite–LDH-derived adsorbent	225	100	0.02	8	25	120	291 ± 8 48 ± 2	Stawiński et al. (2017)
Anionic, nonionic, and cationic dyes	Sodium hexanesulfonate (SHS)–MgAl–LDH Sodium dodecanesulfonate (SDS)–MgAl–LDH	–	100	1	9	30	24	77.5 92	Zhang et al. (2017)
Organic pollutants	Zn–Al LDH 2ZnS/Zn–Al LDH	–	4	0.25	–	25	180	–/75	Li et al. (2017c)

Note: *LDH* layered double hydroxide
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Halloysite is a natural kaolinite clay with tubular aluminosilicate structure (Szczepanik 2017). Halloysite nanotube and its organic- and inorganic-based composites have been extensively utilized in adsorbing the different types of dyes.

Carvalho et al. used cyclodextrin/silica hybrid adsorbent for the adsorption of methylene blue from aqueous solution (De Carvalho et al. 2014). Cheng et al. (2016) synthesized and tested hemicellulose/clay hybrid hydrogels for removal of cationic dyes from aqueous medium.

Chitosan, a natural cationic polysaccharide, and its derivatives have a very high affinity for the direct, reactive, and disperse dyes. However, chitosan-based hybrids are not suitable for basic dyes. Sadeghi-Kiakhani et al. (2013) examined the adsorption behavior of chitosan–PPI dendrimer hybrid toward textile dyes.

Zhao et al. (2013) designed and tested acid red 138/CaF_2 as a low-cost adsorbent for the removing methyl blue and ethyl violet dyes.

Metal–Organic Frameworks

Metal and organic frameworks are a group of high-porosity materials that are synthesized via covalent bonding metal cations and di-, tri-, or tetradendate organic ligands. The metal–organic frameworks have highly ordered crystalline structures and large specific surface area. Due to their excellent properties, the metal–organic frameworks have now found a wide variety of applications in wastewater treatment, catalyst, sensor, energy, pharmaceuticals, etc. (Lee et al. 2014; Ahmed and Jhung 2014; Férey 2008). These materials have a comparative advantage over other porous materials due to their large specific surface area, high porosity, tunable porosity, varying composition, and open metal sites. Such prominent characteristics have made the metal–organic frameworks as favorable adsorbent (Haque et al. 2010). In this regard, cationic metal–organic frameworks exhibited an excellent adsorption capacity toward methyl orange, which is an anionic dye (Haque et al. 2010). Metal–organic framework-235 and MIL-100 (Fe) have been tested to adsorb cationic methylene blue through electrostatic attraction mechanism (Haque et al. 2011; Zhang et al. 2013). The hybridization of metal–organic frameworks (Stock and Biswas 2011; Ostermann et al. 2011) with suitable complementary materials has been reported for the preparation of metal–organic framework-based hybrids (Wee et al. 2011). These metal–organic frameworks hybrids have attracted a great deal of attention for adsorption process (Liu et al. 2016; Ahmed and Jhung 2014).

Yi et al. (2015) used metal–organic frameworks based on hexacarboxylate ligand and tri-cadmium-ion secondary building units to remove the methylene blue, methyl orange, and rhodamine B dyes. The results revealed that methylene blue could be easily adsorbed by the prepared metal–organic frameworks. Rhodamine B could not penetrate the metal–organic framework pore channels because of the large molecule size. Zhang et al. (2015) probed the adsorption behavior of Zn–multicarboxylate ligand metal–organic frameworks toward methylene blue, methyl orange, rhodamine B, and Congo red. It was found out that the MOF could efficiently adsorb Congo red but exhibited a weak performance toward the other dyes. Du et al. (2015)

prepared a bismuth cationic metal–organic framework to remove methylene blue and rhodamine B dyes. The designed metal–organic framework could adsorb both dyes, but a quantitative analysis was not reported. Abbasi et al. (2015) coated silk fiber's surface by a thin film of Zn metal–organic framework and then used it for the adsorption of methyl orange and morphine.

Carbon Nanotubes and Graphene Oxide-Incorporated Adsorbents

Graphene and carbon nanotubes with large external surface area, specific morphology, and well-formed mesopores exhibit a great potential for the removal of various types of environmental contaminants (Ren et al. 2011; Saleh et al. 2011). Graphite oxide is a layered material composed of graphene oxide sheets with oxygenated functional groups on their basal edges and planes. Both graphene and carbon nanotubes are considered as excellent adsorbents for the treatment of dye-contaminated water, benefiting from desirable physical and chemical stability, proper mechanical properties, high selectivity, and high specific surface area. Broad experimental studies have been performed on the adsorption of inorganic or organic pollutants on graphene and carbon nanotubes (Li et al. 2013a). Carbon nanotube-based hybrids are advanced materials that have received much attention due to their outstanding structures and mechanical properties (Pradhan et al. 2015).

The use of graphene oxide and carbon nanotubes in the preparation of metal–organic framework hybrid materials is a promising way to obtain novel adsorbent for wastewater treatment (Li et al. 2013b). The incorporation of graphene oxide and carbon nanotubes can improve metal–organic framework formation by preventing their aggregation, enhancing the dispersive forces in the structure of metal–organic frameworks, and controlling physicochemical properties (size, structure, and morphology) of metal–organic framework (Petit and Bandosz 2012). Abdi et al. synthesized ZIF-8 as a metal–organic framework and its graphene oxide and carbon nanotube-based hybrid nanocomposites as adsorbents for the removal of malachite green dye from wastewater. The results disclosed that the hybrid nanocomposites exhibited higher dye removal rates than the sole metal–organic framework (Abdi et al. 2017).

The significance of adding graphene oxide to the chitin matrix is useful not only in reinforcing the composite but also in improving the adsorption versatility due to the different chemical nature of the two materials. Obtaining a solid-like gel from the two powders has introduced the hybrid as a promising adsorbent for heterogeneous phase wastewater treatment (Kyzas et al. 2011). González et al. synthesized chitin/graphene oxide hybrid gels and then used it for the adsorption of the basic and acidic dyes (González et al. 2015).

Liu et al. (2015) prepared MnO_2/graphene–carbon nanotube hybrid adsorbent for the adsorption of methyl orange. The results showed that the hybrid adsorbent exhibited an excellent adsorption capacity toward methyl orange.

Jiao et al. (2015) synthesized graphene oxide/Fe_3O_4 nanohybrids for rapid and effective adsorption of organic dyes. Ai and Jiang (2012) prepared self-assembled cylindrical graphene– carbon nanotube hybrid for the efficient adsorption of organic dye from aqua medium. The prepared hybrid exhibited a maximum adsorption capacity of 81.97 mg g^{-1}.

Abbasi synthesized a novel magnetic chitosan/SiO_2/carbon nanotube nanocomposite and tested it for the adsorption of reactive blue 19 and direct blue 71 from aqueous solution (Abbasi 2017).

It was found that graphene–carbon nanotube hybrid aerogels were also very promising in removing organic dyes (Sui et al. 2012).

Hassan et al. (2018) prepared a new graphene/hydroxyapatite nanohybrid for removing methylene blue dye from wastewater. This adsorbent exhibited an optimum adsorption capacity of ~333 mg/g.

16.8 Conclusions

This chapter investigated the issues related to dyes, their presence in the effluent and wastewater, environmental problems, and their elimination by using hybrid adsorbents. Studies showed that the development of hybrid adsorbents is a promising solution to the problem of dyeing in wastewater and preventing them from being released into the environment. In the meantime, bimetals adsorbents, compound or mixed metal oxides, layered double hydroxides, organic–inorganic materials, and graphene oxide/carbon nanotube-incorporated adsorbents in the removal of dyes have been investigated more than other hybrid adsorbents. The results showed that these adsorbents exhibit a high adsorption capacity toward dyes. The only question that needs to be answered is: Do these hybrids at large-scale production still retain their quality and can replace the current commercial adsorbents? The current trend of studies is that we should see significant progress in the near future.

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