

Review

Heavy metal adsorption onto agro-based waste materials: A review

Ayhan Demirbas*

Sila Science, Trabzon, Turkey

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Abstract

Adsorption has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low-cost, availability, profitability, easy of operation and efficiency. Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. Biosorption is becoming a potential alternative to the existing technologies for the removal and/or recovery of toxic metals from wastewater. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials. Metal adsorption and biosorption onto agricultural wastes is a rather complex process affected by several factors. Mechanisms involved in the biosorption process include chemisorption, complexation, adsorption–complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption.

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Keywords: Heavy metal ion; Agro waste material; Adsorption; Biosorption

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1. Introduction

Nowadays heavy metals are among the most important pollutants in source and treated water, and are becoming a severe public health problem. Industrial and municipal waste waters frequently contain metal ions. Industrial waste constitutes the major source of various kinds of metal pollution in natural water [1–4]. The application of biosorption in environmental treatment has become a significant research area in the past 10 years. Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity [5,6].

The heavy metal ions are stable and persistent environmental contaminants since they cannot be degraded and destroyed. These metal ions can be harmful to aquatic life and water contaminated by toxic metal ions remains a serious public health problem for human health. Heavy metals removal from aqueous solutions has been traditionally carried out by chemical precipitation [7]. Numerous methods exist to remove detrimental metal ions from aqueous solutions. Activated carbon has been the most used adsorbent, nevertheless it is relatively expensive. In order to obtain cheaper adsorbents, lignocellulosics materials have been studied [8].

The presence of copper, zinc, cadmium, lead, mercury, iron, nickel and others metals, has a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded. Many methods of treatment

* Tel.: +90 462 230 7831; fax: +90 462 248 8508.

E-mail address: ayhandemirbas@hotmail.com.

for industrial wastewater have been reported in literature [9]. Amongst these methods are neutralization, precipitation, ion exchange and adsorption. For low concentrations of metal ions in wastewater, the adsorption process is recommended for their removal. The process of adsorption implies the presence of an “adsorbent” solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable, and cheap [10].

Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams [11,5,12–19].

The sorption capacity of lignocellulosics for metal ions is generally described as adsorption. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials. The major advantages of biosorption over conventional treatment methods include: low-cost; high efficiency; minimization of chemical and/or biological sludge; regeneration of biosorbent; no additional nutrient requirement; possibility of metal recovery [20]. The cost advantage of biosorption technology would guarantee a strong penetration of the large market of heavy metal polluting industries.

In general, raw lignocellulosic biosorbents were modified by various methods to increase their sorption capacities because metal ion binding by lignocellulosic biosorbents is believed to take place through chemical functional groups such as carboxyl, amino, or phenolics. More recently, great effort has been contributed to develop new adsorbents and improve existing adsorbents. Many investigators have studied the feasibility of using low-cost agro-based waste materials [21–29].

Many conventional techniques such as chemical precipitation, membrane filtration, electrolysis, ion exchange, carbon adsorption and co-precipitation/adsorption are used for the removal of heavy metals in wastewater treatment, but they are suitable for high concentrations of metals [30–41]. At low concentrations, these techniques fail in certain cases. Also they are not cost-effective. For this reason, low-cost adsorbents have been evaluated for the removal of heavy metals from aqueous solutions [42].

Modified lignin obtained from lignocellulosic materials is used for the removal of trivalent and hexavalent chromium, lead and zinc from aqueous solutions [1,43–48]. Lignin is known to adsorb many heavy metal ions [49].

Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to some extent to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution [16].

The alkali lignin produced by the alkaline pulping of softwood consequently contains a low content of positions reactive

towards electrophiles. In natural lignin the positions on the aryl rings *para*- and *ortho*- to the hydroxyl groups are usually occupied by alkoxy or alkyl substituents [50].

Lignin has an aromatic, three-dimensional polymer structure with apparent infinite molecular weight [51]. The cellulose is located predominantly in the secondary cell wall [52]. Lignin is covalently linked with xylans in the case of hardwoods and with galactoglucomannans in softwoods. Even though mechanically cleavable to a relatively low molecular weight, lignin is not soluble in water. Lignin has strong resistance to chemical reactions, a high surface area (180 m²/g) [53]. Molecular weight of the polymeric lignin changes from 2000 to 15,000 g/mol [54]. These properties of lignin reveal that it has a potential to be used as a possible adsorption material to remove heavy metals from waste waters.

The removal of heavy metal ions using low-cost abundantly available adsorbents: agricultural wastes such as tea waste and coffee [55], hazelnut shells [56–58], peanut hull [59,21], red fir [60] and maple [61] sawdusts [62,63], pinus bark [64–67] and different bark samples [68–77], palm kernel husk [78] and coconut husk [79,80], peanut skins [81], modified cellulosic materials [82,83], chemically modified cotton [84], corncobs [85] and modified corncob [86], rice hulls [87], apple wastes [88], coffee grounds [89], bark [90,91], modified bark [37], wool fibers [92], tea leaves [93], and wool, olive cake, pine needles, almond shells, cactus leaves, charcoal [94], modified lignin [48,95,96], banana and orange peels [97], modified sugar beet pulp [98], modified sunflower stalk [25], palm fruit bunch [99], maize leaf [20] and different agricultural by-products [100–107] were used and investigated.

2. Chemical properties of agricultural waste materials

The term biomass (Greek, bio, life + maza or mass) refers to wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous species, wood wastes, bagasse, industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, food processing waste, aquatic plants, algae animal wastes, and a host of other materials [108]. It is a rather simple term for all organic materials that seems from plants, trees, crops and algae. Two larger carbohydrate categories that have significant value are cellulose and hemicelluloses (holocellulose). The lignin fraction consists of non-sugar type molecules [109].

Cellulose is a remarkable pure organic polymer, consisting solely of units of anhydroglucose held together in a giant straight chain molecule [110]. These anhydroglucose units are bound together by β -(1,4)-glycosidic linkages. Due to this linkage, cellobiose is established as the repeat unit for cellulose chains (Fig. 1). Cellulose must be hydrolyzed to glucose before fermentation to ethanol.

By forming intramolecular and intermolecular hydrogen bonds between OH groups within the same cellulose chain and the surrounding cellulose chains, the chains tend to be arranged parallel and form a crystalline supermolecular structure. Then, bundles of linear cellulose chains (in the longitudinal direction) form a microfibril which is oriented in the cell wall structure [29].

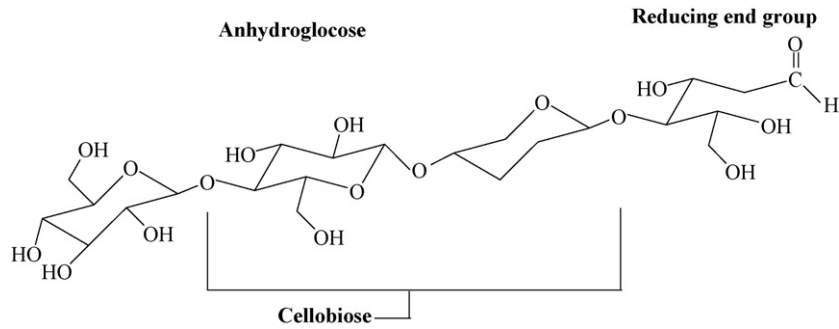


Fig. 1. The structure of cellulose. Anhydroglucose is the monomer of cellulose, cellobiose is the dimer (Ref. [29]).

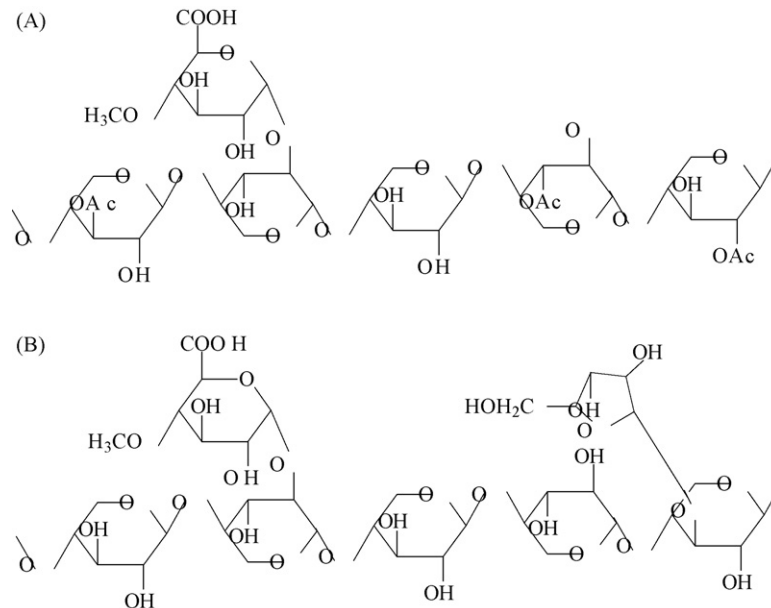


Fig. 2. Schematic illustration of xylans: (A) Partial xylan structure from hardwood and (B) Partial xylan structure from softwood (Ref. [29]).

Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis.

Unlike cellulose, hemicelluloses consist of different monosaccharide units. In addition, the polymer chains of hemicelluloses have short branches and are amorphous. Because of the amorphous morphology, hemicelluloses are partially soluble or swellable in water. Hemicelluloses (arabinoglycuronoxylan and galactoglucomannans) are related to plant gums in composition, and occur in much shorter molecule chains than cellulose. Hemicelluloses are derived mainly from chains of pentose sugars, and act as the cement material holding together the cellulose micells and fiber [111].

Among the most important sugar of the hemicelluloses component is xylose. In hardwood xylan, the backbone chain consists of xylose units which are linked by β -(1,4)-glycosidic bonds and branched by α -(1,2)-glycosidic bonds with 4-*O*-methylglucuronic acid groups [29]. In addition, *O*-acetyl groups sometime replace the OH groups in position C₂ and C₃ (Fig. 2A). For softwood xylan, the acetyl groups are fewer in the backbone chain. However, softwood xylan has additional branches consisting of arabinofuranose units linked by α -(1,3)-glycosidic bonds to the backbone (Fig. 2B). Hemicelluloses are largely

soluble in alkali and, as such, are more easily hydrolysed [112–114].

Lignins are polymers of aromatic compounds. Their functions are to provide structural strength, provide sealing of water conducting system that links roots with leaves, and protect plants against degradation [115]. Lignin is a macromolecule, which consists of alkylphenols and has a complex three-dimensional structure. Lignin is covalently linked with xylans in the case of hardwoods and with galactoglucomannans in softwoods [116]. The basic chemical phenylpropane units of lignin (primarily syringyl, guaiacyl and *p*-hydroxy phenol) as shown in Fig. 3 are bonded together by a set of linkages to form a very complex matrix. This matrix comprises a variety of functional groups, such as hydroxyl, methoxyl and carbonyl, which impart a high polarity to the lignin macromolecule [29,117]. Cellulose and lignin structures were extensively investigated in the earlier studies [118,119,51,120–122].

3. Adsorption models

Isotherm adsorption models have been used in waste stream treatment to predict the ability of a certain adsorbent to remove

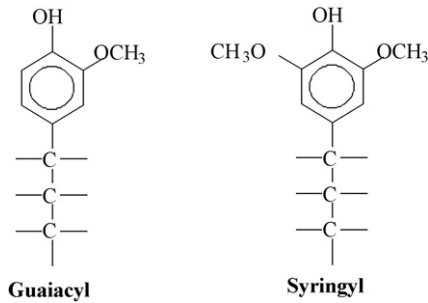


Fig. 3. Schematic illustration of building units of lignin.

a pollutant down to a specific discharge value. When a mass of adsorbent and a waste stream are in contact for a sufficiently long time, equilibrium between the amount of pollutant adsorbed and the amount remaining in solution will develop. For any system under equilibrium conditions, the amount of material adsorbed onto the media can be calculated using the mass balance of Eq. (1):

$$\frac{X}{M} = (C_o - C_e) \frac{V}{M} \quad (1)$$

where X/M (typically expressed as mg pollutant/g media) is the mass of pollutant per mass of media, C_o is the initial pollutant concentration in solution, C_e is the concentration of the pollutant in solution after equilibrium has been reached, V is the volume of the solution to which the media mass is exposed, and M is the mass of the media.

Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as the Langmuir [123] or Freundlich [124] isotherms. The general Langmuir model defined by Eq. (2):

$$\frac{X}{M} = \frac{K_L C_e}{1 + a_L C_e} \quad (2)$$

were K_L and a_L are the isotherm constants. K_L and a_L values can be determined using linear regression. The Langmuir isotherm can be linearized to the following equation:

$$\frac{1}{X/M} = \frac{1}{K_L C_e} + \frac{a_L}{K_L} \quad (3)$$

The general Freundlich equation is:

$$\frac{X}{M} = K_F (C_e)^{1/n} \quad (4)$$

The Freundlich isotherm can also be linearized by the following:

$$\ln \left(\frac{X}{M} \right) = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where K_F and n are adsorption capacity and affinity, respectively.

The Langmuir and Freundlich isotherm models are only applicable to batch adsorber systems where sufficient time is provided to allow equilibrium between the pollutant in solution and the pollutant adsorbed on the media to occur. During the flow through the adsorbent, many of the pollutants are expected to come into contact with active surface sites and thus be retained on the surface of the adsorbing media. Table 1 shows the Langmuir and Freundlich constants for the adsorption of Cu(II) and Cd(II) from aqueous solution onto rice husk and modified rice husk.

The bed depth-service time (BDST) model, this is based on the Bohart and Adams quasi-chemical rate law [125]. The assumption behind the equation (Bohart and Adams Equation, 1920) is that equilibrium is not instantaneous and therefore, the rate of the sorption reaction is proportional to the fraction of sorption capacity still remaining on the media. The linearized BDST model equation is as follows [125–127]:

$$t_b = \frac{N_o}{1000 \varepsilon \nu C_o} D - \frac{1}{k C_o} \ln \left(\frac{C_o}{C_b} - 1 \right) \quad (6)$$

where t_b is the time until breakthrough (min), C_o is the initial concentration of pollutant (mg/L), C_b is breakthrough concentration of pollutant (mg/L), ν is the fluid velocity or loading rate (m/min), ε is the porosity of the filter, k is quasi-chemical rate constant from Bohart and Adams theory (L/mg s), N_o is capacity of the media for each pollutant in a multi-component solution (mg pollutant per cubic meter of filter volume), and D is depth of the filter bed.

Several empirical models proposed in the literature (Bohart–Adams, Yan, Belter and Chu models) were investigated in order to obtain the best fit of column data, describing in a simple manner the breakthrough curves [128].

4. Metal adsorption and biosorption studies

Adsorption has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low-cost, availability, profitability, easy of operation and efficiency, in comparison with conventional methods especially from economical and environmental points of view [29,129–131]. A search for a low-cost and easily available

Table 1

Langmuir and Freundlich constants for the adsorption of Cu(II) and Cd(II) from aqueous solution onto rice husk and modified rice husk

Adsorbent	Heavy metal	K_L	R_L^2	C_e	K_F	$1/n$	R_F^2
Rice husk	Cu	2.48	0.996	0.143	0.693	0.288	0.968
	Cd	8.82	0.936	0.066	0.630	0.454	0.993
Modified rice husk	Cu	9.36	0.994	0.080	0.866	0.480	0.931
	Cd	11.03	0.993	0.069	1.265	0.495	0.952

From Ref. [161]. K_L , C_e and R_L^2 are Langmuir constants. K_F , n and R_F^2 are Freundlich constants.

adsorbent has led to the investigation of materials of biological origin as potential metal biosorbents. Biosorption is becoming a potential alternative to the existing technologies for the removal and/or recovery of toxic metals from wastewater [132,133]. The study of biosorption is of great importance from an environmental point of view, as it can be considered as an alternative technique for removing toxic pollutants from wastewaters [134,135].

In general, raw lignocellulosic biosorbents were modified by various methods to increase their sorption capacities because metal ion binding by lignocellulosic biosorbents is believed to take place through chemical functional groups such as carboxyl or phenolics. Mechanisms and measurement of chemical modification were studied by Kunin et al. [136]. Simple classical pyrolysis technologies that only apply heating will result in conversion of lignin mainly to solid coke with high surface area and gas in a disproportionation process [118,120]. These properties of lignin reveal that it has a potential to be used as a possible adsorption material to remove heavy metals from waste waters.

Chemical modification became popular and many researchers devised elaborate modification procedures [137]. Biomass chemical modifications include delignification, esterification of carboxyl and phosphate groups, methylation of amino groups, and hydrolysis of carboxylate groups. Odozi et al. [138] polymerized corncob, sawdust and onion. Sawamiappan and Krishnamoorthy [139] replaced phenol-formaldehyde cationic matrices with sulfonated bagasse. Freeland et al. [140] used polyethylenimine-modified wood to adsorb mercury. Snyder and Vigo [141] modified cotton ethylenediamine with chlorodeoxycellulose to remove mercury. Gasparini et al. [142] captured mercury ions using cellulose derivatives. Marchant [143] removed mercury using cellulose modified by changing the pH from 1 to 9. Treatment of soybean hulls and sugar beet fiber with epichlorohydrin to improve cation-exchange capacity was studied by Laszlo and Dintzis [144].

Randall et al. [145] chemically modified peanut skins using formaldehyde for heavy metal removal in aqueous waste solutions. The work of Kumar and Dara [146] included bagasse, acacia bark, husk, paddy straw, wheat flour, and waste peanut skin, and Kumar and Dara [147] included onion skin.

The role of lignin in removal of copper is controversial and inconclusive. Camire and Clydesdale [148] found that lignin and pectin have a high metal binding capability. They also tested the effect of pH and heat on removal of the copper ions. Varma et al. [149,150] removed copper between the pH 4.4 and 5.0.

Platt and Clydesdale [151] studied binding of iron by lignin in the presence of other ions. Nasr and MacDonald [152] did stoichiometric studies with carboxylic acids groups on lignin compounds toward aluminum and iron ions at lower pHs. Lignin was used in removal of copper at pH 5.5, cadmium at pH 6.5.

Carbonized coir pith was used as an adsorbent for the removal of toxic ions, dyes and pesticides from wastewaters [153]. Removal of copper(II) by adsorption onto peanut hull carbon from water and copper plating industry wastewater was investigated [154].

4.1. Mechanism of metal biosorption

Metal biosorption is a rather complex process affected by several factors. Mechanisms involved in the biosorption process include chemisorption, complexation, adsorption–complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption [155–157].

In order to understand how metals bind to the biomass, it is essential to identify the functional groups responsible for metal binding. Most of the functional groups involved in the binding process are found in cell walls. Plant cell walls are generally considered as structures built by cellulose molecules, organized in microfibrils and surrounded by hemicellulosic materials (xylans, mannans, glucomannans, galactans, arabogalactans), lignin and pectin along with small amounts of protein [68,158,159].

The behavior of cellulose as a substrate is highly dependent upon the crystallinity, specific surface area, and degree of polymerization of the fibers being studied [160]. The cellulose is located predominantly in the secondary cell wall. Bundles of cellulose molecules are aggregated together in the form of microfibrils in which highly ordered (crystalline) regions exist with less ordered (amorphous) regions. The proportions of crystalline and amorphous regions in cellulose vary depending upon the type of the sample and the method of measurement. Cotton cellulose is usually more crystalline than wood cellulose [119].

Laszlo and Dintzis [144] have shown that lignocellulosics have sorption capacity, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. These are adsorbents for a wide range of solutes, particularly divalent metal cations [144].

Lignocellulosics are hygroscopic and have an affinity for water. Water is able to permeate the non-crystalline portion of cellulose and all of the hemicellulose and lignin. Thus, through absorption and adsorption, aqueous solution comes into contact with a very large surface area of different cell wall components. Because of its disordered structure, amorphous cellulose should be much more accessible to reagents than highly structured crystalline cellulose. Cellulose can also sorb heavy metals from solution [162].

The molecular structure and supramolecular structure have a strong influence on sorption properties. Water adsorption of fibers, orientated in one particular direction, invariably causes swelling. The bigger the amount of water adsorption, the bigger is the swelling. Swelling also depends on the fiber's structure, on the degree of crystallinity and on the amorphous and void regions [163]. Swelling occurs when polar solvents such as water and alcohols are contacted with wood [164]. Wood swelled extremely fast at high temperatures. The polar solvent molecules are attracted to the dry solid matrix and held by hydrogen bonding forces between the –OH or –COOH groups in the wood structure.

More recently sorption potential of pretreated crab and arca shell biomass for lead and copper from aqueous media was explored. The effects of pH, initial concentration, biosorbent dosage and contact time were studied in batch experiments

Table 2
Removal capacity of copper(II) ion (mg/g substrate) at pH 5.5

Common name	Botanical name	Classification	Lignin (%)	Capacity
Sugar cane, bagasse	<i>Saccharum officinarum</i>	Straw fiber	19.9	0.3
Oak	<i>Quercus</i> spp.	Hardwood fiber	23.2	0.5
Aspen	<i>Populus grandidentata</i>	Hardwood fiber	21.8	0.9
Spruce Eastern	<i>Picea orientalis</i>	Softwood fiber	26.3	1.3
Coconut, shell	<i>Cocos nucifera</i>	Shell	35.5	2.6
Flax	<i>Linum usitatissimum</i>	Bast fiber	2.9	5.5
Kudzu, bark	<i>Pueraria lobata</i>	Bast fiber	19.3	8.2
Kenaf, fiber	<i>Hibiscus cannabinus</i>	Bast fiber	9.9	8.5
Hemp	<i>Cannabis sativa</i>	Bast fiber	3.0	9.5
Tobacco, fiber	<i>Nicotina tabacum</i>	Bast fiber	16.5	10.5
Tobacco, bark	<i>Nicotina tabacum</i>	Bast fiber	9.5	14.3

[165]. Effects of common ions like Na, K, Ca and Mg on the sorption capacity of pretreated crab and arca biomasses were also studied. At equilibrium, the maximum uptake by crab shell biomass was 19.83 ± 0.29 and 38.62 ± 1.27 mg/g for lead and copper, respectively. In case of arca shell biomass the maximum uptake capacity was 18.33 ± 0.44 mg/g and 17.64 ± 0.31 mg/g for lead and copper, respectively.

Cellulose is a natural polymer. Cellulosic graft copolymers were prepared by the reaction of bast fibers of the kenaf plant (*Hibiscus cannabinus*) with acrylonitrile and methacrylonitrile monomers in aqueous media initiated by the ceric ion–toluene redox pair. The cellulose–polyacrylonitrile (Cell–PAN) and cellulose–polymethacrylonitrile (Cell–PMAN) graft copolymers were used for the removal of Zn(II) and Cr(III) ions from aqueous solutions at 303 K. Zn(II) ion was more sorbed than Cr(III) ion by both copolymers by an average factor of 1.80 ± 0.40 . For each metal ion, the Cell–PAN graft copolymer was a more effective sorbent than the Cell–PMAN derivative [166]. Chemical modification has either been too expensive or it has caused other problems, such as bleeding of excessive quantities of colored organic compounds, odor, or further pollution through the use of toxic chemicals.

The fiber with the highest level of heavy metal removal was kenaf bast that had a very low level of lignin, showing that removal of heavy metals does not correlate with lignin content. Cotton, with about 1% lignin, was very low in metal ion sorption while all of the fibers containing lignin did remove heavy metal ions showing that lignin does play a role in metal ion sorption [167]. Cellulose, a homopolysaccharide of glucose units, is the most abundant lignocellulosic material and a stable compound. Cotton with high cellulose content shows very low sorption capacity.

Agro-based fibers such as kenaf, roselle, and tobacco have been shown to be effective in sorption of heavy metal ions from stormwater filtration systems. In contrast, most wood-based fibers have a relatively low capacity for filtering heavy metals [168]. Although researchers have tried to increase the sorption capacity of lignocellulosic fibers through chemical modification, more success has been achieved with bark and marine fibers [144,169–171].

Kenaf was most effective at removing cadmium ion. Alfalfa was most effective at removing cadmium, copper and zinc ions. As individual ions, all three ions had about the same ion-

exchange capacity at 40 mg/L and 6 days of residence time. Residence time had the greatest effect on the rate of copper removal. The rate of removal increased with length of residence time. These results suggest that at higher ion concentrations, removal rate increases with an increase in residence time [168]. Removal capacities of different agro wastes for copper(II) ion are given in Table 2.

5. Conclusion

In this review, the inexpensive and effective metal ion adsorbents from agro waste materials to offer these adsorbents as replacements for existing commercial materials were investigated.

Agricultural by-products and in some cases appropriately modified have shown to have a high capacity for heavy metal adsorption. Toxic heavy metals such as Pb(II), Cd(II), Hg(II), Cu(II), Ni(II), Cr(III), and Cr(VI), as well as some elements from lanthanide and actinides groups have been successfully removed from contaminated industrial and municipal waste waters using different agro waste materials.

Biosorption is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. Chemical modification improves the adsorption capacity and stability of biosorbents. Biosorption experiments over Cu(II), Cd(II), Pb(II), Cr(III), and Ni(II) demonstrated that biomass Cu(II) adsorption ranged from 8.09 to 45.9 mg/g, while Cd(II) and Cr(VI) adsorption ranged from 0.4 to 10.8 mg/g and from 1.47 to 119 mg/g, respectively [155].

The Langmuir and Freundlich isotherm models are only applicable to batch adsorber systems where sufficient time is provided to allow equilibrium between the pollutant in solution and the pollutant adsorbed on the media to occur.

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