

## Chapter 15

# Adsorptive Removal and Recovery of Heavy Metal Ions from Aqueous Solution/Effluents Using Conventional and Non-conventional Materials



Ashitha Gopinath, Kadirvelu Krishna, and Chinnannan Karthik

**Abstract** The development of industries over the past few decades has turned the world into a modernized era. The ultimate pros of this industrialization are benefited by humans on one side whereas they are also severely affected by the cons on the other side. The intended release of industrial wastewater into the water bodies often contaminates it heavily with toxic substances particularly heavy metals, as they are non-biodegradable and persistent in the environment. Remediation of heavy metals by various physical and chemical approaches is not advisable as it is uneconomical and generates a large number of secondary wastes. Hence, utilization of low cost conventional and non-conventional adsorbents offers natural and eco-friendly statutory for metal removal. Hence, it is considered an efficient and alternative tool for metal remediation. Based on the facts stated above, the present chapter described the sources and environmental significance of heavy metals as well as remediation strategies using low-cost adsorbents.

**Keywords** Wastewater · Heavy metals · Remediation · Adsorbent · Removal

## 15.1 Introduction

Contamination of the biosphere is a major environmental risk, which has been increased dramatically since the beginning of rapid industrialization and modern lifestyle. A wide variety of organic (hydrocarbons, volatile organic compounds and solvents) and inorganic (heavy metals) pollutants are continuously released into the environment by various industrial activities, long time usage of fertilizer and pesticides in agriculture, mining, burning of fossil fuels and sewage sludge amendments (Abdelatey et al. 2011). Among the pollutants, heavy metals play a crucial role on environment and living organisms due to its toxic nature. The term heavy metal

---

A. Gopinath · K. Krishna · C. Karthik (✉)

DRDO – BU – CLS, Bharathiar University Campus, Coimbatore, Tamil Nadu, India

denotes to any metallic element with high density (higher than  $5 \text{ g cm}^{-3}$ ) and toxic/poisonous to the environment at low concentrations. Heavy metals also called as trace elements, because of their presence in the environment at a trace level (mg/kg) or in ultra-trace level ( $\mu\text{g/kg}$ ). Moreover, they are a heterogeneous group of elements, which greatly differ in their properties and biological functions (Mukesh et al. 2008). Heavy metals enter into the environment through natural (rocks, metalliferous minerals, erosion, volcanic activity, wind-blown dust, rain, snow, and hail) and various anthropogenic resources (metallurgy, energy production, microelectronics, mining, sewage sludge, waste disposal and agriculture). Heavy metals are deliberately released into the environment from anthropogenic resources (Wuana and Okieimen 2011). Moreover, the use of wastewater to irrigate agricultural land is another major environmental risk as it enters the edible as well as nonedible plants via soil posing serious health issues (Kumar Sharma et al. 2007, 2009). Due to these anthropogenic resources, heavy metals enter into the food chain. Heavy metals have been detected in various living forms like microorganisms, plant, animal and human alike through the food chain migration.

## 15.2 Heavy Metal Contamination and Toxicity

Out of naturally occurring 90 elements, 21 nonmetals, 16 light metals and the remaining 53 are considered as heavy metals. Majority of heavy metals are transition elements, with incompletely filled d-orbitals. These d-orbitals provide heavy metal cations with the ability to form complex compounds, which may or may not be redox-active. Among them, the most common toxic heavy metals are Lead (Pb), Cadmium (Cd), Copper (Cu), Chromium (Cr), Mercury (Hg), Zinc (Zn), Aluminum (Al) and Manganese (Mn) (Duruibe et al. 2007). Based on the biological properties, heavy metals are classified into four major groups such as essential, non-essential, less toxic and highly toxic heavy metals. Some of the heavy metals such as Co, Cr, Cu, Mn, Fe, and Zn are classified as essential metals based on their biological functions (Bruins et al. 2000). A lesser quantity of these metals are common in our environment and essential for the metabolic process, good health, growth, disease resistance, vigor production, and reproduction. On the other hand, elevated concentration can be a potential carcinogen to the environment (Gogoasa et al. 2006; Aelion et al. 2008). Heavy metals like Ba, Al, Li, and Zr, are classified as non-essential metals. These non-essential metals are not needed by living organisms for their metabolic process and growth. Similarly, metal ions like Sn and Al classified as less toxic heavy metals based on their toxicity nature. However, heavy metals like Hg, Pb, and Cd are classified as high toxic heavy metals. These metals are well-known toxicants even at lower concentrations, which affect cellular organelles and components mostly, involved in detoxification, DNA or cell damage repair and metabolism (Lim and Schoenung 2010; Mukesh et al. 2008). Because of its mutagenic and carcinogenic nature, heavy metals are considered as a “Priority pollutant”

(USEPA 1997). Toxicity and biological significance of the primary heavy metals have been discussed elaborately in Table 15.1. This imposes massive pressure on the society for the removal and recovery of it from the contaminated site. Henceforth, it is essential to establish a method suitable and practicable for the removal of heavy metals on-site, which can be performed by the common man as well.

In the last few decades, several heavy metal removal strategies such as ion exchange, reverse osmosis, electrodialysis, flocculation and chemical precipitation have been extensively explored for their effectiveness in the removal of metals in industrial effluents. However, these strategies become uneconomical and unsuitable for a large quantity of heavy metal removal from industrial wastewater. Hence, the development of an alternative, low cost, and eco-friendly strategies are highly desirable for heavy metal removal. In this scenario, utilization of various conventional and non-conventional adsorbents could be cost-effective and more efficient approach over the traditional methods. Thus, the current chapter has been discussed in detail about the efficiency of various conventional and non-conventional adsorbents in heavy metal removal from aqueous solution.

### 15.3 Conventional Technologies for Heavy Metal Removal

Given the above context, a vast array of techniques has been witnessed by the scientist's for the removal of heavy metals from aqueous solution. Selection of a method depends on many factors such as cost, time and easiness to operate, safety, efficiency, long term and short-term environmental effects. This section presents an overview of different techniques adopted for the elimination of heavy metals from wastewater. Heavy metals can be specifically removed with the aid of ion exchangers that employs acidic and basic resins (Sofinska-Chmiel and Kolodynska 2017). Each heavy metal requires the use of unique resins implying that multi-components cannot be removed in a single process or single resin. This makes the treatment process impractical for high-end applications. Chemical precipitation arises to be a well-known method due to its safety, ease of operation and it does not demand the use of any sophisticated types of equipment as well. The method employs a precipitating agent such as lime to convert the dissolved metal ions into an insoluble metal hydroxide (Marchioretto et al. 2005). However, it suffers from many limitations including slow settling rate, huge sludge generation and the expense incurred during its disposal. A similar method which generates an excessive amount of sludge is coagulation-flocculation since it uses a large amount of coagulating agents such as alum and ferric salts to increase the particle size (flocules) for fast settling (Ferhat et al. 2016). Henceforth, the above mentioned two methods are not acceptable for large-scale remediation purposes. The reverse process of coagulation involves flotation or collection of heavy metals from suspension when it is in the floating stage rather than by settling of particles (Salmani et al. 2013). This reduces the retention time but utilizes a huge amount of collectors to remove low

**Table 15.1** Toxicity effects of major heavy metals on living forms

Heavy metals	Source	Effects on human	Effects of plant	Effects on microorganisms	Reference
As	Industrial manufacturing, wood preservatives, cosmetics, agrochemicals, glass and glass wares	Respiratory, nervous and cardiovascular disorders, skin cancer, dermatitis, conjunctivitis, brain, and kidney damage	Reduce the metabolic activity, inhibition of growth, and photosynthesis rate and induced the oxidative stress	Inhibit the cell division and growth, enzymatic activities	Bissen and Frimmel (2003)
Cd	Agro-chemicals, pigments, and plastics, mining, refining, welding	Bone & kidney diseases, gastroenteric distress, and pain, lung and prostate cancer, lymphocytosis, coughing, emphysema, and vomiting	Reduce the nutrient uptake, alter the stomatal function and photosynthesis, inhibition of seed germination rate and growth behavior	Long time exposure induces DNA and protein damage, inhibit the transcription and cell division	Nagajyoti et al. (2010), Fashola et al. (2016)
Cr	Dyeing, tanning, electroplating, textile, steel fabrication and paint	Lung cancer, liver diseases, nausea, skin irritation, itching of the respiratory track, inflamed mucosa, reproductive toxicity, bronchopneumonia, chronic bronchitis, diarrhea	Inhibition of seed germination rate, growth, and photosynthesis rate, affect the antioxidant expression and induce lipid peroxidation and proline	Growth inhibition, elongated lag phase, modulation in physiological and biochemical processes	Karthik et al. (2016), Cervantes et al. (2001)
Cu	Industrial machinery, electrical equipment, mining, painting, combustion of fossil fuels and wastes, wood production	Liver and kidney disorders, modulating the metabolic activities, nose, mouth, and eyes irritation, diarrhea, vomiting, stomach cramps, headaches, dizziness, and nausea,	Growth retardation, imbalanced antioxidant expression, chlorosis and reduce the water and nutrient transport and genotoxicity	Reduce the size of microbial biomass, enzymatic activities and disrupt cellular function	Nagajyoti et al. (2010), Saleem et al. (2011)
Co	Smelting process, phosphate fertilizers, fossil fuels, vehicular exhaust and other industrial activities	Lungs disorder including asthma, pneumonia and wheezing, vomiting, skin rashes, allergy and hearing problems	Decrease plant growth, biochemical functions and change the antioxidant system expression	Induce cell surface modifications, imbalanced metabolic process	Gopal et al. (2003)

Mn	Mining and mineral processing, emissions from ferroalloy, steel and iron production as well as combustion of fossil fuels	Neurodegenerative disorder, behavioral changes, lungs irritation, loss of sex drive and sperm damage.	At higher concentration decrease growth rate, induce chlorosis, necrosis, modulating both enzymatic and non-enzymatic antioxidant expression, Affect seed germination, growth, antioxidant system, photosynthesis, and chlorosis	At elevated concentration inhibit the growth and metabolic process of the cells	Zhao et al. (2012), Moroni et al. (2003)
Pb	Batteries manufacturing, mining, paint and pigment industries, automobile exhaust of leaded petrol and soldering	Modulation in various enzymatic function, high blood pressure, neurons damage, reduced fertility, anorexia, hyperactivity and damage in the renal system		Cell membrane disruption, denaturation of DNA and protein and inhibits transcription	Wuana and Okieimen (2011)
Hg	Coal burning, mining, paint, paper, electrical and electronic industries, methylmercury fungicides and batteries	Psychological changes, neurological damage, Minamoto disease, fertility problems, gastrointestinal irritation and loss of immunity	Retardation of growth, inhibition of seed germination, growth and photosynthesis rate, modulate the antioxidant system and affect nutrient uptake	Inhibit cell cycle, reduce the biomass and disrupt cell membrane biochemical processes	Fashola et al. (2016), Wuana and Okieimen (2011)
Ni	Electroplating, power plants, and trash incinerators,	Allergy, lung and nasal cancer, kidney disease, nausea, cardiovascular diseases, asthma	Decrease the growth, biomass, chlorophyll content, reduce enzymatic activities induce reactive oxygen species and genotoxicity	Affect the morphological and physiological behavior, inhibit enzyme activities and oxidative stress	Chibuikwe and Obiora (2014), Fashola et al. (2016), Malik (2004)
Zn	Mining, oil refinery, steel production, fertilizer, coal burning, burning of wastes and fertilizers.	Anemia, kidney and liver damage, stomach cramps, skin irritation, vomiting, nausea, and depression	Affect the reproductive percentage, induce reactive oxygen species, physiology, morphology, and genotoxicity, reduced the germination, photosynthesis and chlorophyll content.	Reduce the growth rate and biomass, induce cell death (at higher concentration) and inhibit the cell cycle.	Chibuikwe and Obiora (2014), Gumpu et al. (2015)

concentration of heavy metals efficiently. Membrane filtration, the process that underlies the size of the particles is another option to separate heavy metals from contaminated water. Specific particles of varying size could be retained depending on the nature of the filtration membrane, which is being categorized as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Vinodhini and Sudha 2017; Mehdipour et al. 2015; Mohsen-Nia et al. 2007). UF retains macromolecules but rejects low molecular weight compounds whereas NF process lies in between that of UF and RO. RO involves pressure dependent rejection of water and retention of heavy metals, which makes it more suitable for the different membrane processes. Although membrane filtration can be used at large scale, its long time efficiency is doubtful, as fouling is a common problem encountered in filtration processes that necessitates frequent cleaning and replacement of membrane. This leads to operational as well as maintenance costs, which makes the process non-economical. A more recent technique, which has been practiced, is an electro-based treatment that includes electrolysis, electroprecipitation, electro dialysis (Gherasim et al. 2014; Yasri and Gunasekaran 2017) and electrocoagulation (Mansoorian et al. 2014). This technique is known to reduce treatment time but demands a lot of energy which boosts up capital as well as maintenance cost and requires trained personnel. Adsorption turns out to be a viable option due to its simplicity, utility, safety, feasibility and more importantly its economical nature (Chen et al. 2012). In addition to this, adsorption is the individual process that can be employed to extract a soluble material from solution as it provides an option for desorbing the adsorbed materials for the further use of adsorbent and adsorbate. It is important to study this possible method, which is discussed in the following sections.

## 15.4 Adsorption

Adsorption means the mass transfer of a molecule from the aqueous or gaseous matrix to a solid interface but a complex process involving many factors (Fig. 15.1). It is a phenomenal surface- interplay between two components namely adsorbent and adsorbate. A solid surface acts as the adsorbent on which an adsorbate occupies its position depending on the favorable conditions. Adsorption takes place in two different means in which the adsorbate associates with adsorbent either through a physical attraction (physisorption) or forms a chemical bond with the latter (chemisorption). The former process is a rapid process involving multilayer adsorption and is of reversible nature whereas the latter is an irreversible reaction with a single layer adsorbed specifically on the adsorbent. This purely depends on the nature of affinity between adsorbate and adsorbent specific sites as few metal ions occupy specific sites whereas the rest compete for non-specific sites (Jiang et al. 2010). Adsorption continues to occur till equilibrium is reached between metal ions (adsorbate) and the adsorbent. The equilibrium condition relies on whether the adsorption process is in static mode or dynamic mode (Goel et al. 2005).

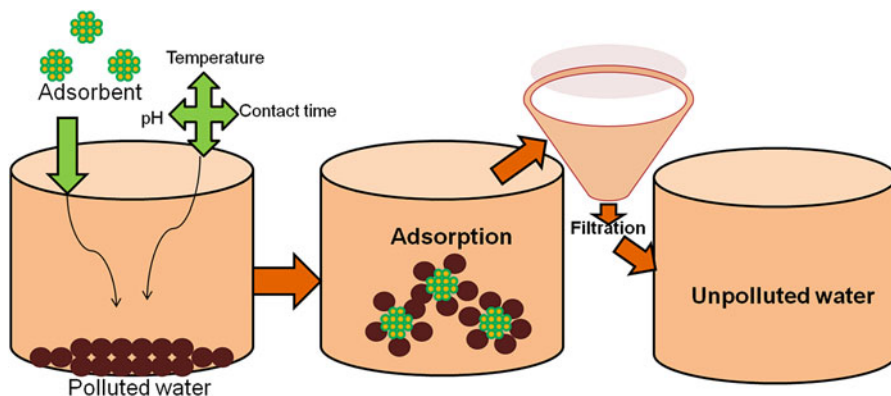


Fig. 15.1 Overview of adsorption

### 15.4.1 Factors Affecting Adsorption

The complexity of the adsorption process relies typically on the internal and external factors surrounding the adsorbent and adsorbate. The governance of the internal factors such as nature of adsorbent and adsorbate necessitates the proper selection of both whereas the pH, temperature and contact time being the external factors assist in driving the adsorption towards the equilibrium condition. These factors are discussed in the subsequent sections.

#### 15.4.1.1 Nature of Adsorbate

The size and charge of the metal ions have great influence on its adsorption on a substrate. Metal with higher ionic radius subside on the surface of adsorbent and introduce steric hindrances resulting in fast saturation of adsorbent sites (Kadirvelu et al. 2000). Heavy metal ions have a positive charge on their surface and are likely to get attracted to an adsorbent surface possessing negative charge and vice versa (Pillay et al. 2009). Adsorption generally increases with increase in initial adsorbate concentration since the driving force for diffusion is larger in the initial stage and continues until the adsorbent sites are saturated with the adsorbate (Najafi et al. 2012).

#### 15.4.1.2 Nature of Adsorbent

An adsorbent is characterized by several physicochemical properties that determine its adsorption capacity for a metal ion. Primarily, the surface area and pores size play a major role in deciding the adsorbent capacity. The high surface area represents number of adsorption sites available for the attachment of metal ions and enables

faster kinetics. Mesoporous materials have gained popularity in adsorption due to its large surface area, and uniform pores distribution (Aguado et al. 2009; Li et al. 2011). However, microporous materials present much more efficiency in adsorption when compared to mesoporous materials as it exhibits faster film transfer diffusion (Kadirvelu et al. 2000). Presence of significant functional groups on the adsorbent is beneficial as it aids in chemisorption between the functional group present on the adsorbent and metal ions (Jain et al. 2013). Consequently, nature of functional groups determines the surface charge of an adsorbent which is a parameter of utmost importance for adsorption of metal cations (Wang Hongjie et al. 2009; Wu et al. 2009; Jain et al. 2014; Karthik et al. 2016, 2017; Zarghami et al. 2016). The amount of adsorbent also determines the rate of adsorption as higher amount provides number of adsorption sites thereby ensuring higher removal of cations (Motsi et al. 2009).

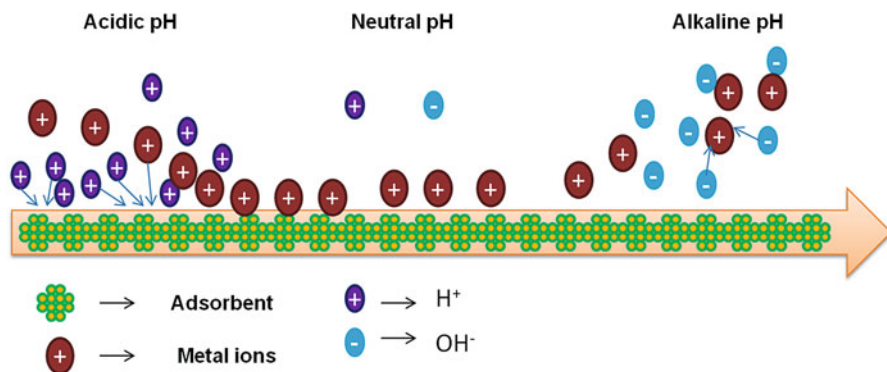
#### 15.4.1.3 pH

pH is one of the crucial factors that govern the rate of adsorption of metal ions in solution. Generally, at lower pH the concentration of  $H^+$  ions is very high; hence, the competition between metal ions for the adsorbent would be high. This greatly reduces adsorption rate at low pH whereas at higher pH, the reduction in competition ultimately favors adsorption of metal ions efficiently (Kadirvelu et al. 2000; Wingenfelder et al. 2005; Wu et al. 2009). Adsorption trend is severely changed if the pH goes beyond neutral, as the metals tend to precipitate due to the presence of more hydroxyl ions. This reduces the solubility of metals in water and hence a higher amount of metal uptake in hydrated forms (Malandrino et al. 2006). Moreover, functional groups present on the adsorbent alter the surface charge at various pH as ionization occurs and aid in the binding of metal ions process via ion exchange (Argun et al. 2007; WANG Hongjie et al. 2009; Karthik et al. 2016, 2017). The changes in adsorption pattern under various pH conditions are well depicted in Fig. 15.2.

#### 15.4.1.4 Contact Time

Time is a factor that helps determine the strength of interaction between adsorbent and adsorbate (Jain et al. 2009). Generally, the initial process of adsorption is assumed to be very rapid but the time required to reach equilibrium varies with adsorbent and adsorbate (Meena et al. 2008; Abdel Salam et al. 2011). A good adsorbent with the large surface area, porosity, and ideal pH and temperature conditions drive the reaction in the forward reaction to attain equilibrium at a faster pace.





**Fig. 15.2** Adsorption of metal ions at various pH

### 15.4.1.5 Temperature

The dependence of temperature on the adsorption of heavy metals on a substrate is being studied using thermodynamic parameters. It gives insight knowledge on the energy changes occurring during adsorption. The equations relate the Gibbs free energy ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ) and temperature ( $T$ ) in Kelvin. Gibbs free energy ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ) and temperature ( $T$ ) in Kelvin.

$$\Delta G = -RT \ln K_l \quad (R \text{ is the molar gas constant } 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \text{ and } K_l \text{ is the Langmuir constant})$$

$$\text{Also } \ln K_l = -\frac{\Delta H}{RT} + C \text{ and}$$

$$\Delta G = \Delta H - T\Delta S$$

It is imperative to determine the spontaneity of a reaction as it very well predicts the reaction rate which indirectly gives adsorption capacity for heavy metals with change in a temperature. A negative value of  $\Delta G$  indicates that the reaction is spontaneous and it increases with increase in temperature (Eloussaief et al. 2009; Karthik et al. 2016, 2017). This suggests that the rate of heavy metal removal increases with temperature and vice versa. For a positive value of  $\Delta S$ , an increase in adsorption was reported as the circulation of rotational and transitional energy increases (Argun et al. 2007; An et al. 2017). Positive value enthalpy is a strong indication of endothermic the nature of metal adsorption process. This can be explained in terms of regarding the reaction between water molecules and metal cations (Shaker 2014). However, the amount of water being displaced varies with different metals.

### 15.4.2 Adsorption Isotherms

Isotherms are linear graphs that give accurate information about the adsorbent and adsorbate. It usually represents the adsorption capacity of a material in terms of regarding the equilibrium concentration of metal ions. The classic isotherm equations that are used to describe adsorption process are Langmuir, Freundlich, Sips, Temkin and Dubinin, Radushkevich (DR) (Xiang et al. 2016; Zarghami et al. 2016; An et al. 2017).

Langmuir model is a theoretical model and describes monolayer adsorption since it assumes adsorption takes place on a homogenous surface with all the sites equally available for metal ions (Jain et al. 2013). It is expressed according to the following equation:  $q_e = \frac{q_m K_l C_e}{1 + K_l C_e}$ , where  $q_e$  is the equilibrium adsorption capacity in  $\text{mmol g}^{-1}$ ,  $q_m$  is the maximum monolayer adsorption capacity in  $\text{mmol g}^{-1}$ ,  $C_e$  is the equilibrium concentration in  $\text{mmol L}^{-1}$ ,  $K_l$  is the Langmuir constant. Furthermore, a dimensionless parameter  $R_l$  could be related with Langmuir constant by the equation:  $R_l = (1 + K_l C_0)$ . If the value of  $R_l$  lies between 0 and 1, it represents favorable adsorption whereas  $R_l > 1$  represents unfavorable adsorption.

Freundlich model is an empirical model, which describes multilayer adsorption on heterogeneous surfaces with different adsorption sites on the adsorbent possessing different adsorption energy (Jain et al. 2009, 2013). It is represented by the equation:  $\ln q_e = \frac{1}{n} \ln C_e + \ln K_f$  where  $q_e$  is the amount of solute on adsorbent in  $\text{mmol g}^{-1}$ ,  $C_e$  is the equilibrium concentration in  $\text{mmol L}^{-1}$ ,  $K_f$  is the Freundlich constant which indicates adsorption capacity whereas  $n$  is constant indicative of adsorption intensity. Adsorption process is favorable if  $n > 1$ , whereas  $n = 1$  shows linear adsorption and  $n < 1$  depicts unfavorable conditions for adsorption.

The Sips model is a combination of Langmuir and Freundlich and is described by the equation as follows:  $q_e = \frac{q_m K_s C_e^m}{1 + K_s C_e^m}$ ,  $K_s$  is the sips equilibrium constant and  $m$  is the dissociation parameter. Sips isotherm becomes Langmuir isotherm when the value of  $m$  is close to 1 whereas when the value is closer to 0, it becomes Freundlich isotherm.

Temkin isotherm describes adsorption as a uniform distribution of bonding energies up to some maximum binding energy and heat of adsorption decreases linearly with an increase in adsorbent-adsorbate interactions. The equation is generally represented as  $q_e = B \ln K_T + B \ln C_e$  where  $B = \frac{RT}{b_T}$  and it is related to heat of adsorption the  $n$ ,  $K_T$  is the Temkin equilibrium binding constant,  $R$  is the molar gas constant,  $T$  is the temperature in Kelvin,  $b_T$  is the Temkin isotherm constant.

Dubinin- Radushkevich (DR) model is used to express the adsorption in terms of free energy of adsorption. This model helps to differentiate the physisorption and chemisorptions of metal ions onto a substrate. The prediction can determine from the following equation:  $\ln q_e = \ln q_m - K_{DR} \varepsilon^2$ , where  $K_{DR}$  is the Dubinin-Radushkevich constant,  $\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)$ .

The apparent free energy is given by  $E = (2K_{DR})^{-0.5}$ , if the value of E is in between 1 and 8  $\text{kJmol}^{-1}$  then adsorption is governed by the physical attraction between adsorbent and adsorbate but chemisorptions happens if the value is exceeds above 8  $\text{kJ mol}^{-1}$ .

## 15.5 Adsorption on Conventional Sources

Conventional adsorbents have been successfully used for the last few decades by the industries in the large-scale removal of contaminants. These adsorbents are known for their excellent surface adsorption properties due to its high surface area and porous nature they possess. Some of the conventional sources as well as its modified forms are discussed in the following sections.

### 15.5.1 Activated Carbon

Among the carbon family, activated carbon (AC) is the most prominently used porous adsorbent for the removal of contaminants from wastewater due to its large adsorption capacity. It is available in different forms including powder, granular, fiber and felt. A greater part of the investigations on this resourceful adsorbent has been done using granular in the batch model due to its ease of availability. However, column studies have also been found to be successful in removing heavy metals from water (Goel et al. 2005; Park et al. 2007; Natale et al. 2015). Modifications on AC has out lifted the adsorption capacity for the removal of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Cu}^{2+}$  in batch as well as column mode (Park et al. 2007). Hachao Liu et al. (2014) has investigated the effects of humic acid modified AC and reported that increase in humic acid on AC increased its adsorption capacity for copper. Modification on AC by either sulfur or oxidation by nitric acid has proven to be advantageous for the removal of  $\text{Cd}^{2+}$  as the introduced functional aid in proper bonding of AC with the metal ion (Liang et al. 2016; Tajar et al. 2009). Advancement in the carbon industry gave rise to the addition of activated carbon in fiber form possessing high flexibility and low mass transfer resistance (Kadirvelu et al. 2000).

### 15.5.2 Silica Gel

Silica gel is the amorphous version of silicon dioxide and present in the form of granules or beads. The distinct feature of silica gel is its highly porous nature providing large surface area necessary for adsorption. Moreover, it is non-toxic, odorless, thermally resistant and does not undergo any side reactions with the adsorbate. Among the porous form, mesoporous are known to possess excellent

features including large surface area, distinct pore size, and pore volume. This prompted the researchers to exploit them as an adsorbent for the removal of heavy metals. Functionalized silica is more prominently used to improve the affinity and specificity towards a particular metal ion (WANG Hongjie et al. 2009; Mureseanu et al. 2008). Silica gel modified with amine groups has shown significant adsorption of Cu, Cd, Pb, Ni and Zn from aqueous solution (Aguado et al. 2009). Chen et al. (2012) introduced amidoxime groups on silica gel by homogenous and heterogeneous methods have proved it to be an excellent material for the removal of specific removal  $\text{Hg}^{2+}$  ions from an aqueous solution containing Hg-Pb, Hg-Ag, Hg-Ni, Hg-Cu binary systems. Thiol-functionalized reusable silica adsorbent has been proved well effective for the removal of Hg and Pb from both acid and alkaline conditions (Li et al. 2011). Later, Ren et al. (2013) attempted to develop magnetic EDTA modified silica for the adsorption of Cu, Pb and Cd ions and it could be reused up to 12 cycles, and thereafter its efficiency decreased. Silica gel acts as an excellent support material for chelating agents for solid phase extraction as well as recovery of noble metals (Kondo et al. 2015).

### 15.5.3 Zeolites

Zeolites are porous aluminosilicates exhibiting crystalline nature with honeycomb structure formed by the assemblage of  $\text{SiO}_4$  and  $\text{AlO}_4$  via sharing of oxygen atoms. Due to the introduction of Si by Al, it possesses a net negative charge, which must be balanced by some cations. Low density, hydrothermal stability, resistance to the acidic solution and its abundance in nature makes it a widely used material for adsorption of heavy metals. A typical composition of the zeolite may contain  $\text{SiO}_2$  (45.09),  $\text{Al}_2\text{O}_3$  (14.43),  $\text{Fe}_2\text{O}_3$  (10.59), CaO (5.79) and MgO (4.49) (Abdel Salam et al. 2011). The most commonly use zeolite clinoptilolite as it has gained immense research interest due to its higher thermal stability than other zeolites. The affinity of different zeolites towards metal ions varies depending on the composition of the former. The dependence of pH on  $\text{Pb}^{2+}$  removal varies with the type of zeolites used for adsorption (Kabwadza-Corner et al. 2015). Ibrahimi and Sayyadi (2015) have well explained the use of natural and synthetic zeolites for the removal of heavy metal ions. Murthy et al. (2013) investigated the significance of different adsorption isotherms for the removal of  $\text{Hg}^{2+}$  using different zeolites.

### 15.5.4 Clay

Clay is composed of finely grained particles containing phyllosilicates, organic matter and few other matters that give plasticity to the clay. They are known to be hydrous aluminosilicates containing silicon-oxygen tetrahedron and aluminum octahedron arranged in hexagonal patterns. The four major types of clay materials used

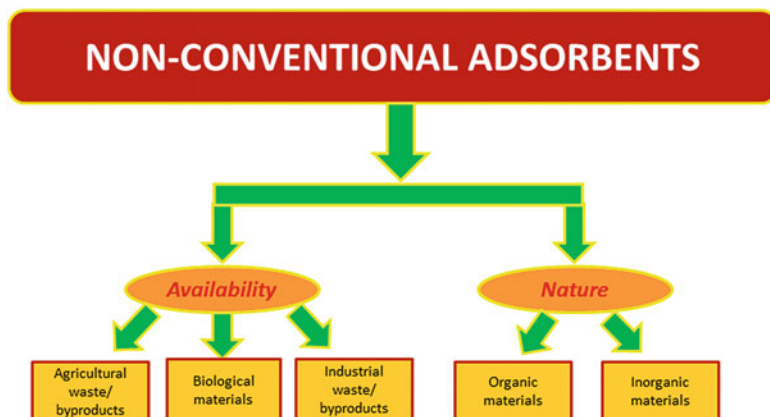
for the adsorption of metal ions from aqueous media are bentonite, montmorillonite, kaolinite, and sepiolite (Adeyemo et al. 2017). Abollino et al. (2008) investigated the adsorption behavior of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  on montmorillonite and vermiculite and reported the latter exhibited more adsorption capacity than the former. Kaolinite presents various adsorption sites responsible for the competition that exists in multielement system (Srivastava et al. 2005). For an equilibration time of 30 min, kaolinite presented strong ion exchange capacity towards Pb preceded by Ni, Cd, and Cu (Jiang et al. 2010). De-Pablo et al. (2011) reported that the adsorption capacity of montmorillonite and Ca-montmorillonite varies for different metal ions. Ca montmorillonite was found to be a superior adsorbent for Pb, Zn, Cr, Ba, Hg, Mn, and Ag, whereas montmorillonite exhibited good adsorption capacity for Cd, Cu, and Ni. Eloussaief et al. 2009 investigated the significance of pH and temperature for the adsorption of copper on pristine and acid treated clays.

## 15.6 Non – conventional Technologies for Heavy Metal Removal

Various conventional adsorbents have been found as potential adsorbents for metal removal from the aqueous environment. On the other hand, usage of these adsorbents is restricted because of its high operating cost. In this circumstance, where functional cost factor plays a crucial role, researchers are in need of low-cost eco-friendly adsorbent for wastewater treatment. Previously, few attempts have been made towards the development of cost-effective non-conventional adsorbents for heavy metals removal. These adsorbents can be classified based on their availability (agricultural waste, biological material, and industrial waste/by-products) and nature of the adsorbents (organic and inorganic materials). Figure 15.3 provides information about various non-conventional adsorbents for heavy metal removal.

### 15.6.1 Agricultural Waste/Byproducts

Recently, utilization of low-cost agriculture waste and byproducts as adsorbents for heavy metals is a growing interest for researchers. Agro-materials are considered as a promising material for heavy metal adsorption, due to its ease of availability and low cost (Jain et al. 2009, 2013, 2014; Meena et al. 2008). Various agro-materials such as rice husk, sugarcane bagasse, coconut waste, orange peel, sawdust, maize cob, jackfruit, sunflower head waste, sawdust, hazelnut and almond shell can be utilized as a low cost adsorbent for heavy metal removal after chemical treatment or conversion by heating into activated carbon (Ibrahim et al. 2006; Hameed et al. 2008; Hameed 2009). These agro-materials are mainly composed of cellulose,



**Fig. 15.3** Classification of non-conventional adsorbents

hemicellulose, lipids, protein, lignin, sugars components, water, and hydrocarbons, which consists of various functional groups such as carboxy, hydroxyl, sulphhydryl, amide, and amine (Bhatnagar and Sillanpää 2010). In general, the adsorption process occurs through complexation, hydrogen bonding, and ion exchange. Easy availability, the presence of large surface area and functional groups make different agricultural waste and byproducts good alternative to the expensive commercial adsorbents for heavy metal removal.

These agro-materials can be used directly (natural form) or after some physical/chemical modifications. Different types of agents such as organic compounds (ethylenediamine, formaldehyde, epichlorohydrin and methanol), organic acids (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid and citric acid) oxidizing agents (hydrogen peroxide), base solutions (sodium hydroxide, calcium hydroxide and sodium carbonate) and dyes have been used for pretreatment process (Grassi et al. 2012). Previously, various researchers demonstrated the heavy metal adsorption ability of agro-materials. Jain et al. (2009, 2013) successfully removed Cr from industrial wastewater by utilizing sunflower head waste as an adsorbent. Similarly, chemically modified sunflower waste has been used for Ni removal from aqueous solution (Jain et al. 2014). Zuorro et al. (2013) investigated the heavy metal adsorption ability of spent tea leaves for heavy metal adsorption. Spent tea leaves have adsorbed almost 2 g/l of Pb at 40 °C. Hegazi (2013) results highlighted that rice husk could be a better candidate for simultaneous removal of Fe, Pb, and Ni. Earlier, Meena et al. (2008) suggested that mustard husk would be a better component for Pb and Cd removal from aqueous solution.

### ***15.6.2 Biological Materials***

Adsorption of heavy metals by biological materials is an emerging area in the field of water treatment as it is a passive uptake process and is mostly reversible and metabolism-independent processes. The adsorption of heavy metals onto the cell surface of biological materials (bacteria, fungi and algal biomass) is known as biosorption (Arivalagan et al. 2014). The significant advantages of microbial biosorption are their low operational cost, simplicity, highly effective and environmentally friendly methodology (Fomina and Gadd 2014).

Cell wall composition of the microorganisms plays a crucial role in metal adsorption. Functional groups such as hydroxyl, carboxyl, sulfonate, amide and phosphate groups are mainly the metal uptake process from aqueous solutions (Karthik et al. 2016, 2017). The anionic nature of microbial surface enables them to bind metal cations through electrostatic forces. Gram-positive bacteria contain a thicker cell wall composed of peptidoglycan, teichoic and teichuronic acid, whereas in Gram-negative bacteria, teichoic, teichuronic acid is absent and the peptidoglycan layer is thinner. Gram-positive bacteria are more efficient in trapping metal ions compared to Gram-negative bacteria. Moreover, fungi are well known to tolerate and detoxify heavy metal contaminated effluents. Fungal cell wall consists of chitin and other polysaccharides along with proteins, lipids, polyphosphates as well as inorganic ions cementing the cell wall. Owing to greater cell-to-surface ratio, fungi have a greater tendency to come in physical and enzymatic contact with the surroundings. Fungal biomass is a good sorption material, as it can be easily cultured on a large scale using simple fermentation technique (Congeevaram et al. 2007). Similarly, the living and non-living biomass of algae is a predominant candidate for metal adsorption. Metal adsorption in living algae biomass is more complex than non-living biomass since adsorption and intracellular localization occur during the growth phase. On the other hand, uptake by non-living biomass takes place on the surface of the cell membrane, and it is considered as an extracellular process. Non-living algal biomass consists of sugar, cellulose, pectins, glycoproteins which are capable of binding to heavy metals as a cost-effective wastewater treatment. Several researchers have studied the usage of living and non-living microorganisms as adsorbent extensively (Arief et al. 2008).

### ***15.6.3 Industrial Waste/by-Products***

Industries are producing a large number of solid waste materials and byproducts, due to the numerous industrial activities. Various waste materials such as fly ash, red mud, magnetite, activated slags, iron waste and slags, hydrous titanium oxide and bagasse are being released into the environment, which can be utilized for heavy metal removal from wastewater (Ahmaruzzaman 2011). Industrial wastes are available easily, with free of cost and cause significant disposal problem. Utilization of

these industrial waste/byproducts will provide twofold benefits in environmental pollution management. Previously, many researchers reported that the use of various industrial waste and byproducts in heavy metal adsorption from aqueous solution. Pengthamkeerati et al. (2008) utilized biomass fly ash as an adsorbent for wastewater treatment. Mohammed et al. (2017) reported the heavy metal adsorption ability of various industrial wastes such as slag, fly ash and biomass ash in acid mine drainage in continuous stirred tank experiments. Among the industrial waste materials, fly ash showed maximum adsorption efficiency of Mn, Fe, Ni, Cu, Pb, Cd, Zn and As meanwhile slag and biomass ash showed significant adsorption efficiency of heavy metals. Similarly, Hegazi (2013) also documented the heavy metal (Cd and Cu) adsorption efficiency of fly ash.

### 15.6.3.1 Conclusion and Future Prospects

Heavy metal toxicity induces serious health risk on all kind of living forms. Several, remediation strategies have been implemented in the treatment of heavy metal ions. Technologies such as physicochemical have their advantages over metal remediation from environmental matrices. In recent years, development of eco-friendly, low-cost adsorbents for heavy metal removal from aqueous solutions have gained potential interest among the public and research community. Several conventional and non-conventional adsorbents have been investigated for their heavy metal adsorption ability from industrial wastewater. These adsorbents found to be more suitable for heavy metal adsorption from the aqueous environment.

On the other hand, before concluding them as a potential adsorbents need to carryout extensive research in following points: (i) enhance the removal efficiency of these adsorbents after appropriate treatment or modification, (ii) before going field application, cost factor should be analyzed and (iii) very few research literatures available about safe disposal of spent adsorbents. It should dispose of in an eco-friendly way. Thus, more research work should be made in this direction. If we could manage the above-stated characteristics, then these conventional and non-conventional adsorbents may offer significant advantages over the currently existing expensive physicochemical approaches.

## References

- Abdelatey LM, Khalil WKB, Ali TH, Mahrous KF (2011) Heavy metal resistance and gene expression analysis of metal resistance genes in gram positive and gram negative bacteria present in Egyptian soil. *J Appl Sci Environ Sanit* 6:201–211
- Abollino O, Giacomino A, Malandrino M, Mentasti E (2008) Interaction of metal ions with montmorillonite and vermiculite. *Appl Clay Sci* 38(3):227–236
- Adeyemo AA, Adeoye IO, Bello OS (2017) Adsorption of dyes using different types of clay: a review. *Appl Water Sci* 7(2):543–568



- Aelion CM, Davis HT, McDermott S, Lawson AB (2008) Metal concentrations in rural topsoil in South Carolina: potential for human health impact. *Sci Total Environ* 402:149–156
- Aguado J, Arsuaga JM, Arencibia A, Lindo M, Gascón V (2009) Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica. *J Hazard Mater* 163(1):213–221
- Ahmaruzzaman M (2011) Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Adv Colloid Interf Sci* 166(1–2):36–59
- An FQ, Wu RY, Li M, Hu TP, Gao JF, Yuan ZG (2017) Adsorption of heavy metal ions by iminodiacetic acid functionalized D301 resin: kinetics, isotherms, and thermodynamics. *React Funct Polym* 118:42–50
- Argun ME, Dursun S, Ozdemir C, Karatas M (2007) Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. *J Hazard Mater* 141(1):77–85
- Arief VO, Trilestari K, Sunarso J, Indraswati N, Ismadji S (2008) Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters, and mechanism studies. *Clean Soil Air Water* 36(12):937–962
- Arivalagan P, Singaraj D, Haridass V, Kaliannan T (2014) Removal of cadmium from aqueous solution by batch studies using *Bacillus cereus*. *Ecol Eng* 71:728–735
- Bhatnagar A, Sillanpää M (2010) Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment – a review. *Chem Eng J* 157:277–296
- Bissen M, Frimmel FH (2003) Arsenic – a review. Part I: occurrence, toxicity, speciation, mobility. *Acta Hydrochim Hydrobiol* 31:9–18
- Bruins MR, Kapil S, Oehme FW (2000) Microbial resistance to metals in the environment. *Ecotoxicol Environ Safe* 45:198–207
- Cervantes C, Campos-García J, Devars S, Gutiérrez-Corona F, Loza-Tavera H, Torres-Guzmán JC, Moreno-Sánchez R (2001) Interactions of chromium with microorganisms and plants. *FEMS Microbiol Rev* 25:335–347
- Chen J, Qu R, Zhang Y, Sun C, Wang C, Ji C, Yin P, Chen H, Niu Y (2012) Preparation of silica gel supported amidoxime adsorbents for selective adsorption of Hg (II) from aqueous solution. *Chem Eng J* 209:235–244
- Chibuie G, Obiora S (2014) Heavy metal polluted soils: effect on plants and bioremediation methods. *Appl Environ Soil Sci* 2014:1–12
- Congeevaram S, Dhanarani S, Park J, Dexilin M, Thamaraiselvi K (2007) Biosorption of chromium and nickel by heavy metal resistant fungal and bacterial isolates. *J Hazard Mater* 146(1–2):270–277
- De-Pablo L, Chávez ML, Abatal M (2011) Adsorption of heavy metals in acid to alkaline environments by montmorillonite and Ca-montmorillonite. *Chem Eng J* 171(3):1276–1286
- Di Natale F, Erto A, Lancia A, Musmarra D (2015) Equilibrium and dynamic study on hexavalent chromium adsorption onto activated carbon. *J Hazard Mater* 281:47–55
- Duruibe JO, Ogwuegbu MO, Egwurugwu JN (2007) Heavy metal pollution and human biotoxic effects. *Intern J Phy Sci* 2(5):112–118
- Eloussaief M, Jarraya I, Benzina M (2009) Adsorption of copper ions on two clays from Tunisia: pH and temperature effects. *Appl Clay Sci* 46(4):409–413
- Fashola M, Ngole-Jeme V, Babalola O (2016) Heavy metal pollution from gold mines: environmental effects and bacterial strategies for resistance. *Int J Environ Res Public Health* 13:1047
- Ferhat M, Kadouche S, Lounici H (2016) Immobilization of heavy metals by modified bentonite coupled coagulation/flocculation process in the presence of a biological flocculant. *Desalination Water Treat* 57(13):6072–6080
- Fomina M, Gadd GM (2014) Biosorption: current perspectives on concept, definition, and application. *Bioresour Technol* 160:3–14
- Gherasim CV, Krivčík J, Mikulášek P (2014) Investigation of batch electro dialysis process for removal of lead ions from aqueous solutions. *Chem Eng J* 256:324–334
- Goel J, Kadirvelu K, Rajagopal C, Garg VK (2005) Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies. *J Hazard Mater* 125(1):211–220
- Gogoasa I, Gergen I, Rada MA, Pârvu D, Ciobanu CA, Bordean D, Marunoiu C, Moigradea D (2006) AAS detection of heavy metals in sheep cheese (the Banat area, Romania). *Buletinul USAMV-CN* 62:240–245

- Gopal R, Dube BK, Sinha P, Chatterjee C (2003) Cobalt toxicity effects on growth and metabolism of tomato. *Commun Soil Sci Plant Anal* 34(5–6)
- Grassi M, Kaykioglu G, Belgiorno V, Lofrano G (2012) Removal of emerging contaminants from water and wastewater by adsorption process. In: Lofrano G (ed) *Emerging compounds removal from wastewater*, SpringerBriefs in green chemistry for sustainability, pp 15–37
- Gumpu MB, Sethuraman S, Krishnan UM, Rayappan JBB (2015) A review on detection of heavy metal ions in water – an electrochemical approach. *Sens Actuators B Chem* 213:515–533
- Hameed BH (2009) Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent. *J Hazard Mater* 162:344–350
- Hameed BH, Mahmoud DK, Ahmad AL (2008) Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (*Cocos nucifera*) bunch waste. *J Hazard Mater* 158:65–72
- Hegazi HA (2013) Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC J* 9(3):276–282
- Hongjie WA, Jin KA, Huijuan LI, Jiahui QU (2009) Preparation of organically functionalized silica gel as an adsorbent for copper ion adsorption. *J Environ Sci* 21(11):1473–1479
- Ibrahim SC, Hanafiah MAKM, Yahya MZA (2006) Removal of cadmium from aqueous solution by adsorption on sugarcane bagasse. *Am-Euras. J Agric Environ Sci* 1:179–184
- Ibrahimi MM, Sayyadi AS (2015) Application of natural and modified zeolites in removing heavy metal cations from aqueous media: an overview of including parameters affecting the process. *Int J Geo Earth Env Sci* 3:1–7
- Jain M, Garg VK, Kadirvelu K (2009) Equilibrium and kinetic studies for sequestration of Cr (VI) from simulated wastewater using sunflower waste biomass. *J Hazard Mater* 171(1–3):328–334
- Jain M, Garg VK, Kadirvelu K (2013) Chromium removal from aqueous system and industrial wastewater by agricultural wastes. *Bioresour J* 17(1):30–39
- Jain M, Garg VK, Kadirvelu K (2014) Removal of Ni (II) from aqueous system by chemically modified sunflower biomass. *Desalination Water Treat* 52(28–30):5681–5695
- Jiang MQ, Jin XY, Lu XQ, Chen ZL (2010) Adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite clay. *Desalination* 252(1):33–39
- Kabwadza-Corner P, Johan E, Matsue N (2015) Ph dependence of lead adsorption on zeolites. *J Environ Protect* 6(01):45
- Kadirvelu K, Faur-Brasquet C, Cloirec PL (2000) Removal of Cu (II), Pb (II), and Ni (II) by adsorption onto activated carbon cloths. *Langmuir* 16(22):8404–8409
- Karthik C, Oves M, Thangabalu R, Sharma R, Santhosh SB, Arulselvi PI (2016) *Cellulosimicrobium funkei*-like enhances the growth of *Phaseolus vulgaris* by modulating oxidative damage under Chromium (VI) toxicity. *J Adv Res* 7(6):839–850
- Karthik C, Ramkumar VS, Pugazhendhi A, Gopalakrishnan K, Arulselvi PI (2017) Biosorption and biotransformation of Cr (VI) by novel *Cellulosimicrobium funkei* strain AR6. *J Taiwan Inst Chem Eng* 70:282–290
- Kondo K, Kanazawa Y, Matsumoto M (2015) Adsorption of Noble metals using silica gel modified with surfactant molecular assembly containing an Extractant. *Sep Sci Technol* 50(10):1453–1460
- Li G, Zhao Z, Liu J, Jiang G (2011) Effective heavy metal removal from aqueous systems by thiol functionalized magnetic mesoporous silica. *J Hazard Mater* 192(1):277–283
- Liang J, Liu M, Zhang Y (2016) Cd (II) removal on surface-modified activated carbon: equilibrium, kinetics and mechanism. *Water Sci Technol* 74(8):1800–1808
- Lim SR, Schoenung JM (2010) Human health and ecological toxicity potentials due to heavy metal content in waste electronic devices with flat panel displays. *J Hazard Mater* 177:251–259
- Liu H, Feng S, Zhang N, Du X, Liu Y (2014) Removal of Cu (II) ions from aqueous solution by activated carbon impregnated with humic acid. *Front Environ Sci Eng* 8(3):329–336
- Malandrino M, Abollino O, Giacomino A, Aceto M, Mentasti E (2006) Adsorption of heavy metals on vermiculite: influence of pH and organic ligands. *J Colloid Interface Sci* 299(2):537–546
- Malik A (2004) Metal bioremediation through growing cells. *Environ Int* 30:261–278

- Mansoorian HJ, Mahvi AH, Jafari AJ (2014) Removal of lead and zinc from battery industry wastewater using electrocoagulation process: influence of direct and alternating current by using iron and stainless steel rod electrodes. *Sep Purif Technol* 35:165–175
- Marchioretto MM, Bruning H, Rulkens W (2005) Heavy metals precipitation in sewage sludge. *Sep Sci Technol* 40(16):3393–3405
- Meena AK, Kadirvelu K, Mishraa GK, Rajagopal C, Nagar PN (2008) Adsorption of Pb (II) and Cd (II) metal ions from aqueous solutions by mustard husk. *J Hazard Mater* 150(3):619–625
- Mehdipour S, Vatanpour V, Kariminia HR (2015) Influence of ion interaction on lead removal by a polyamide nanofiltration membrane. *Desalination* 362:84–92
- Mohammed NH, Atta M, Yaacub WZW (2017) Remediation of heavy metals by using industrial waste by products in acid mine drainage. *Am J Eng Appl Sci* 10(4):1001.1012
- Mohsen-Nia M, Montazeri P, Modarress H (2007) Removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from wastewater with a chelating agent and reverse osmosis processes. *Desalination* 217(1–3):276–281
- Moroni J, Scott B, Wratten N (2003) Differential tolerance of high manganese among rapeseed genotypes. *Plant Soil* 253:507–519
- Motsi T, Rowson NA, Simmons MJ (2009) Adsorption of heavy metals from acid mine drainage by natural zeolite. *Intern J Miner Process* 92(1):42–48
- Mukesh KR, Kumar P, Singh M, Singh A (2008) Toxic effect of heavy metals in livestock health. *Veterin World* 1:28–30
- Mureseanu M, Reiss A, Stefanescu I, David E, Parvulescu V, Renard G, Hulea V (2008) Modified SBA-15 mesoporous silica for heavy metal ions remediation. *Chemosphere* 73(9):1499–1504
- Murthy ZV, Parikh PA, Patel NB (2013) Application of  $\beta$ -Zeolite, Zeolite Y, and Mordenite as adsorbents to remove mercury from aqueous solutions. *J Dispers Sci Technol* 34(6):747–755
- Nagajyoti P, Lee K, Sreekanth T (2010) Heavy metals, occurrence and toxicity for plants: a review. *Environ Chem Lett* 8:199–216
- Najafi M, Yousefi Y, Rafati AA (2012) Synthesis, characterization and adsorption studies of several heavy metal ions on amino-functionalized silica nano hollow sphere and silica gel. *Sep Purif Technol* 85:193–205
- Park HG, Kim TW, Chae MY, Yoo IK (2007) Activated carbon-containing alginate adsorbent for the simultaneous removal of heavy metals and toxic organics. *Process Biochem* 42(10):1371–1377
- Pengthamkeerati P, Satapanajaru T, Chularuengoksorn P (2008) Chemical modification of coal fly ash for the removal of phosphate from aqueous solution. *Fuel* 87(12):2469–2476
- Pillay K, Cukrowska EM, Coville NJ (2009) Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution. *J Hazard Mater* 166(2):1067–1075
- Ren Y, Abbood HA, He F, Peng H, Huang K (2013) Magnetic EDTA-modified chitosan/SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> adsorbent: preparation, characterization, and application in heavy metal adsorption. *Chem Eng J* 226:300–311
- Salam OE, Reiad NA, Elshafei MM (2011) A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *J Adv Res* 2(4):297–303
- Salmani MH, Davoodi M, Ehrampoush MH, Ghaneian MT, Fallahzadah MH (2013) Removal of cadmium (II) from simulated wastewater by ion flotation technique. *Iran J Environ Health Sci Eng* 10(1):16
- Shaker MA (2014) Dynamics and thermodynamics of toxic metals adsorption onto soil-extracted humic acid. *Chemosphere* 111:587–595
- Sharma RK, Agrawal M, Marshall F (2007) Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. *Ecotoxic Environ Safe* 66(2):258–266
- Sharma RK, Agrawal M, Marshall FM (2009) Heavy metals in vegetables collected from production and market sites of a tropical urban area of India. *Food Chem Toxic* 47(3):583–591
- Sofinska-Chmiel W, Kolodynska D (2017) Application of ion exchangers for purification of galvanic wastewater from heavy metals. *Sep Sci Technol*. Accepted
- Srivastava P, Singh B, Angove M (2005) Competitive adsorption behavior of heavy metals on kaolinite. *J Colloid Interface Sci* 290(1):28–38

- Tajar AF, Kaghazchi T, Soleimani M (2009) Adsorption of cadmium from aqueous solutions on sulfurized activated carbon prepared from nut shells. *J Hazard Mater* 165(1):1159–1164
- USEPA (United States Environmental Protection Agency) (1997) Mercury study report to congress, vol 3. USEPA, Washington, DC
- Vinodhini PA, Sudha PN (2017) Removal of heavy metal chromium from tannery effluent using ultrafiltration membrane. *Text Cloth Sustain* 2(1):5
- Wingenfelder U, Hansen C, Furrer G, Schulin R (2005) Removal of heavy metals from mine waters by natural zeolites. *Environ Sci Technol* 39(12):4606–4613
- Wu P, Wu W, Li S, Xing N, Zhu N, Li P, Wu J, Yang C, Dang Z (2009) Removal of Cd<sup>2+</sup> from aqueous solution by adsorption using Fe-montmorillonite. *J Hazard Mater* 169(1):824–830
- Wuana RA, Okieimen FE (2011) Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *ISRN Ecol*:1–20
- Xiang B, Fan W, Yi X, Wang Z, Gao F, Li Y, Gu H (2016) Dithiocarbamate-modified starch derivatives with high heavy metal adsorption performance. *Carbohydr Polym* 136:30–37
- Yasri NG, Gunasekaran S (2017) Electrochemical Technologies for Environmental Remediation. In: Enhancing cleanup of environmental pollutants. Springer, Cham, pp 5–73
- Zarghami Z, Akbari A, Latifi AM, Amani MA (2016) Design of a new integrated chitosan-PAMAM dendrimer biosorbent for heavy metals removing and study of its adsorption kinetics and thermodynamics. *Bioresour Technol* 205:230–238
- Zhao H, Wu L, Chai T, Zhang Y, Tan J, Ma S (2012) The effects of copper, manganese and zinc on plant growth and elemental accumulation in the manganese-hyperaccumulator *Phytolacca americana*. *J Plant Physiol* 169(13):1243–1252
- Zuorro A, Lavecchia R, Medici F, Piga L (2013) Spent tea leaves as a potential low-cost adsorbent for the removal of Azo dyes from wastewater. *Chem Eng Trans* 32:19