POLYMERIC MATERIALS FOR METAL SORPTION FROM HYDRIC RESOURCES

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Introduction

Pure water is crucial for global population. However, there are many sources of pollutants that contribute to the upscaling contamination of hydric resources. Among the pollutants, heavy metals are the highest concern since they are responsible for several diseases and disorders in living beings. A wide range of industrial activities, such as mining, metal processing, petroleum refining, electroplating, battery manufacturing, textiles, tanneries, pigment manufacture, paint manufacture, printing, photography industries, and pesticides, are responsible sources for the releasing of metals into the environment (Ahmaruzzaman, 2011). Thus, it is of extreme importance to remove these pollutants from water for its consumption. Several physical and chemical methods, such as chemical precipitation, filtration, coagulation, membrane processes, ion exchange, and adsorption have been used to remove metal ions from water (Kołodyńska, 2013). Nevertheless, these methods have limitations. For instance, when the metal's concentration is in the range of $1-100\,mg/L$, precipitation and coagulation lose effectiveness and became more expensive. The high costs, associated to the complexity and low removal efficiency, limit the use of membrane processes for heavy metal removal (Mark et al., 2006). Therefore, among the techniques, the adsorption process can be highlighted.

Adsorption is a highly efficient method that provides flexibility in the design and it is easy to operate (Zhong et al., 2014). Activated carbon is one of the most widely used materials for this purpose, but it still suffers from costly regeneration and high attrition rate (Pan et al., 2009). Due to their vast surface area, perfect mechanical rigidity, adjustable surface chemistry and pore size distribution, and feasible regeneration under mild conditions, polymeric adsorbents emerged as potential alternatives to activated carbon (Pan et al., 2009). Polymers with chelating properties are of great interest since they are suitable for metal-ion removal by ultrafiltration (Barakat and Schmidt, 2010) and can also be incorporated in a solid support, such as membranes (Bessbousse et al., 2012). Several polymers based on polysaccharides, specially chitosan, are reported as metal sorbents (Pontoni and Fabbricino, 2012), but more can be found with different chelating groups (Repo et al., 2013; Biçak et al., 2000; Hussein et al., 2014; Rahman et al., 2014; Reddy and Reddy, 2003).

Fig. 8.1 depicts the increased interest in the removal of several metal ions from hydric resources. It is the result of searching in Scopus database using the following combination of words, present in the publication title: "metal or symbol (i.e., lead or Pb)," "water," and "sorption or removal." Although it may only be

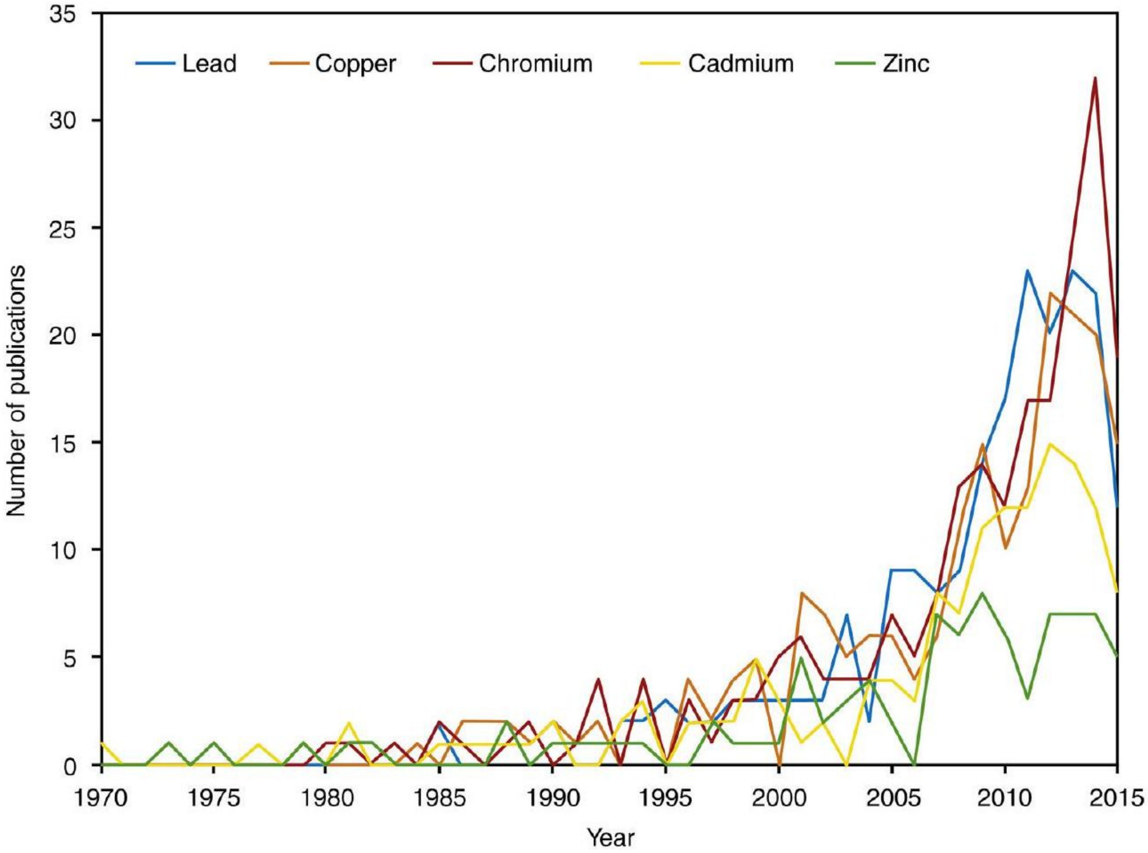

Figure 8.1. Evolution of the publication number along the years in the field of water remediation, specifically in lead, copper, chromium, and cadmium removal. Data obtained on July 27, 2015.

representative of this research field, since it is dependent on the searching keywords that were used, it is possible to observe an increasing number of publications from the 1990s to 2014. Comparing the five metal ions represented in the image, it is possible to notice that zinc, probably due to its well-known biochemistry, is the one that attracts less attention from researchers. The remaining metal ions, lead, copper, and chromium, are those that most concern the scientific society, being in 2014, chromium the one with the highest number of publications.

This chapter will focus on the adsorption process, which is a highly efficient method that provides flexibility in the design and is easy to operate (Zhong et al., 2014). It will be given a description of several phases related with this purification method. Moreover, it will also be described several parameters that can influence the adsorption process and several isotherm models used in the assessment of the sorption efficiency of adsorbent materials.

Polymeric adsorbents arise as potential alternatives to activated carbon, the most used adsorbent. For that reason, this chapter will give special emphasis to polymeric materials with chelating properties, most of them biopolymers obtained from natural wastes, that have been reported as adsorbents of metal ions from hydric resources, specifically for $Cu(II), Cd(II), Zn(II), Cr(VI)$, and $Pb(II)$, and their efficiency as metal adsorbents. Fig. 8.2 depicts a periodic table where lead (Pb) and the transition metals copper (Cu), cadmium (Cd), zinc (Zn), and chromium (Cr) are highlighted. Since the sorption of heavy metals is related to the formation of coordination compounds, it is important to give same insights about coordination chemistry to better understand the sorption process.

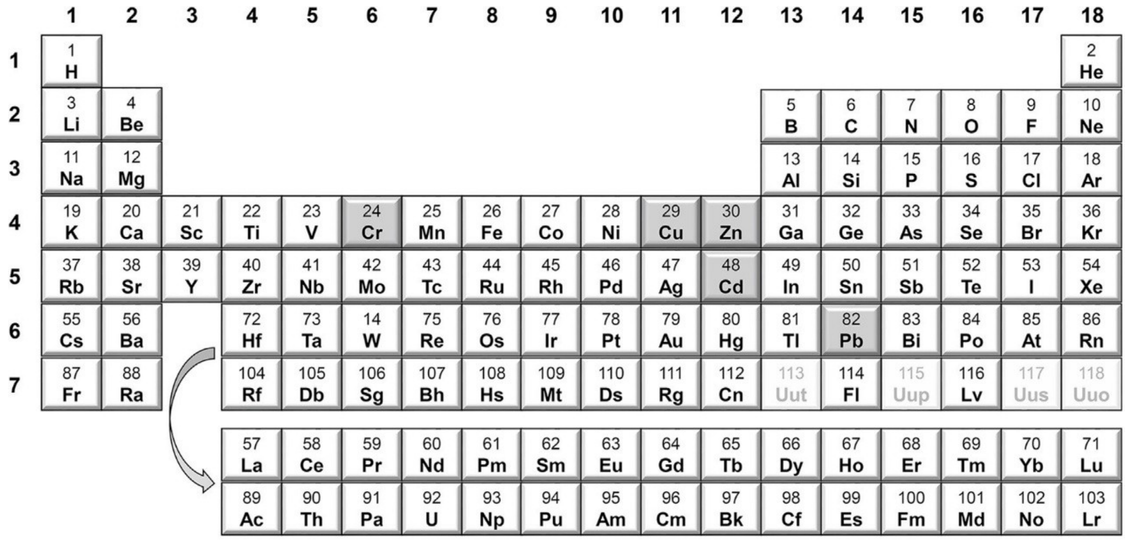

Figure 8.2. Periodic table. Elements discussed in the text are highlighted. Faded elements are under revision by IUPAC. Adapted from IUPAC, 2015. International Union of Pure and Applied Chemistry (IUPAC). Available from: http://www.iupac.org/

The Adsorption Process

The adsorption process is one of the several strategies that can be used in wastewater treatment. The concept of this method is based on removing pollutants from the water by promoting their adsorption at the adsorbent surface. It can be applied for organic or inorganic pollutants and, in both cases, the sorption process and its efficiency can be evaluated using several isotherm models (Section 4).

Wastewater treatment by adsorption involves several steps that can be divided into four stages, according to Fig. 8.3.

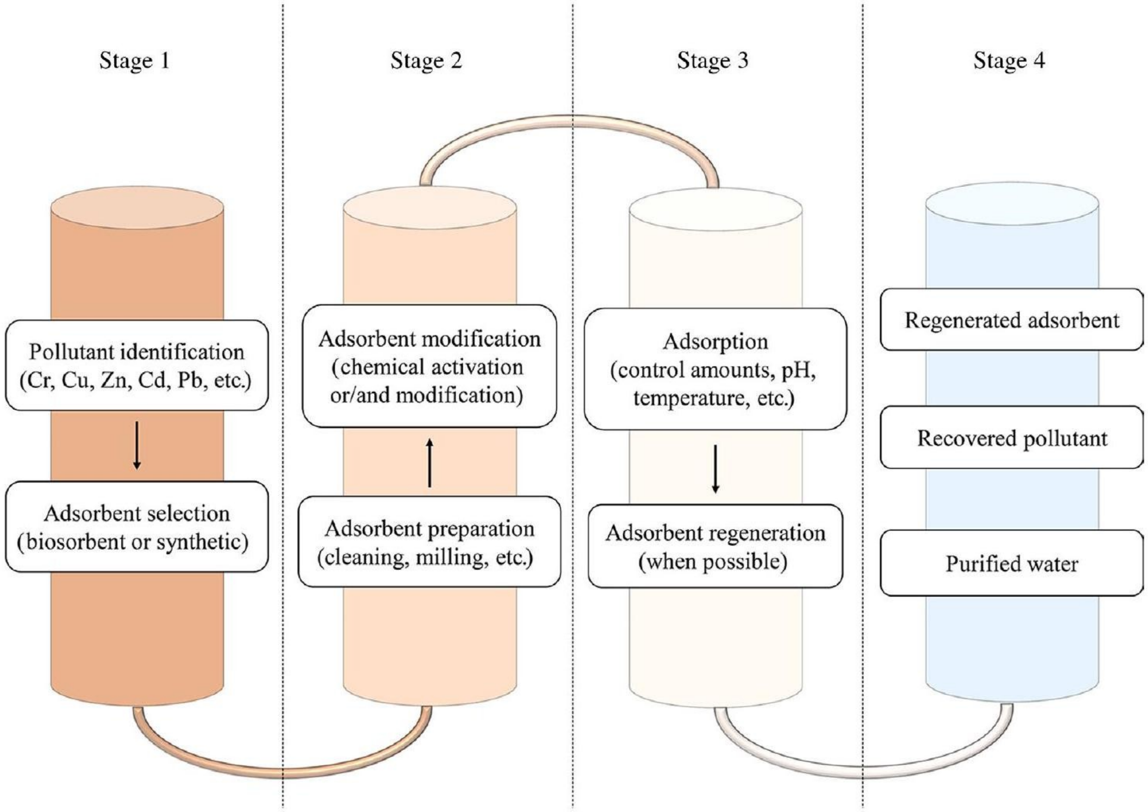

Figure 8.3. Adsorption process divided into stages, from identification of the pollutant to obtaining the toxin-free water.

Stage 1 corresponds to the identification of the problem (pollutant) and its solution (adsorbent). The pollution may be due to one or several toxins, which in the context of this chapter is a heavy metal, that upon identification will allow to select an adsorbent that can be obtained from natural resources, such as plants or crustacean shells wastes, or synthesized.

Stage 2 is associated with the preparation of the adsorbent that should accomplish several requirements. Adsorbents obtained from natural resources need to be cleaned before usage, in order to eliminate contaminants, such as dirt or undesired residues. In this stage, the adsorbents are also submitted to a milling process to obtain materials with controlled size. Additionally, the materials can be submitted to a chemical treatment that will activate functional groups on their surface or introduce new and/or more efficient functional groups. It is crucial to perform a full characterization of the adsorbent material in order to obtain information about its properties, such as chemical composition, surface morphology, and thermal stability, among others, thus its adsorption capacity can be easily predicted and understood.

Stage 3 corresponds to the sorption process itself. In this stage, the adsorption process is studied, testing different conditions, such as amounts of adsorbent and adsorbate, pH , and temperature, among others, in order to optimize the process. As part of this study, isotherm models are used to evaluate the adsorption efficiency. Also in this stage, the possibility of reuse the adsorbent material is evaluated. The coordination compounds formed during the adsorption are hydrolyzed allowing the recovery of the initial adsorbent and to obtain a concentrated solution of the pollutants, which can be properly eliminated or transformed in industries. If the material allows the regeneration, it is necessary to determine the number of cycles sorption/regeneration that can be performed without losing efficiency. It is also important to characterize the regenerated material in order to determine if its properties remain unchanged.

In the final stage, the purification is completed and heavy met-al-free water is obtained, as well as the pollutant and the regenerated adsorbent, when regeneration is possible.

Insights in Coordination Chemistry

Specifically for inorganic pollutants, the adsorption purification consists of the coordination of the metal ions by the adsorbent and, for that reason, in this section basic insights into coordination chemistry will be given.

Transition metals, and other metals, such as lead or aluminum, are known for their Lewis acids metal ions that have the capacity to form coordination compounds. These coordination compounds correspond to Lewis acid-base pairs in which the Lewis base is a molecule or ion that can donate a pair of electrons, known as ligands.

Both Lewis acids and bases are classified as hard or soft accordingly to Pearson concept. Hard metals are those with high charge/ ionic radii ratio and with high polarizing capacity (early to middle d block and f block) and are preferably coordinated by hard donors, which have high electronegativity and are not easily polarized (F, O, N, Cl, HO-, and π-donors). Soft metals (zero-oxidation state or late d- and p-block metals), have low charge/ionic radii ratio and low polarizing capacity, are preferably coordinated by soft donors (I, S, P, $H^{-¿¿}$, CO, and alkenes), due to medium electronegativity are easily polarized and are π-acceptors.

Although of being cations, due to their electronegativity, metal ions do not form ionic bonds, since there are pair of electrons being shared with the donor atom. However, it is not shared equally by the two atoms, likewise it happens in a covalent bond. Thus, metal ions form coordination bonds, which are chemicals bonds with intermediate character between ionic and covalent bonds.

Due to the empty orbitals in their valence shell, metal ions can accept several pairs of electrons. Nevertheless, the number of ligands in a coordination compound, which is known by coordination number (CN), is limited by the metal's ionic radii, its electronic configuration, and the ligands' size. Thus, it is possible to found coordination compounds with CN ranging from 2 up to 12, being 6 the most common CN.

The ligands found in coordination compounds can be classified as mono- or polydentates ligands or chelators, accordingly to their denticity (number of donor atoms). Fig. 8.4 depicts the coordination of a metal ion by mono- and bidentate ligands. As it can be seen in Fig. 8.4B, when a polydentate ligand coordinates a metal ion they form a ring resulting in coordination compounds known as chelates. Nevertheless, polydentate ligands can themselves be cyclic compounds prior the coordination. They are known as macrocyclic chelators if they fulfill the requirements of having a minimum of nine atoms of which, at least, three of them are donor atoms (Fig. 8.4C). Thus, these type of ligands can be subdivided into open chain or macrocyclic chelators.

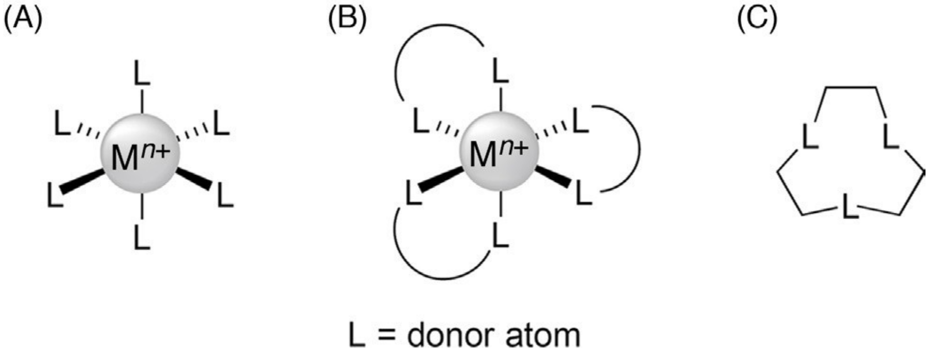

Figure 8.4. Schematic representation of monodentate ligands (A) and bidentate ligands (B) coordinating a metal ion with coordination number 6 and the basic structure of a macrocyclic chelator (C).

Another issue that is important to take into account in what concerns coordination compounds is their thermodynamic stability, usually associated to its formation constant $(\log \beta)$. Taking into consideration the variation of the Gibbs free energy (ΔG) Eq. (8.1), where ΔH is the variation of enthalpy, T the temperature, and ΔS the entropy of the system, which gives insights about the spontaneity of the formation reaction, it possible to find out that only three parameters are affecting it. Thus, taking as an example the coordination of a given metal ion ($M^{n+¿¿}$) with $CN=6$ by ammonia (NH_3) or ethylenediamine (en) [Eq. (8.2 and 8.3)] in aqueous solution, and performing the reaction at the same temperature, it is easy to understand that enthalpy and entropy assume higher importance. Nevertheless, ammonia and ethylenediamine are very similar and ΔH will not diverge considerably, but they have very different contribution to ΔS, which is in fact the most important parameter involved in the formation of coordination compounds. This effect is even more pronounce for chelators with higher denticity. When the chelator is a macrocyclic ligand, in addition to the entropic contribution, the fact that the chelator has less degrees of conformation, the formation constant is even higher. This is known as the macrocyclic effect.

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

(8.1)

¿¿

¿

Adsorption Isotherms

The phenomenon of retention/release or mobility of a certain substance from aqueous medium to a solid phase at a constant temperature and pH can be described by an invaluable curve, known as adsorption isotherm (Memon et al., 2007). In particular to metal ions, their distribution between the sorbent matrix and the solution, at equilibrium, is crucial for the determination of matrix's maximum adsorption capacity (Karnitz et al., 2007).

Several equilibrium isotherm models have been proposed for the analysis of the adsorption process, including Langmuir, Freundlich, Brunauer-Emmett-Teller, Redlich-Peterson,

Dubinin-Radushkevich, Temkin, Toth, Koble-Corrigan, Sips, Khan, Hill, Flory-Huggins, and Radke-Prausnitz isotherm. These models can be divided according to their fundamental approach: kinetics, thermodynamics, or potential theory (Kumar and Bandyopadhyay, 2006).

Since this chapter is dedicated to polymeric materials used to metal adsorption and these models are reviewed elsewhere (Kumar and Bandyopadhyay, 2006), only the Langmuir and Freundlich isotherm models will be briefly described.

The Freundlich Isotherm

The Freundlich isotherm, presented by Freundlich in 1906 (Gaballah et al., 1997), was the first isotherm model proposed for sorption processes. It can be applied for nonideal sorption on heterogeneous surfaces, as well as, multilayer sorption.

Eq. (8.4) represents the linear form of the Freundlich equation that can be fitted according to Eq. (8.5), where q is the metal's uptake per unit weight of sorbent (mg/g), C_e corresponds to the residual concentration at equilibrium of the metal ion in solution (mg/L), K_f is the sorption capacity (mg/g), and $1/n$ the sorption intensity (Karnitz et al., 2007). The slope, $1/n$, allows to understand the adsorption process. A variation in the slope between 0 and 1 is associated with a chemisorption process, which is more heterogeneous as the value gets closer to 0 . When a slope above 1 is observed, it is consistent with a cooperative adsorption (Kumar and Bandyopadhyay, 2006).

$$q = K_f C_e^{1/n}$$

(8.4)

$$\log q = \log K_f + \frac{1}{n} \log C_e$$

(8.5)

Due to lack in fundamental thermodynamic basis, since there is no approach to Henry's law at vanishing concentrations, this represents a limitation of this isotherm model (Huang et al., 2013).

The Langmuir Isotherm

The Langmuir isotherm was first described by Irving Langmuir (Zein et al., 2010) when studying the gas-solid adsorption onto activated carbon. This model proposes a monolayer adsorption occurring at finite and definite localized sites. These adsorption sites are identical and equivalent, and there is no lateral interaction and steric hindrance between adsorbed molecules (Huang et al., 2012). Graphically, Langmuir isotherm displays a typical plateau that corresponds to the equilibrium saturation point at which a molecule occupies one site and there is no further adsorption (Kumar and Bandyopadhyay, 2006).

The nonlinear form of the Langmuir adsorption isotherm is expressed according to Eq. (8.6), in which q_e is the amount adsorbed at equilibrium (mg/g), Q_0 the maximum adsorption capacity of the adsorbent (mg/g), b the Langmuir isotherm constant (dm^3/mg), and C_e the concentration at the equilibrium (mg/L). Langmuir isotherm has four linear forms that are represented by Eqs. (8.7-8.10).

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{8.6}$$

$$\frac{C_e}{q_e} = \frac{1}{b Q_0} + \frac{C_e}{Q_0} \tag{8.7}$$

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{b Q_0 C_e} \tag{8.8}$$

$$q_e = Q_0 - \frac{q_e}{b C_e} \tag{8.9}$$

$$\frac{q_e}{C_e} = b Q_0 - b q_e \tag{8.10}$$

Limitations to the Adsorption Process

The adsorption process is affected by several parameters, including the chemical nature of the adsorbent, its surface properties, and operational parameters (Pathak et al., 2015).

As it can be seen in Section 2, the coordination phenomenon of a metal ion is dependent on the type of ligand (mono or polydentate ligand) and on the functional groups present on those ligands. Thus, the chemical nature of the adsorbent is an aspect that should be taken into account to understand which functional groups will provide better results for a given metal ion. More suitable chelating groups will for sure increase the efficiency in removing the heavy metal. Nevertheless, it is also an important aspect of the adsorbents that they can be reused for the larger number of cycles sorption/regeneration as possible, and a highly efficient sorbent material can have its regeneration limited due to the high affinity for the metal ion. Thus, when new adsorbents are developed, it is important to reach an equilibrium between sorption efficiency and regeneration capacity.

In what concerns the surface of the adsorbent, there are several conditions affecting the adsorption process. The surface area of the adsorbent limits the contact area between adsorbent and adsorbate. Nevertheless, a large surface area is not important if the functional groups on the surface are not suitable for coordinating a metal ion. The pH of the surface is also important, since it can compromise the functional groups affinity for the metal ion. Other parameters, such as porosity, particle and bulk densities, and thermal properties can limit the adsorption process of a given material.

The adsorption process is also highly limited by the operation parameters used, such as amount of adsorbent, initial concentration of the adsorbate, particle size, pH of the medium, contact time, temperature, and stirring speed (Pathak et al., 2015). Increasing the amount of adsorbent in the adsorption results in higher number of binding sites for metal ions, which results in the enhancement of the removal percentage. Nevertheless, upon reaching an equilibrium, it is not possible to further increase the removal percentage by adding more adsorbent. The initial concentration of adsorbate influences the mass transfer between the bulk phase and the adsorbent. Thus, using higher initial concentration of adsorbate will result in higher loading capacities. The particle size of the adsorbent controls the surface area, and, as it was already referred, this parameter has high influence on the sorption process. The pH of the medium is of high importance in these type of processes, since it can influence the functional groups affinity for the metal ions and the chemical speciation of the cations. A controlled increasing of the pH can provide better sorption results. However, high pH may also promote the precipitation of other inorganic compounds rather than promoting adsorption of the metal ions. Each metal ion or chelator has its specific properties that influence the chemical processes occurring during adsorption, thus, not all systems respond in a similar way. These dissimilarities may result in systems that require longer time to reach an equilibrium. Therefore, it is of high importance that absorbent and adsorbate can be in contact for a time period suitable that makes possible the occurrence of the adsorption process. It is known that temperature influences the thermodynamic parameters of chemical reactions. At higher temperatures, the medium displays lower viscosity and the adsorbate has higher mobility in solution. This fact enhances the adsorption rates, which will influence the sorption process. Some authors observed in their works that the stirring speed used in the sorption assays influenced the adsorption process. This parameter can overcome the boundarylayer mass-transfer resistance that the adsorbate experiences, resulting in higher adsorption rates (Pathak et al., 2015).

As it is possible to notice, there are several parameters that can influence the adsorption capacity of a given adsorbent. Thus, different results can be achieved just by changing one parameter. Due to this, there are in the literature several works studying the same systems but reporting different efficiencies. This can be attributed to the problems in establishing a standard procedure for the determination of sorption efficiencies. However, it is of high concern that this standard can be established, so more accurate results' comparisons can be performed.

Polymeric Materials for Metal Sorption

As known, activated carbon is the most-used material as adsorption matrix for water remediation, however, due to its high cost other materials are attracting the researchers' attention. Among these materials, cellulose, chitin, and starch (Fig. 8.5), the most-abundant biopolymers on earth (Wan Ngah and Hanafiah, 2008; Wang and Huang, 2012), are ecofriendly adsorbents that have been tested for metal sorption. Cellulose is one of the main constituents of plants while chitin is found, for instance, in exoskeletons of crustaceous and starch, which is a mixture of amylopectin and amylose, is the energy storage material of living plants.

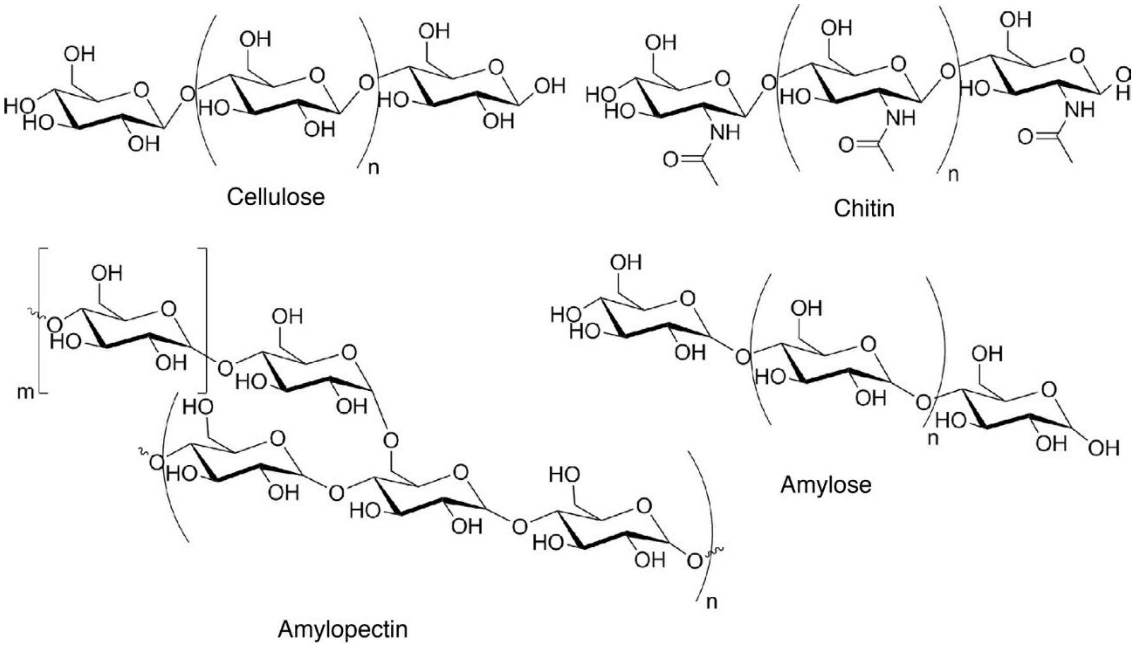

Figure 8.5. Chemical structure of biopolymers present in plants and crustaceous shells wastes used in adsorption studies.

The excellent adsorption behavior of these polysaccharides is related to the high number of hydroxyl groups that confer high hydrophobicity, the presence of large number of functional groups and their high reactivity, and the flexibility of the polymer's chain (Wang and Huang, 2012).

The advantage of using such materials is related to their availability, associated low costs, being easily regenerated, ecofriendly nature, and the minimization of toxic sludge (Singha and Guleria, 2014).

Cellulosic materials for removal of toxic metal ions include agricultural wastes, such as tea and coffee waste, saw dusts, pinus bark, coconut husk, modified cellulosic materials, corncobs, sugarcane bagasse, agave bagasse, and different agricultural byproducts (Singha and Guleria, 2014).

Although plant wastes can be directly used in the removal of heavy metals from wastewaters, it has several disadvantages. Since these wastes contain soluble organic compounds that are released during the sorption process, they can influence the oxygen content of the water causing problems to aquatic life (Wan Ngah and Hanafiah, 2008). Thus, it is of high concern to avoid this environmental threat, which can be achieved by chemical modification of these wastes. Additionally, this modification can also be of high importance since, depending on the method applied, can result in materials with enhanced sorption capacity (Gaballah et al., 1997). Among others, treatment with alkaline solutions, acid solution, and oxidizing agents are commonly reported in the literature. Usually, treatment of plant wastes with alkaline solutions result in materials with higher chelation capacity than those treated with acids. This is due to the fact that bases promote deprotonation of functional groups, which consequently results in better metal-ion coordinating groups.

Chromium

Chromium, with the electronic configuration $[Ar]3\ d^5 4\ s^1$, belongs to group 6, fourth period, of the periodic table. It can be found in several oxidation states, and among them, Cr (III) and $Cr(VI)$ are the most important. This metal is suggested as micronutrient for humans, but it is found in such low quantities in human body that its deficiency determination is based on observation of beneficial changes with chromium supplementation (Vincent, 2000). Cr(VI), due to it solubility, permeability through biological membranes, and interactions with biological molecules, such as proteins and nucleic acids, constitutes higher risk to human health than Cr (III) (El-Sherif et al., 2013). Cr (VI) is associated to several diseases, including liver, kidney, lung, and gastrointestinal cancers (Saygi et al., 2008). Among others, tannery industry widely uses Cr(III) and is responsible for its release in nature. However, it has been shown that Cr (III) can be oxidized to $Cr(VI)$ in the tannery sludge (Apte et al., 2005) that increases health risks. Thus, it is necessary to remove this contaminant from hydric resources, and several studies with polymeric materials can be found in literature. Table 8.1 summarizes the sorption capacity of several materials that have been reported for $Cr(III)/$¿ (VI) removal.

Gupta and Babu (2009) tested sawdust as biosorbent for removal of $Cr(VI)$, finding a sorption capacity of $41.52\,mg/g$ for this material. Baral et al. (2006) studied sawdust from Shorea robusta pretreated with formaldehyde and sulfuric acid. The authors observed that this material has a Cr (VI) sorption capacity of $9.55\,mg/g$. Sawdust from oak tree was also tested, by Argun et al. (2007), for Cr(VI) sorption. In this case, the authors found a sorption capacity of only $1.74\,mg/g$. The sorption of Cr (III) was studied by Li et al. (2007) using two plant wastes, sawdust from poplar trees, and peanut husk. In the case of sawdust, the authors did not preform any type of chemical modification, only washed the material with deionized water, and found that it shows a Cr (III) sorption capacity of $5.52\,mg/g$. In the case of the peanut husk, formalin and sulfuric acid were used to pretreat the wastes. In this case, a sorption capacity of $7.67\,mg/g$ was found. Nasernejad et al. (2005), also for Cr(III), tested carrot residues pretreated with hydrochloric acid as metal-ion biosorbents, and found that this material has a maximum sorption capacity of $45.09\,mg/g$. Rao et al. (2014) used Artimisia absinthium's seeds as biosorbents for Cr(VI), among others, and found that this material has a sorption capacity of $46.99\,mg/g$. Deseeded sunflower head was tested by Jain et al. (2013) for Cr(VI) removal, who had shown that, upon treatment with formaldehyde, this waste has a sorption capacity of $7.9\,mg/g$. A highest sorption capacity of $31.45\,mg/g$, at 319 K , was evidenced by Doke et al. (2012) when tested wood apple shell for the $Cr(VI)$ biosorption. Chen et al. (2009) pretreated tobacco leaf with several solvents in order to extract its polyphenols. The material obtained was tested for $Cr(VI)$ showing a sorption capacity of $113.2\,mg/g$. A phosphoric acid treatment, followed by

Table 8.1 Polymeric Materials Tested for Cr(III)/(VI) Removal Discussed in the Text

Material	$Q_0(mg/g)$	References
Sawdust		
Sawdust	41.52	Gupta and Babu (2009)
S. robusta treated with formaldehyde in sulfuric acid	9.55	Baral et al. (2006)
Oak treated with hydrochloric acid	1.74	Argun et al. (2007)
Poplar trees	5.52	Li et al. (2007)
Peanut husk treated with formalin in sulfuric acid	7.67	Li et al. (2007)
Carrot treated with hydrochloric acid	45.09	Nasernejad et al. (2005)
A. absinthium seeds	46.99	Rao et al. (2014)

Sunflower head treated with formaldehyde	7.9	Jain et al. (2013)
Wood apple shell	31.45	Doke et al. (2012)
Tobacco-leaf treated with distilled water, ethanol, and acetone	113.2	Chen et al. (2009)
T. nudiflora's fruit peel treated with phosphoric acid	294.12	Bhattacharya et al. (2013)
Olive pomace	4.0	El-Sheikh et al. (2011)
L. japonica	59.35	Wang et al. (2008)
P. yezoensis Ueda	56.32	
Rice bran	58.89	
Wheat bran	40.48	
Pine needles treated with ammonia	477.2	Chauhan et al. (2005)
Cellulose-g-poly(GMA)	393.6	
Cellulose-g-poly(GMA-co-AAm)	983.6	
Cellulose-g-poly(GMA-co-AAc)	655.6	
Cellulose-g-poly(GMA-co-AN)	852.4	
Starch-g-poly(DMA-co-AAc)	6.70	Kolya et al. (2015)
CAPE	48.5	Saleh et al. (2015)
GCB	202.4	Wang and Ge (2014)
CGP	165.6	Karthik and Meenakshi (2014b)
CCGP	179.2	
α-Cyclodextrin	24.2	Sikder et al. (2013)
β-Cyclodextrin	21.0	
γ-Cyclodextrin	18.6	
PVA/PANI composite	111.2	Karthik and Meenakshi (2014a)

heat exposure, was the method adopted by Bhattacharya et al. (2013) in order to activate the surface of Trewia nudiflora's fruit peel, which was tested for Cr (VI) sorption. The authors were able to prepare a material with a higher sorption capacity than those already mentioned, $294.12\, mg/g$. Olive pomace was described by El-Sheikh et al. (2011) to have a $Cr(VI)$ sorption capacity of $4.0\, mg/g$ that can be enhanced by pyrolysis of the material. Wang et al. (2008) studied Cr(VI) sorption by four biomaterials: Laminaria japonica, Porphyra yezoensis Ueda, rice bran, and wheat bran. While the first-three materials revealed, at $30^{\circ} C$, similar sorption capacity ($59.35, 56.32$, and $58.89\, mg/g$, respectively), wheat bran can only reach $40.48\, mg/g$. Chauhan et al. (2005) investigated the possibility of using cellulose extracted form pine needles and four derived grafted copolymers, cell-g-poly(GMA), cell-g-poly(GMA-co-AAm), cell-g-poly(GMA-co-AAc), and cell-g-poly(GMA-co-AN), for the sorption of $Cr(VI)$ and $Cu(II)$ (discussed further in the chapter), among other metal ions. The authors found that the cellulose itself has a sorption capacity of $477.2\, mg/g$ for $Cr(VI)$, which is compromised and decrease to $393.6\, mg/g$ when glycidyl methacrylate (GMA) is grafted onto cellulose surface. Nevertheless, the copolymerization of acrylamide (AAm), acrylic acid (AAc), and acrylonitrile (AN) increased considerably the sorption capacity, achieving $983.6\, mg/g$ in the case of cell-g-poly(GMA-co-AAm). Kolya et al. (2015) reported the grafting of poly(N,N-dimethylacrylamide-co-acrylic acid) [poly(DMA-co-AAc)] onto maize starch. This material revealed a sorption capacity of $6.70\, mg/g$. Sikder et al. (2013) preformed the crosslinking of the three most-common cyclodextrins (α, β, and γ-cyclodextrin) with epichlorohydrin in order to produce Cr (VI) sorption matrices. The authors showed that as the size of cyclodextrin increases (α to γ) their sorption capacity decreases, obtaining a maximum of $24.2\, mg/g$ for the α-cyclodextrin derivative. Polyvinyl alcohol (PVA) was used by Karthik and Meenakshi (2014a) in the preparation of a composite with polyaniline (PANI) that showed a sorption capacity of $111.2\, mg/g$ for Cr(VI). This group also reported the synthesis of two chitosan derivatives, chitosan-grafted-polyaniline (CGP) and glutaraldehyde crosslinked-chitosan-grafted-polyaniline (CCGP) (Karthik and Meenakshi, 2014b). These two polymers revealed higher sorption capacity than PVA/PANI composite, being 165.6 and $179.2\, mg/g$ the sorption capacities determined for CGP and CCGP, respectively. More recently, Saleh et al. (2015) published a crosslinked tetrapolymeric anionic polyelectrolyte that was tested for Cr (III) removal. With this polymer, it was possible to obtain a sorption capacity of $48.5\, mg/g$. Wang and Ge (2014) produced the glutaraldehyde crosslinked chitosan biguanidine (GCB) polymer, for which a sorption capacity of $202.4\, mg/g$ was determined.

Copper

Copper belongs to group 11, fourth period, of the periodic table. It has the electronic configuration $[Ar] 3d^{10} 4s^{1}$ and can be found in two oxidation states, $Cu(I)$ and $Cu(II)$, being the latter the most common. Copper is an essential element that acts as electron donor/acceptor in metalloenzymes in mammalians (Stern et al., 2007). Normally, copper intake occurs via food or water ingestion. Several disorders are related to copper deficiency but high exposure is also a problem of high concern. High concentrations of Cu are associated, among others problems, to Alzheimer's and Wilson diseases (Llanos and Mercer, 2002). Table

8.2 presents some sorbents, either of natural sources or synthetic, proposed for the removal of $Cu(II)$ from wastewaters and their sorption capacity.

There is a high number of studies involving natural sorbents. Wong et al. (2003), in their search for a Cu (II) biosorbent, reported the use of rice husk pretreated with tartaric acid. This material revealed maximum sorption capacity of $31.85\,mg/g$ for Cu(II). Acar and Eren (2006) found that sawdust from the poplar tree Samsun clone can be used to remove Cu¿ II ¿ from water, reaching a sorption capacity of $5.43\,mg/g$. However, the authors observed an enhancement to $13.5\,mg/g$ upon pretreat the biosorbent with sulfuric acid. Šćiban et al. (2006) also proposed sawdust as Cu (II) biosorbent. In this case, the material was obtained from poplar and fir tree and tested with and without pretreatment with sodium hydroxide. The nontreated materials revealed similar sorption capacities, 2.54 and $2.35\,mg/g$, respectively for poplar and fir tree, while the pretreatment increased these values, with higher impact for the fir treebase material, reaching $12.71\,mg/g$. Sawdust from poplar tress was also used by Li et al. (2007), without pretreatment, for Cu (II), revealing a sorption capacity of $6.585\,mg/g$. The same authors also tested peanut husk, which was treated with formalin and sulfuric acid, resulting in a $Cu(II)$ sorbent with sorption capacity of $10.15\,mg/g$. Horsfall et al. (2006) used cassava (Manihot sculenta Cranz) tuber bark waste in the removal of Cu (II) from water. The authors tested the influence of two treatments in the sorption capacity of the material. Treating the cassava wastes with nitric acid allowed the material to reach a sorption capacity of $33.3\,mg/g$. However, when the cassava wastes were further treated with thioglycollic acid, its sorption capacity was enhanced to $90.9\,mg/g$. Özer et al. (2004) worked with wheat bran treated with sulfuric acid, observing an enhancement in its sorption capacity from 42.0 to $51.5\,mg/g$, by increasing the temperature from 20 to $60^\circ C$, at pH 5 . Chemical

Table 8.2 Polymeric Materials Tested for Cu(II) Removal Discussed in the Text

Material	$O_0(mg/g)$	References
Sawdust		
Poplar tree	5.43	Acar and Eren (2006)
	2.54	Šćiban et al. (2006)
	6.58	Li et al. (2007)
Poplar tree treated with	13.5	Acar and Eren (2006)

	6.93	Šćiban et al. (2006)
Fir tree	2.35	
Fir tree treated with sodium hydroxide	12.71	
Rice husk treated with tartaric acid	31.85	Wong et al. (2003)
Peanut husk treated with formalin in sulfuric acid	10.15	Li et al. (2007)
Cassava treated with Nitric acid Nitric acid and thioglycollic acid	33.3	Horsfall et al. (2006)
	90.9	
Wheat bran treated with sulfuric acid	51.5	Özer et al. (2004)
Sugarcane bagasse treated with	114	Karnitz et al. (2007)
	139	
	133	
Pine needles treated with ammonia	179.6	Chauhan et al. (2005)
Cellulose-g-poly(NIPAM)	74.98	Kasgoz et al. (2013)
β-Cyclodextrin crosslinked with epichlorohydrin	111.11	Sikder et al. (2014)
Cellulose-g-poly(GMA)	134.8	Chauhan et al. (2005)
Cellulose-g-poly(GMA-co-AAm)	495.2	
Cellulose-g-poly(GMA-co-AAc)	912.8	
Cellulose-g-poly(GMA-co-AN)	213.6	
Cell-g-poly(GMA-PEI)	102	Tang et al. (2013)
Chitosan-tripolyphosphate beads	208.3	Wu et al. (2013)
Polyethyleneiminemethylene phosphonic acid	85.69	Ferrah et al. (2011)

modified biomass from sugarcane bagasse was studied by Karnitz et al. (2007) as biosorbent of several metal ions, including $Cu(II)$. With these materials, it was possible to obtained sorption capacities ranging from 114 to $139\,mg/g$. Chauhan et al. (2005) studied the possibility of using cellulose extracted form pine needles for the sorption of several metal ions including Cu (II) and discovered that this material can reach a sorption capacity of $179.6\,mg/g$.

Synthetic materials also assume high importance in Cu (II) sorption. Kasgoz et al. (2013) reported a study with a cellulose-based copolymer, the cell-g-poly(N-isopropyl acrylamide) (NIPAM), in which the copolymer was used in combination with sodium dodecyl benzene sulfonate (SDBS) to remove Cu (II) from aqueous solutions. SDBS was responsible for the coordination of the metal ion and upon the metal complex formation adsorption takes place onto the copolymer surface. With this, the authors were able produce a system with a maximum sorption capacity of $74.98\,mg/g$. Chauhan et al. (2005) also studied four grafted copolymers derived from the cellulose extracted from pine needles, cell-g-poly(GMA), cell-g-poly(GMA-co-AAm), cell-g-poly(GMA-co-AAc), and cell-g-poly(GMA-co-AN). By grafting GMA onto cellulose surface the authors compromised the sorption capacity of their cellulose, reaching $134.8\,mg/g$. However, further copolymerization of acrylamide (AAm), acrylic acid (AAc), and acrylonitrile (AN) enhanced considerably the sorption capacity of the initial cellulose to $495.2, 912.8$, and $213.6\,mg/g$, respectively. Cell-g-poly(GMA) was used by Tang et al. (2013) as an anchor for the immobilization of poly(ethylene imine) (PEI). In this case, an adsorption capacity of $102\,mg/g$ was achieved. Sikder et al. (2014) prepared a water insoluble β-cyclodextrin crosslinked with epichlorohydrin for $Cu(II)$ sorption. This material was found to have a sorption capacity of $111.11\,mg/g$. Wu et al. (2013) were able to produce a sorbent for Cu (II) that has $208.3\,mg/g$ sorption capacity by forming porous chitosan-tripolyphosphate beads. Ferrah et al. (2011) found that the polymer polyethyleneiminemethylene phosphonic acid can be used to remove Cu (II) from water, showing a sorption capacity of $85.69\,mg/g$.

Zinc

Zinc (Zn), belongs to the fourth period, group 12 of the periodic table, and has an electronic configuration $[Ar]3d^{10}4s^{2}$. Its most common oxidation state is Zn¿ II), which is considered an essential element for all organisms. In humans, $Zn(II)$ is part of more than 300 metalloenzymes, thus there is a requirement for a regular uptake to maintain an ideal concentration for a proper biochemistry. Nonetheless, injection of high doses of Zn can result in multiple illnesses, such as gastrointestinal disorders, copper deficiency, and immunologic effects (Plum et al., 2010).

There are several anthropogenic activities responsible for releasing Zn (II) into the environment, such as paper production, electroplating, pipes galvanization, and metal alloys production (Sulaiman et al., 2011). Therefore, it is imperative to remove this pollutant from the environment.

In Table 8.3 are summarized several studies involving biopolymers and synthetic that are under investigation for Zn (II) removal from water. Sulaiman et al. (2011) treated Semantan bamboo (Gigantochloa scortechinii) with hydrochloric acid and tested its sawdust in Zn(II) removal from water. They found out that this bamboo can reach a maximum sorption capacity, at $30^{\circ}C$, of $107.52\,mg/g$. Pehlivan et al. (2006) observed that sugar beet pulp can be used in the Zn (II) removal from water and were able to determine a maximum sorption capacity of $35.6\,mg/g$. Wang et al. (2006) observed a sorption capacity of $14.17\,mg/g$ when tested the efficiency of rice bran in removing Zn (II) from water. Mitić-Stojanović et al. (2012), upon performing acid (nitric acid) and alkaline (sodium hydroxide) washing procedures to Lagenaria vulgaris, tested the biomass in Zn (II) sorption. The authors noticed a sorption capacity of $6.41\,mg/g$. Conrad and Bruun Hansen (2007) investigated the possibility of use coir, fibers from Coco nucifera, in metal sorption. Their study revealed that this biomass has a maximum sorption capacity of $8.6\,mg/g$. Horsfall et al. (2006) tested cassava tuber bark in sorption experiments. The biomass was treated with nitric acid showing a maximum sorption capacity for Zn (II) of $22.2\,mg/g$. Nevertheless, upon further modification with thioglycollic acid, the resulting material had an enhancement on its efficiency to $88.3\,mg/g$. Singha and Guleria (2014) extracted cellulose fibers form okra plant and treated it with sodium hydroxide in order to prepare a biosorbent for $Zn(II)$. The authors showed that this cellulose was able to reach a maximum sorption capacity of $16.85\,mg/g$. Šćiban et al. (2006), in the same study already referred in Section 6.2, proposed poplar and fir tree sawdust for Zn (II) sorption. The biomass were used either with or without sodium hydroxide treatment. The nontreated materials had the same sorption capacity, $0.98\,mg/g$. However, pretreating the materials with sodium hydroxide increased their efficiency to 15.82 and $13.40\,mg/g$ for poplar and fir tree-derived materials, respectively. Paulino et al. (2013) modified cotton fiber with citric acid and tested the resulting material for removal of several metal ions, including Zn(II), from water. The authors observed that their material has a sorption capacity for Zn (II) of $4.53\,mg/g$. Nasernejad et al. (2005) tested carrot residues, which were pretreated with hydrochloric acid, as Zn (II) biosorbent. The maximum sorption capacity of this material was found to be $29.61\,mg/g$. Water hyacinth weed (Eichhornia crassipes) biomass, treated with nitric acid, was studied by Mahamadi and Nharingo (2010) as $Zn(II)$

Table 8.3 Polymeric Materials Tested for Zn(II) Removal Discussed in the Text

Material	$Q_0(mg/g)$	References
Sawdust		
Semantan bamboo treated with hydrochloric acid	107.52	Sulaiman et al. (2011)
Poplar tree	0.98	Šćiban et al. (2006)

Poplar tree treated with sodium hydroxide	15.82	
Fir tree	0.98	
Fir tree treated with sodium hydroxide	13.40	
Sugar beet pulp	35.6	Pehlivan et al. (2006)
Rice bran	14.17	Wang et al. (2006)
L. vulgaris treated with nitric acid and sodium hydroxide	6.41	Mitić-Stojanović et al. (2012)
Coir	8.6	Conrad and Bruun Hansen (2007)
Cassava treated with Nitric acid	22.2	Horsfall et al. (2006)
Nitric acid and thioglycollic acid	88.3	
Cellulose extracted from okra plant	16.85	Singha and Guleria (2014)
Cotton fiber modified with citric acid	4.53	Paulino et al. (2013)
Carrot treated with hydrochloric acid	29.61	Nasernejad et al. (2005)
Water hyacinth weed treated with nitric acid	12.55	Mahamadi and Nharingo (2010)
Hazelnut shell	9.15	Demirbaş and Karadağ (2013)
Rapeseed	13.859	Paduraru et al. (2015)
A. fatua	23.54	Areco et al. (2013)
6-(2'-aminomethylpyridine)-6-deoxycellulose	4.64	Silva Filho et al. (2013)
Ch/IA/MAA hydrogel	105.5	Milosavljević et al. (2011)
PVA/EDTA resin	38.7	Zhang et al. (2010)
Chlorosulfonated styrene-DVB resin modified with TETA	173.26	Biçak et al. (2000)
Corn-cob cellulose	8.63	Rahman et al. (2014)
Corn-cob cellulose-g-PAN	2.67	

Polyamidoxime	190.99	
Amidoximated polymerized banana stem	85.89	Anirudhan et al. (2010)

biosorbent. These authors detected that water hyacinth has a sorption capacity of $12.55 mg/g$ for this metal ion. Demirbaş and Karadağ (2013) tested the waste of one of the most important agricultural products in Turkey, hazelnut (Corylus avellana L.). The authors performed Zn (II) sorption tests using hazelnut shell in order to evaluate its efficiency for this purpose and were able to determine a sorption capacity of $9.15 mg/g$. Paduraru et al. (2015) evaluated the efficiency of rapeseed in the removal of Zn(II) from water, finding a maximum sorption capacity of $13.859 mg/g$. Dead biomass of Avena fatua was used by Areco et al. (2013) in sorption experiments with several metal ions. Specifically for $Zn(II)$, the authors found a maximum sorption capacity of $23.54 mg/g$. Silva Filho et al. (2013) performed chemical modification on cellulose surface, inserting 2 - aminomethylpyridine units, and obtained the 6-(2'-aminomethylpyridine)-6-deoxycellulose polymer. Upon obtaining this sorbent, the authors have determined its maximum sorption capacity for several metal ions, including zinc, founding a value of $4.64 mg/g$ for the latter. Milosavljević et al. (2011) prepared pH -sensitive hydrogels based on chitosan, itaconic acid, and methacrylic acid (Ch/IA/MAA) and tested them for Zn (II) sorption. The author found a maximum sorption capacity of $105.5 mg/g$, at $25^\circ C$, for the hydrogel with Ch/IA/MAA ration 1:1.56:7.5. Zhang et al. (2010) prepared a resin based on PVA and chloromethylated polystyrene grafted by EDTA that was tested as Zn (II) sorbent. The authors concluded that the PVA/EDTA resin has a maximum sorption capacity of $38.7 mg/g$. Biçak et al. (2000) modified chlorosulfonated styrene-divinyl benzene (DVB) resin with triethylene tetramine (TETA) in order to prepare a polymer with EDTA-like moieties that could be used to remove metal ions from water. The resulting polymer was tested as sorbent for several toxins and it was determined a maximum sorption capacity of $173.26 mg/g$, specifically for Zn(II). Rahman et al. (2014) extracted cellulose from corn cob, performed several chemical modifications to its structure, and tested all the materials as metal sorbents. In the case of Zn(II), the starting cellulose achieved a sorption capacity of $8.63 mg/g$. However, when acrylonitrile (AN) was grafted onto the cellulose surface (cellulose-g-PAN) the efficiency of the material dropped to $2.67 mg/g$. The last modification performed by the authors, converting cellulose-g-PAN in the polyamidoxime ligand lead to a remarkable enhancement of the maximum sorption capacity to $190.99 mg/g$. Anirudhan et al. (2010) performed chemical reactions with banana stem obtaining an amidoximated polymerized banana stem. This material was then used in $Zn(II)$ sorption assays with which was possible to determine a maximum sorption capacity of $85.89 mg/g$.

Cadmium

Cadmium is found in the fifth period, group 12, of the periodic table with electronic configuration $[Kr]4\ d^{10}5\ s^{2}$. It has two oxidation states, $Cd(I)$ and $Cd(II)$. Cd is a nonessential element for humans, thus human body is not prepared for its proper metabolization. When exposure occurs, cadmium tends to accumulate in organs, resulting in kidneys' damage and provoking harmful effects on red blood cells and nervous system (Brown et al., 2000). Table 8.4 summarizes several polymeric sorbents that have been tested as Cd (II) sorption agents. Kumar and Bandyopadhyay (2006) proposed rice husk for sorption of Cd(II). These authors compared the efficiency of the raw material against it pretreated with different modifying agents. It was observed that by treating the rice husk with 0.5 M NaOH during 4 h the sorption efficiency was increased from 8.58 to $20.54 mg/g$. Also with rice husk, Ye et al. (2010) obtained a sorption capacity of $73.96 mg/g$ for the raw material, while a pretreatment with 1 M NaOH during 3 days increased the value for $125.94 mg/g$. The difference in the sorption capacity of both rice husk raw materials may be related to the origin and chemical composition of both wastes. Sawdust is one type of plant waste that attracts the attention from researchers. Memon et al. (2007) reported the use of Cedrus deodara wood sawdust. Like Kumar and Bandyopadhyay (2006) observed that the material pretreated with sodium hydroxide is more efficient than the raw material in the Cd (II) sorption. The authors were also able to produce a material with a maximum sorption capacity of $73.62 mg/g$. Taty-Costodes et al. (2003) treated sawdust of Pinus sylvestris with formaldehyde, in acidic medium, in order to avoid the leaching of phenolic compounds that would stain the water, and obtained a matrix that showed sorption capacity of $9.29 mg/g$. Horsfall et al. (2006) performed sorption experiments with cassava tuber bark. The authors treated the wastes with nitric acid and thioglycollic acid. When only nitric acid was applied, the material showed a sorption capacity of $5.88 mg/g$. However, further treatment of the wastes with thioglycollic acid enhanced their sorption capacity almost five times, to $26.3 mg/g$. Wheat bran, pretreated with sulfuric acid, was proposed by Özer and Pirinççi (2006). The sorption tests with this material showed the highest sorption capacity, $101 mg/g$, being achieved at $25^{\circ} C$. Min et al. (2004) reported assays of Cd(II) sorption using juniper (Juniperous monosperma) fibers. The authors compared the efficiency of the raw fibers against those treated with sodium hydroxide during 24 h . The results demonstrated that pretreating the fibers improves the sorption capacity from 9.2 to $29.5 mg/g$. Corncob was used by Leyva-Ramos et al. (2005) who studied the effect of oxidizing

Table 8.4 Polymeric Materials Tested for Cd(II) Removal Discussed in the Text

Material	O_0/g)	References
Rice husk	8.58	Kumar and Bandyopadhyay (2006)

	73.96	Ye et al. (2010)
Sodium hydroxide	20.24	Kumar and Bandyopadhyay (2006)
	125.94	Ye et al. (2010)
Sodium bicarbonate	16.18	Kumar and Bandyopadhyay (2006)
Epichlorohydrin	11.12	
Sawdust		
Cedrus deodar wood treated with sodium hydroxide	73.62	Memon et al. (2007)
P. sylvestris treated with formaldehyde in sulfuric acid	9.29	Taty-Costodes et al. (2003)
Nitric acid	5.88	Horsfall et al. (2006)
Nitric acid and thioglycollic acid	26.3	
Wheat bran treated with sulfuric acid	101	Özer and Pirinççi (2006)
J. monosperma	9.2	Min et al. (2004)
J. monosperma treated with sodium hydroxide	29.5	
Corncob	5.12	Leyva-Ramos et al. (2005)
Nitric acid	19.3	
Citric acid	55.2	
Sodium bicarbonate	196	Karnitz et al. (2007)
Ethylenediamine	164	
Triethylenetetraamine	313	
Mangosteen (dye removed)	3.15	Zein et al. (2010)
Calcium hydroxide	39.3	Huang et al. (2013)
Thiosemicarbazide	39.37	Huang et al. (2012)
Diethylenetriamine	20.49	Wang and Huang (2012)

Platanus leaf	3.69	Siswoyo et al. (2014)
Citric acid	15.31	
Agar encapsulated	6.89	
H. verticillata treated with hydrochloric acid	37.46	Li et al. (2013)
Mustard husk	42.85	Meena et al. (2008)
Chitosan from crab shell	138.3	Khan et al. (2015)
Glutaraldehyde crosslinked chitosan pyruvic acid	98.04	Boamah et al. (2015)
Chitosan modified with glycidylmethacrylate followed by 1,2-ethanedithiol	229.3	Khan et al. (2015)
Maize straw grafted succinic anhydride	196.1	Guo et al. (2015)
Polystyrene-diethylenetriamine	89.1	Zhang et al. (2013)
Poly(AAm-co-SMA)	24.05	Milosavljević et al. (2014)
Starch-g-poly(AA)	588	Abdel-Halim and Al-Deyab (2014)

the sorption matrix with nitric acid and citric acid on the sorption efficiency. It was detected that by using citric acid, the content of carboxylic sites on the corncob increased more than what was observed with nitric acid. The modifications increased the sorption capacity of the corncob from 5.12 to $19.3\,mg/g$, when pretreated with nitric acid, while citric acid pretreatment gave $55.2\,mg/g$. The introduction of carboxylate and amines groups into sugarcane bagasse was performed by Karnitz et al. (2007), by reacting the material with succinic anhydride followed by sodium bicarbonate, ethylenediamine, or triethylenetetraamine, to produce more-efficient sorption matrices. With carboxylate groups available to coordinate Cd(II) ions, the material revealed a sorption capacity of $196\,mg/g$, while the introduction of ethylenediamine decreased the efficiency to $164\,mg/g$. However, increasing the number of amine groups with triethylenetetraamine, the sorption capacity was enhanced to $313\,mg/g$. Mangosteen shell is also being tested by several research groups as metal-ion sorbents. Zein et al. (2010) found that, upon removal of the dyes, mangosteen shell has a Cd(II) sorption capacity of $3.15\,mg/g$. In an another study, Wang and Huang (2012) treated the mangosteen shell with diethylenetriamine and found that this increases, to $20.49\,mg/g$, the sorption capacity. In the same year, Huang et al. (2012) used mangosteen shell treated with thiosemicarbazide and obtained a sorption capacity of $39.37\,mg/g$. This result is very similar to the one found by Huang et al. (2013) with mangosteen shell treated with calcium hydroxide, $39.3 mg/g$. Platanuś leaf was studied by Siswoyo et al. (2014) as it is, treated with citric acid and encapsulated in agar. The authors found that this waste has a sorption capacity of $3.69 mg/g$ without any treatment. However, treating the leaf powder with citric acid enhanced the sorption of Cd(II) to $15.31 mg/g$, being this value reduced to $6.89 mg/g$ upon encapsulation of the treated material onto agar. Li et al. (2013) proposed the use of Hydrilla verticillata as Cd (II) sorbent and have determined a sorption capacity of $37.46 mg/g$, upon washing the biomass with $3\% HCl$. Meena et al. (2008) tested untreated mustard husk for Cd(II) removal from water and found that it has a sorption capacity of $42.85 mg/g$. Boamah et al. (2015) used a low molecular weight chitosan modified with pyruvic acid and crosslinked with glutaraldehyde as sorbent for $Cd(II)$. This material was able to reach a sorption capacity of $98.04 mg/g$. Khan et al. (2015) performed chemical modifications in chitosan (crab shell) by reacting it with glycidylmethacrylate followed by 1,2-ethanedithiol. This chitosan-based material was tested for Cd(II) removal and its efficiency was compared with the starting material. The unmodified chitosan showed a sorption capacity of $138.3 mg/g$ while the chemical modifications enhanced this value to $229.3 mg/g$.

Guo et al. (2015) reported the grafting of succinic anhydride onto maize straw and subsequent activation with sodium carbonate. The polymer was tested for Cd (II) sorption, revealing a high sorption capacity of $196.1 mg/g$. Zhang et al. (2013) modified polystyrene (PS) resin with diethylenetriamine (DETA) producing the new polymer PS-DETA. This new resin was tested for Cd(II) removal and showed maximum sorption capacity of $89.1 mg/g$. A hydrogel of poly(acrylamide-co-sodium methacrylate) [poly(AAm-co-SMA)] was reported by Milosavljević et al. (2014) as Cd(II) sorbent with a sorption capacity of $24.05 mg/g$. Abdel-Halim and Al-Deyab (2014) also prepared a hydrogel for Cd (II) removal. In this case, the authors preformed the grafting of polyacrylic acid [poly(AA)] onto starch obtaining the starch-g-poly(AA), which was further treated with epichlorohydrin to form the hydrogel. This material was found to have a sorption capacity of $588 mg/g$.

Lead

Lead is a metal that belongs to group 14, sixth period, of the periodic table. It has the electronic configuration $[Xe]4f^{14}5\ d^{10}6\ s^{2}6p^{2}.Pb$ (II) is the most-common oxidation state of this metal. Lead is one of the most-toxic heavy metals and several health problems are associated to lead exposure, including, for instance, dysfunctions in several organs (Kim et al., 2014). A lot of work has been carried out, involving both polymers present in natural wastes and synthetic ones, in $Pb(II)$'s removal form water. Table 8.5 resumes several examples than can be found in literature. Wong et al. (2003), in the same work already referred to copper, tested rice husk treated with tartaric acid in Pb (II) sorption, and found out a maximum sorption capacity of $120.48 mg/g$. Taty-Costodes et al. (2003), in their research with sawdust from P. sylvestris, were able to determine a sorption capacity of $9.29\,mg/g$ of Pb (II) upon treating the material with formaldehyde in sulfuric acid. Li et al. (2007) found that sawdust, from poplar tree, can reach a Pb (II) sorption capacity of $21.05\,mg/g$ while peanut husk, treated with formalin in sulfuric acid, can reach $29.14\,mg/g$. Noeline et al. (2005) treated pseudo stem of Musa paradisiaca L. (banana) with formaldehyde and sulfuric acid to produce a biosorbent material for $Pb(II)$. This material, when tested for $Pb(II)$ sorption, revealed a maximum sorption capacity of $91.74\,mg/g$. In the same study already referred for Cu(II) and Cd(II), Karnitz et al. (2007) also verified the efficiency of sugarcane bagasse with three different treatments for Pb (II) sorption. The authors did not find differences in the sorption capacity of the material treated with sodium bicarbonate and ethylenediamine, determining a value of $189\,mg/g$. However, increasing the

Table 8.5 Polymeric Materials Tested for $Pb(II)$ Removal Discussed in the Text

Material	O_0 (mg/g)	References
Rice husk treated with tartaric acid	120.48	Wong et al. (2003)
Sawdust		
P. sylvestris treated with formaldehyde in sulfuric acid	9.29	Taty-Costodes et al. (2003)
Poplar tree	21.05	Li et al. (2007)
Peanut husk treated with formalin in sulfuric acid	29.14	Li et al. (2007)
Pseudo stem of banana treated with formaldehyde and sulfuric acid	91.74	Noeline et al. (2005)
Sugarcane bagasse treated with Sodium bicarbonate	189	Karnitz et al. (2007)
Ethylenediamine	189	
Triethylenetetraamine	313	
Wheat straw modified with urea	31.85	Farooq et al. (2010)
L. vulgaris treated with nitric acid and sodium hydroxide	26.94	Mitić-Stojanović et al. (2012)
Cashew nut shell	28.653	Coelho et al. (2014)
Apple pomace	16.39	Chand and Pakade (2013)

Custard apple	91.74	Isaac and Sivakumar (2013)
PVC membranes with 50% D2EHPA inclusion	60.78	Gherasim et al. (2011)
Poly(AAm-co-SMA) crosslinked with PEGDA	68.92	Kalagasidis Krušić et al. (2012)
Cotton-fiber modified with citric acid	21.62	Paulino et al. (2013)
Pigeon-peas hulls treated with sodium hydroxide and sulfuric acid	23.64	Ramana et al. (2012)
Water-hyacinth weed treated with nitric acid	26.32	Mahamadi and Nharingo (2010)
Cellulose acetate	9.4	Abdelwahab et al. (2015)
CA-g-(AA-co-AAm)	66.67	
EDTA/chitosan/PMMS	211	Tan et al. (2015)
Marula (Sclerocarya birrea) seed husk	20	Moyo et al. (2015)

number of amine groups with triethylenetetraamine resulted in higher sorption efficiency, reaching $313\,mg/g$. Farooq et al. (2010) used the straw of Triticum aestivum (wheat) modified with urea to remove Pb (II) from wastewater, finding a maximum sorption capacity of $31.85\,mg/g$. Mitić-Stojanović et al. (2012) performed acid (nitric acid) and alkaline (sodium hydroxide) washing to L. vulgaris in order to obtain a metal-free biomass that could be used to remove $Pb(II)$ from water. This biomass showed a sorption capacity of $26.94\,mg/g$. Coelho et al. (2014) reported the use of cashew nut (Anarcadium occidentale L.) shell as biosorbent for $Pb(II)$. The authors separated the shell form the nut and extracted the oils from the shell using hexane. The biomass obtained was then tested in the Pb (II) sorption, a sorption capacity of $28.653\,mg/g$ was achieved with this material. Apple pomace was used by Chand and Pakade (2013), who tested its efficiency in Pb (II) removal from water. The authors were able to determine a sorption capacity of $16.39\,mg/g$. Isaac and Sivakumar (2013) performed Pb (II) sorption tests using custard apple (Annona squamosa) shell. The fruits waste was found to be able to remove $Pb(II)$ from water, having a sorption capacity of $91.74\,mg/g$. Gherasim et al. (2011) prepared inclusions of bis-(2-ethylhexyl) phosphate (D2EHPA) onto polyvinyl chloride (PVC) membranes to be used in Pb (II) sorption. With membranes containing 50% D2EHPA, the authors achieved a maximum sorption capacity of $60.78\,mg/g$. Kalagasidis Krušić et al. (2012) used a hydrogel based on poly(AAm-co-SMA) crosslinked with poly(ethylene glycol) diacrylate (PEGDA) in Pb (II) sorption tests, finding a sorption capacity of $68.92\,mg/g$ for this material. Paulino et al. (2013) produce a

Pb (II) sorbent derived from natural sources by modification of the surface of natural cotton fibers with citric acid. The resulting material was tested in Pb (II) removal assays and a sorption capacity of $21.62\,mg/g$ was noticed. Pigeon peas hulls were tested by Ramana et al. (2012), who treated the biomass with sodium hydroxide, to remove the lignin materials, followed by sulfuric acid. The sorption efficiency of the resulting biosorbent for $Pb(II)$ was experienced, being possible to determine a sorption capacity of $23.64\,mg/g$. Mahamadi and Nharingo (2010) performed metal sorption tests with water-hyacinth weed (E. crassipes) biomass, treated with nitric acid. These authors detected that, for $Pb(II)$, water hyacinth has a sorption capacity of $26.32\,mg/g$. Abdelwahab et al. (2015) performed sorption studies of Pb (II) using cellulose acetate (CA) and CA grafted with acrylic acid and acrylamide, CA-g-(AA-co-AAm). The authors found that CA can only reach a maximum sorption capacity of $9.4\,mg/g$ while in the CA derivative case, the sorption capacity increased sevenfold, reaching a value of $66.67\,mg/g$. Tan et al. (2015) reported the preparation of a magnetic adsorbent (EDTA/chitosan/PMMS) for Pb (II) that showed maximum sorption capacity of $211\,mg/g$. Chitosan functionalized with EDTA moieties, responsible for the coordination of the metal ion, were obtained by reaction of EDTAanhydride with chitosan in the presence of PEI-coated magnetic microspheres (PMMS). Moyo et al. (2015) tested marula seed husk as Pb (II) biosorbent. The biomass, only washed to remove dirt and without any chemical treatment, revealed a maximum sorption capacity of $20\,mg/g$.

Conclusions

The presence of heavy metals in drinking water is a problem of high concern to society, since it is a source of exposure to very harmful toxins that are related to several diseases and disorders.

Fortunately, the society, with special emphasis to scientific society, recognized that problem and started to create methodologies to improve the quality of our hydric resources. Several methods have been developed to remove heavy metal from water, being the adsorption method the one that has received higher attentions, due to its features.

Polymers, due to their properties, are assuming high importance as an alternative to activated carbon for water remediation. There are a high number of studies reporting the use of natural polymers, mainly cellulose-based materials, for the sorption of metal ions. Actually, this has several benefits including the fact that these polymers exist in high abundance in nature and are biodegradable, which contributes to sustainability. Moreover, the use of these materials opens a new window to a high-society concern, add value to the high amount of residues that are produced worldwide. Nevertheless, the sorption efficiency of these polymers can be enhanced with some chemical modifications that will provide better affinity to metal ions. Furthermore, new polymers can be developed with improved structure and appropriated features for this application, which has already being performed by several research groups.

However, it is important to remember that the sorption studies reported in literature do not follow a standard procedure, which limits the comparison of results reported by different authors. There are several parameters that influence the adsorption of metal ions, as it was referred earlier. Despite the fact that some of these parameters, such as pH or contact time, are dependent on the chemical nature of the adsorbent and adsorbate, there are some that can be standardized, including amounts of adsorbent used, initial concentration of adsorbate, particle size, temperature, or even stirring speed.

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