Pure Appl. Chem., Vol. 76, No. 4, pp. 801–813, 2004.

Use of phytofiltration technologies in the removal of heavy metals: A review*

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Abstract: Biosorption is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. Microorganisms as well as plant- and animal-derived materials have been used as biosorbents by many researchers. Biomaterial immobilization and 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^{-1}, while Cd(II) and Cr(VI) adsorption ranged from 0.4 to 10.8 mg g^{-1} and from 1.47 to 119 mg g^{-1}, respectively.

Mechanisms involved in the biosorption process include chemisorption, complexation, surface and pore adsorption-complexation, ion exchange, microprecipitation, hydroxide condensation onto the biosurface, and surface adsorption. Chemical modification and spectroscopic studies have shown that cellular components including carboxyl, hydroxyl, sulfate, sulfhydryl, phosphate, amino, amide, imine, and imidazol moieties have metal binding properties and are therefore the functional groups in the biomass. Column studies using support matrices for biomass immobilization such as silica, agar, polyacrilamide, polysulfone, alginates, cellulase, and different cross-linking agents have been performed to improve the biomass adsorption capacity and reusability. In this review, the salient features of plant-derived materials are highlighted as potential phytofiltration sources in the recovery of toxic heavy and precious metals.

INTRODUCTION

Several industrial and agricultural processes as well as mining activities have increased the concentration of toxic contaminants in water and wastewaters around the world [1,2]. Beginning in the 1960s, industrialized countries became aware of a health threat provoked by water contamination, which led to immediate legislation by various governments to control those harmful activities primarily responsible for such pollution. The development of proper clean-up methods also became a priority in the legislation process. In 1969, the U.S. Congress approved the National Environmental Policy Act with the purpose "…to promote efforts which will prevent or eliminate damage to the environment and biosphere and stimulate the health and welfare of man…" (Congressional Declaration of National Environmental Policy, Sec. 101 [42 USC§ 4331]). Since then, significant efforts have been made in developing appropriate methodologies for cleaning polluted water and wastewater.

Current methodologies used in the removal of toxic contaminants found in both water and wastewater include procedures such as chemical precipitation, membrane filtration, ion exchange, carbon adsorption, and coprecipitation/adsorption [3]. While precipitation is the most common among such meth-

*Plenary lecture presented at the Southern and Eastern Africa Network of Analytical Chemists (SEANAC), Gaborone, Botswana, 7–10 July 2003. Other presentations are published in this issue, pp. 697–888.
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ods, the disadvantage is that it only reduces the dissolved metal concentration to the solubility product level, which is frequently out of compliance with rigorous discharge permit standards and thus requires additional cleaning stages. These aforementioned techniques are all generally expensive and might possibly generate by-products dangerous to human health, such as in the case of leachates, which originate from ion-exchange resins [4].

Biosorption is a relatively new technique that emerged in the 1980s and gained a considerable amount of attention since it has shown to be very promising in the removal of contaminants from effluents in an environmentally friendly manner [5,6]. Biosorption refers to the passive or physicochemical attachment of chemical species to the biopolymers present in a biomass [7]. Biosorbents are generally inexpensive because they are either naturally abundant or found as waste material from certain process [3]. It has been shown that different kinds of inexpensive dead biomasses can be used as biosorbents to sequester toxic contaminants from waters and wastewaters. Biosorbents might be classified according to the following sources: bacteria, algae, fungi, plant-derived, and animal-derived. Dead biomass offers several advantages over living organisms since the former does not need maintenance and is not affected by high concentrations of pollutants. Living organisms, on the other hand, need nutritional supply and are usually affected by a high concentration of contaminants [8].

Biomaterials have been used as biosorbents either in raw or chemically modified forms. Chemical modification generally improves the adsorption capacity and stability of biosorbents. Biomaterials have also been immobilized in different matrices for similar purposes. Examples of current chemical modifications include chitosan, which is the acetylated derivative of chitin and alginate, which are linear, nonbranched polymers derived from algae [3]. A variety of biomaterials have been used to remove a wide variety of contaminants. In fact, one can practically find a specific biomaterial for the adsorption of each pollutant found in aqueous effluents. Table 1 shows examples of biomaterials that have been successfully used in the removal of organic and inorganic pollutants. As seen in this table, bacteria, algae, and fungi have been extensively used by several researchers for toxic heavy and precious metal recovery. Organic pollutants have been treated with bacteria and fungi, while plant-derived biomass has demonstrated a high capability for toxic and precious metal recovery. In this review, the salient features of plant-derived materials used as phytofiltration sources for toxic heavy and precious metal recovery are highlighted.

Table 1 Reported ability of different biomaterials to remove pollutants from aqueous effluents.

Pollutant	Biomaterial	Source
Heavy metals	Plant-derived	[8,28,31,38,44,46,47,55,56]
	Bacteria	[57,58]
	Fungi	[5,54,59,60]
	Crab shell	[61]
	Algae	[62–65]
Precious metals	Plant-derived	[26,66,67]
	Fungi	[68]
	Algae	[69]
Lanthanides and actinides	Plant-derived	[50]
	Bacteria	[70]
Organic pollutants	Fungi	[71]
	Bacteria	[72]
Organic dyes	Fungi	[73–75]

BIOMATERIALS TESTING

Batch experiments are initially performed in order to test the biomaterial potential for contaminant removal from aqueous solutions. The biomaterial testing methodology consists of a series of experiments. These experiments provide information about factors such as the optimal pH for metal binding, time dependency, capacity of the biomass to bind metal ions, efficiency of stripping (desorbing) agents, multimetal competition, as well as interference studies [9,10]. Several factors considered in the evaluation of the biosorption capability of a biomass are described below.

pH Studies

Most natural waters have pH values between 4 and 8.5, and the main acids present in these waters are weak (i.e., some organic acids, carbonic acid, bicarbonate ion). Waters with pH < 4 usually contain strong acids (H_2SO_4, HCl); the pH level of seawater is about 8.15 and waters with pH values higher than 8.5 typically contain sodium carbonate and bicarbonate along with other strong bases [11]. Most industrial effluents remain in the acid range, and since acidity favors the solubility of heavy metals, it is expected that the lower the pH, the higher the concentration of heavy metals.

The pH condition of the solutions is an extremely important factor in metal biosorption since it governs a series of phenomena such as site dissociation and chemistry of the heavy metals. At low pH values, binding sites in the biomass are generally protonated or positively charged, thus repulsion occurs between the metal cations and the biomass. At higher pH values, binding sites start deprotonating, making different functional groups available for metal binding. In general, cation-binding increases as pH increases. As previously mentioned, pH not only influences functional group dissociation, but also the chemistry of metals in a solution. Hydrolysis, complexation, precipitation, and redox reactions are pH-dependent phenomena that will influence the speciation and availability of heavy metal for biosorption [12].

Hydrolysis refers to the reaction between water and another chemical species. In this reaction, one or both of the O–H water bonds are broken and a hydrogen, oxygen, or hydroxyl group is incorporated into one or more of the products [13]. A typical hydrolysis reaction is shown in eq. 1, where M^{n+} refers to the metal cation

$$M^{n+} + xH_2O \rightleftarrows [M(H_2O)_x]^{n+} \rightleftarrows [\, M(H_2O)_{x-1}\, OH]^{(n-1)+} + H^+ \quad [1]$$

As shown in eq. 1, hydrogen ions are released, and consequently the solution pH is lowered in the hydrolysis process. This equation also shows that the metal cation is not "free", but instead surrounded by water molecules, a phenomenon that consequently interferes with the metal biosorption process.

Complexation reactions occur when a cation or atom is bound to an anion or neutral molecule by sharing pairs of electrons, forming a coordinate covalent bond [14]. This cation, or atom, is called a central metal ion, or atom, and the attaching groups are called ligands. Some elements such as Cu^{2+}, Hg^{2+}, U^{4+}, Fe^{3+}, and Pb^{2+}, are more often found forming complexes than free ions [11]. Complexation reactions are important for biosorption since the formation of complexes in aqueous solutions might either favor or inhibit the adsorption process, depending on the characteristic of the product.

Hydrolysis and complexation reactions are pH-dependent, and as pH increases, the formation of hydroxyl compounds also increases. The pH required for hydroxide precipitation depends on the chemical nature of the metals. However, when this condition (optimal pH) is reached, hydroxides precipitate and metals are removed from solution, thus avoiding any possible metal biosorption.

The pH also influences redox reactions. In a redox reaction, one chemical species transfers electrons (oxidizes), thus reducing another. Sometimes, redox reactions occur in acidic or basic solution and H^+ or OH^- species participate in the process [14]. Such is the case of the reduction of Cr(VI) to Cr(III), where an acidic pH and the presence of organic matter are important factors in the reaction [15].

Heavy metals generally tend to bind to the biomass at pH values that are somewhat more acidic than the pH at which the metal precipitates in the hydroxide form [16]. However, a pH profile is necessary since unknown reactions between the metal ions and the biomass might occur, modifying to some extent the "normal" metal behavior. Table 2 shows a summary of the optimum pH values for metal binding to different types of biomasses. As shown in this table, most of the heavy metals studied bind better to the biomass at pH values between 4.0 and 6.0.

Table 2 Optimum pH for metal binding to different plant-derived materials.

Biomass	Metal ions	Optimum pH	Source
Alfalfa	Ni(II)	5.0–6.0	[9]
	Cd(II), Cr(III), Pb(II), Zn(II)	5.0	[76]
	Eu(III)	5.0	[50]
	Pt (II,IV)	6.0	[26]
C. Sphagnum peat moss, its Humin and Humic acids	Cu(II), Cd(II), Cr(III), Pb(II), Ni(II)	4.0–5.0	[28,34]
Hops (*Humulus lupulus*)	Pb(II)	5.0	[46]
Oat (*Avena monida*)	Cr(III)	6.0	[44]
	Cr(VI)	2.0	[44]
Petiolar felt-sheath of palm	Pb(II), Ni(II), Cd(II), Cu(II), Cr(III), Zn(II)	4.0	[17]
Sorghum *(Sorghum bicolor)*	Cr(III)	4.5–5.0	[77]
Thuja orientalis	Cu(II)	7.7	[78]

Time-dependency and capacity studies

Time-dependency studies offer data about the changes in metal adsorption related to time. In these studies, the minimum time necessary for the biomass to be in contact with the metal ion solution is identified. As for binding capacity, it is particularly important to determine the maximum amount of metal that the biomass is able to adsorb. If the biomaterial is capable of binding a considerable amount of contaminant, it might be considered an appropriate candidate for phytofiltration.

Binding capacity might be reported in milligrams per gram (mg g^{-1}), and moles or micromoles per gram. Table 3 shows a compilation of different plant biomasses that have been studied for their use in metal recovery from aqueous solutions as well as their reported adsorption capacity in mg g^{-1} for a variety of heavy metals. As shown in Table 3, Cu(II), Cd(II), Pb(II), Cr(III), and Ni(II) have been the most studied metals. Cu(II) adsorption capacity varies from 8.09 mg g^{-1}, obtained using petiolar felt-sheath palm, an arecaceae [17], to 45.9 mg g^{-1}, obtained with silverleaf nightshade *Solanum eleagnifolium* [18]. However, the results for Cd(II) adsorption, the second most studied metal, are low compared to those obtained for Cu(II). For Cd(II), the adsorption ranged from 0.4 mg g^{-1}, obtained with cactus powder [19], to 10.8 mg g^{-1}, obtained using petiolar felt-sheath palm [17]. As shown in Table 3, Cr(VI), one of the most toxic metal species, has received less attention. Orhan and Buyukgungor [20] found that nut shell has a Cr(VI) adsorption capacity of 1.47 mg g^{-1}, while Sharma and Forster [21] found that Irish sphagnum peat moss has a Cr(VI) adsorption capacity of 119 mg g^{-1} at pH 1.5. Perhaps researchers have avoided studying Cr(VI) due to its instability and oxidizing power, characteristics that make it difficult to study Cr as Cr(VI).

Table 3 Reported metal adsorption capacities for selected biomaterials.

Material	Cu(II)	Cd(II)	Cr(III)	Cr(VI)	Fe(II)	Fe(III)	Ni(II)	Zn(II)	Pb(II)	Source
Canadian S. peat moss	16.1									[34]
Irish S. peat moss	16.4			119			9.18			[21,79]
Humic acid	28.2									[34]
Humin	17.9	1.34	8						31.2	[34,80]
Sorghum			10							[77]
Cactus powder	9.5	0.4				0.2	8.3	1.5	2.9	[19]
Petiolar palm	8.09	10.8	5.32				6.89	5.99	11.4	[17]
Alfalfa	19.7	7.1	7.7		2.88	4.47	4.1	4.9	43	[9,18,76]
Solanum eleagnifolium	45.9		43.1				13.3	11.5	31.9	[36]
Hops									74.2	[46]
Cocoa shell									2.58	[81]
Pine bark		9.2								[31]
Pine cone		7.5								[31]
Pine needles		7.1								[30]
Nut shell		1.3		1.47						[20]
Paper mill	13.4									[82]

Metal recovery

A stripping agent is a chemical mediator used in the recovery of the adsorbed metal from the biomaterial. When determining the optimal stripping agent, one should consider the following: the capacity to recuperate the metal(s) in a high percentage by using a small volume of such agent in solution, the "benevolence" of the stripping agent in terms of not causing physical damage to the biomaterial, its potential toxicity, and the possible reduction to the metal uptake capacity that the stripping agent might cause.

Stripping agents work by precipitating or complexing the heavy metal attached to the biomass, or by an ion-exchange mechanism [22]. Table 4 presents varieties of stripping agents that have been explored for their use in desorption of metals and are organized according to the mechanism of metal recovery.

Table 4 Mechanism of metal recovery for different stripping agents.

Mechanism	Stripping agent	Source
Complexation/chelation	Ethylenediaminetetracetic acid disodium salt (Na_2EDTA)	[84]
	Sodium citrate	[46]
	Nitrilotriacetic acid (NTA)	[82]
	$NaHCO_3$, Na_2CO_3	[54]
Precipitation	Sulfide	[22]
Ion exchange	HCl	[8,17,83–85]
	H_2SO_4	[82]
	NaOH	[54]

Compounds such as Na_2EDTA, sodium citrate, NTA, and sodium carbonate salts are used as stripping agents since they have the ability to complex heavy metals and put them back into the solu-

tion. These compounds possess pairs of electrons that are available to complex metals. Figure 1 shows the chemical structure of Na_2EDTA where the pairs of electrons that are used in the metal complexation are the ones forming the sodium carboxylate salt.

As Table 4 indicates, desorption of the heavy metals attached to the biomass might be achieved by using a precipitating agent. Crist et al. [22] performed the desorption of Cd adsorbed to *Vaucheria* biomass by immersing the Cd-laden biomaterial in a sulfide solution. In this way, CdS, which is insoluble in water, was formed. The disadvantage of using this method is that the metal is not dissolved in the aqueous solution, and therefore it is not possible to directly quantify the degree of desorption since most of the precipitate is adhered to the biomass.

Another way of desorbing metals is by using chemical species that allow for an ion exchange between the metals bound to the biomass and the cations in the solution. These chemical species could be strong acids or bases, which provide positive species able to displace the metal ions. In most of the cases shown in Table 4, experiments performed with different biomasses and heavy metals report about an 80–100 % rate of metal recovery.

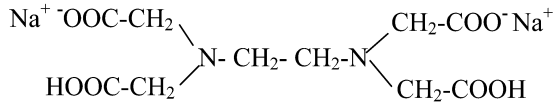

Fig. 1 Chemical structure of ethylenediaminetetracetic acid disodium salt.

Multimetal competition and biosorption interference

Wastewater effluents typically contain more than one toxic metal as well as light metal ions, which could reduce the ability of the biomaterial to eliminate the toxic species from the solution. Thus, multimetal competition and interference experiments are usually performed in order to find out if the presence of other species might interfere with the binding of the target metal ion to the biomass. Competition between chemical species for the binding sites depends on factors such as the chemistry of the metal, pH of the solution, the nature of the binding sites, the amount of binding sites, the diversity of chemical species, metal ion concentration, and the selectivity of the biomass to bind certain species. Hard water components (Ca(II) and Mg(II)) frequently decrease the effectiveness of synthetic resins to recover heavy metal ions present in wastewaters. However, different research groups have shown that even when Ca(II) somewhat interferes with heavy metal binding, most of the time ions such as (Na(I), Ca(II), and Mg(II) do not substantially affect heavy metal biosorption [10,23–26].

Heavy metal biosorption at low concentrations

Traditional methods for heavy metal removal from wastewaters are usually inappropriate or very expensive if applied to effluents containing low levels of contaminants. Several research groups have found that some biosorbents are very effective in recovering a variety of heavy metals from wastewaters when they are present at ppb (parts per billion) concentrations. Spinti et al. [27] reported on the use of S. peat moss to eliminate heavy metals present at low concentrations in acid mine drainage. Gardea-Torresdey et al. [24,25] have reported on the trace level Cu(II) and Au(III) binding to alfalfa biomass with excellent results. In addition, De la Rosa et al. [28] have shown that Canadian S. peat moss, its humin and humic acids efficiently remove Cu(II), Cd(II), Cr(III), Ni(II), and Pb(II) when these elements are found at trace level in an aqueous solution. Therefore, biosorption displays another advantage over conventional methods for heavy metal removal from aqueous effluents.

MECHANISM OF METAL BIOSORPTION

Metal biosorption is a rather complex process affected by several factors. Mechanisms such as chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, micro-precipitation, heavy metal hydroxide condensation, as well as surface adsorption, are involved in the biosorption process [6,16,29].

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 noncellulosic polysaccharides, such as lignin and pectin along with small amounts of protein and some hemicellulosic materials (xylans, mannans, glucomannans, galactans, arabogalactans) [30–32]. In summary, these biomolecules contain carboxyl, hydroxyl, sulfate, sulfhydryl, phosphate, amino, amide, imine, and imidazol moieties that are the functional groups in the biomass with metal binding properties.

As previously mentioned, pH affects the selectivity of the biomass to bind a variety of metals. While binding sites remain different at different pH levels, it is still necessary to identify which functional groups are actually participating in metal binding in order to understand the mechanisms involved. The techniques that have been used in order to gain information about the nature of those binding sites include chemical modification of the biomass as well as a variety of spectroscopic techniques.

Chemical modification

Biomass chemical modifications include esterification of carboxyl and phosphate groups, methylation of amino groups, and hydrolysis of carboxylate groups [33–35]. Esterification is usually performed through the reaction of the biomass with acidic methanol (eq. 2). In this process, an ester is formed and the carboxyl groups are blocked [34]. Esterification of phosphate groups, on the other hand, is accomplished by treating the biomass with a triethyl phosphite/nitromethane mixture (eq. 3). Methylation of amino groups is achieved by a reaction of the biomass with a mixture of formaldehyde/formic acid (eq. 4). Finally, the formation of carboxylate moieties from esters is carried out by exposing the biomass to NaOH solutions (eq. 5).

$$RCOOH + CH_3OH \xrightarrow{H^+} RCOOCH_3 + H_2O \quad [2]$$

$$R\text{-}O\text{-}P(=O)(O^-)\text{-}O^- \xrightarrow[CH_3NO_2]{(CH_3CH_2)_3PO_3} R\text{-}O\text{-}P(=O)(OCH_2CH_3)\text{-}O\,CH_2CH_3 \quad [3]$$

$$RCH_2NH_2 \xrightarrow{HCHO/HCOOH} RCH_2N(CH_3)_2 + CO_2 + H_2O \quad [4]$$

$$RCOOCH_3 \xrightarrow{NaOH} RCOO^-Na^+ + CH_3OH \quad [5]$$

Through these modifications, the variation in metal binding capacity by a variety of biomaterials has been studied. Experimental results have shown that esterification of *Solanum eleagnifolium* biomass and S. peat moss and its humic fractions decreased the capacity of the biomaterial to bind a variety of heavy metals. Hydrolysis of these biomasses, however, enhanced the cited capacity [34,36]. By modifying carboxyl and amino groups in *A. niger* biomass, Kapoor and Viraraghvan [37] found that biosorption of heavy metals was significantly reduced, while esterification of phosphate moieties did not show noted variation in biosorption capacity. Tobin et al. [33], on the other hand, demonstrated that phosphate structures present in *Rhizopus arrhizus* are especially important in metal binding.

Auxiliary spectroscopic techniques

Infrared spectroscopy (IR) [19,38], nuclear magnetic resonance spectroscopy (NMR) [39,40], electron paramagnetic resonance (EPR) [41], and X-ray absorption spectroscopy (XAS) [42–44] are useful techniques that have provided very important information regarding the nature of metal binding to different biomass types. Among these techniques, XAS is probably the most powerful tool available for the elucidation of chemical environments in different materials.

Overview on XAS

Synchrotron-based X-ray absorption spectroscopy (XAS) is a nondestructive technique that provides information about the oxidation state as well as the local environment of elements in a given sample [42,43]. Synchrotron X-ray sources produce X-ray radiation by accelerating pulses of electrons to a speed that approaches that of light. When performing these analyses, a monochromatic X-ray beam is directed to the sample and the energy is gradually increased until it is strong enough to excite the core electrons that are subsequently ejected. This is the absorption edge energy and is specific for each element. In general, impurities do not cause interference, and by analyzing the absorption edge and the oscillations it is possible to obtain information about the environment of the absorbing atom [45]. XAS spectra are divided in two regions, X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS). XANES gives information about the oxidation state of the atom, and the coordination environment, while EXAFS provide data about interatomic distances as the number and identity of neighboring atoms within a 5 Å range [42,43].

XAS studies on metal binding to plant biomass

XAS has revealed very important information about the chemical environment of heavy metals adsorbed to different biomaterials. By using these data, it is possible to determine the functional groups most likely involved in metal binding as well as more detailed information about the chemical identity and the number of atoms attached to the absorbing element. In addition, any change in the oxidation state of the studied metal can be determined. Table 5 presents the results of various XAS experiments performed with a variety of plant-derived materials.

Table 5 shows that the moieties containing oxygen atoms are the main structures participating in metal biosorption. In addition, N and S structures also contribute to metal sequestration. By combining XAS data with information about metal binding by chemically modified biomass, it is apparent that carboxyl moieties are the main functional groups responsible for heavy metal binding to a variety of plant-derived materials such as peat moss, humic substances, and alfalfa [34–36,38,42,46–48,49–51].

Table 5 XAS studies for metal binding to different biomasses.

Heavy metal	Biomass	Bond network	Source
Au(III) reduced to Au(0)	Alfalfa	Au–O; Au–N	[47]
Co(II)	Humic substances	Co–O; Co–C	[42]
Cu(II)	Humic substances	Cu–O; Cu–C	[42]
		Cu–O	[49]
	Hops	Cu–O; Cu–N; Cu–S	[51]
	S. eleagnifolium	Cu–O; Cu–S	[36]
Cr(III)	Hops	Cr–O	[86]
	S. eleagnifolium	Cr–O	[36]
	Alfalfa	Cr–O	[38]
Cr(VI) reduced to Cr(III)	*Avena monida*	Cr–O	[44]
Eu(III)	Alfalfa	Eu–O; Eu–N	[50]
Fe(II), Fe(III)	Alfalfa	Fe–O	[18]
	Hops	Cr–O	[51]
Ni(II)	Humic substances	Ni–O; Ni–C	[42]
	S. eleagnifolium	Ni–O	[36]
Pb(II)	*S. eleagnifolium*	Pb–O	[36]
	Humic substances	Pb–O	[48]
	Alfalfa	Pb-O	[35]
Zn(II)	Humic substances	Zn–O; Zn–C	[42]
	Hops	Zn–O; Zn–S	[51]
	S. eleagnifolium	Zn–O	[36]

COLUMN EXPERIMENTS

Since batch processes are usually limited to the treatment of small amounts of wastewater, a more practical alternative to eliminate metal ions from aqueous solution on a larger scale is required. For this purpose, column experiments are performed in order to evaluate the removal and recovery of metal ions under flow conditions. These experiments also allow testing of the recycling capacity of the packed biomass beads columns.

For the column experiments, the biomaterial might also be used in the raw form or immobilized in a matrix. The biomaterial is packed into columns by which a flow rate is achieved. In some cases, the biomaterial already possesses the appropriate characteristics; most of the time, however, the immobilization needs to be accomplished in order to improve the native biomass mechanical strength, particle size, and resistance to chemicals that could be either present in the aqueous effluent or that might be used for metal desorption. The particle size aspect is important since very small particles will tend to clog the columns avoiding a continuous flow through the apparatus.

Immobilization methods include either entrapment into polymers or natural adsorption onto inert and porous support materials [52]. Support matrices for biomass immobilization include silica, agar, polyacrilamide, polysulfone, alginates, cellulase, and different cross-linking agents [8,52–54]. However, in choosing the matrix, it is necessary to consider the cost of the material, the toxicity and the relative facility to perform the immobilization procedure.

Just as in batch experiments, biosorbents used in column techniques should keep the same adsorption capacity after various adsorption/desorption cycles and maintain the original physical characteristics. Desirable characteristics in a biosorbent include the same adsorption capacity after various adsorption/desorption cycles, the original physical characteristics (particle size, mechanical strength), and the ability to concentrate metals after stripping [6].

In summary, column techniques involve the packing of the column with a biosorbent, preferably immobilized by one of the methods previously mentioned. After packing, a solution containing the metal(s) is passed through the column at a given flow rate until saturation of the biomaterial is achieved. Once the column is saturated, the contaminant attached to the biomass is recovered by using a stripping agent. Biomass saturation is determined by obtaining a breakthrough curve where the concentration of the contaminant in the effluent is plotted against the bed volume of the target solution. A typical breakthrough curve is shown in Fig. 2. This figure shows that at 200 bed volumes, the target contaminant has not appeared in the effluent, meaning that the biomass is adsorbing it. At about 220 bed volumes, the pollutant starts appearing; this is the breakthrough point, and at 310 bed volumes the column becomes saturated. As previously mentioned, a good stripping agent should be able to recover the adsorbed metal in a few bed volumes allowing the concentration of the metal in a small amount of effluent. Column techniques facilitate the treatment of wastewaters to remove toxic pollutants at the site of emission and before contaminants reach water bodies and soils.

The use of biosorbents for water treatment has proven to have considerable advantages over traditional materials. Research is still in progress as different areas related to biosorption are being explored.

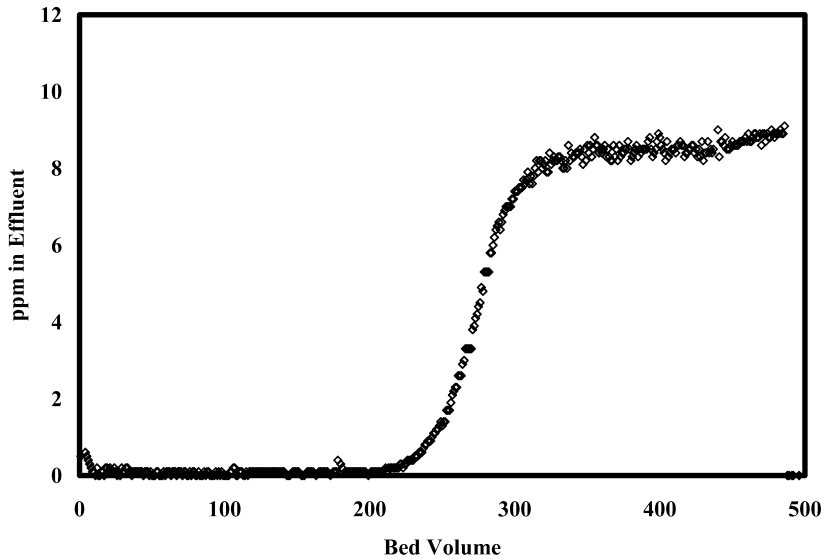

Fig. 2 Typical breakthrough curve for the adsorption of a heavy metal onto a biomass.

CONCLUSIONS

Experimental results have demonstrated that biomass of different natures can be utilized as cost-effective and environmentally friendly techniques in the removal of contaminants from water and wastewater. Plant biomass and biomass from 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), 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 aqueous solutions using different agricultural biomasses. Procedures such as incineration and landfill burial are common for the disposal of heavy metal laden biomass. However, heavy metals entrapped in biomass-packed columns can be recovered using stripping agents such as EDTA-disodium salt, sodium citrate, HCl, and others. This review demonstrates that the use of biosorbents for water treatment might have considerable advantages

over traditional materials. Research is still in progress as different areas related to biosorption are being explored.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the National Institutes of Health (Grant S06GM8012-33). We also acknowledge the financial support from the University of Texas at El Paso (UTEP)'s Center for Environmental Resource Management (CERM) through funding from the Office of Exploratory Research of the EPA (Cooperative Agreement CR-819849-01-04). We also acknowledge the HBCU/MI Environmental Technology Consortium that is funded by the Department of Energy. Guadalupe de la Rosa acknowledges the support of the Consejo Nacional de Ciencia y Tecnologia of Mexico (CONACyT) (Grant 131996). Dr. Jorge Gardea also acknowledges the financial support of the National Institute of Environmental Health Sciences (Grant R01 ES11367-01).

REFERENCES

1. J. Sienkiewicz. *Sci. Total Environ*. **55**, 339–349 (1986).
2. H. W. Woolhouse. In *Encyclopedia of Plant Physiology*, Vol. 12C, O. L. Lange, P. S. Novel, C. B. Osmond, H. Ziegler (Eds.), pp. 246–300, Springer-Verlag, New York (1983).
3. S. E. Bailey, T. J. Olin, R. M. Bricka, D. Adrian. *Wat. Res.* **33** (11), 2469–2479 (1999).
4. D. Petruzzelli, G. Mascolo, G. Barile, G. Tiravanti, A. Marton. *React. Funct. Polym*. **35** (1–2), 89–98 (1997).
5. J. L. Gardea-Torresdey, I. Cano-Aguilera, R. Webb, K. J. Tiemann, F. Gutierrez- Corona. *J. Hazard. Mater.* **48**, 171–180 (1996).
6. B. Volesky. *Hydrometallurgy* **59**, 203–216 (2001).
7. D. Aderhold, C. J. Williams, R. G. J. Edyvean. *Bioresource Technol*. **58**, 1–6 (1996).
8. J. L. Gardea-Torresdey, K. J. Tiemann, J. H. Gonzalez, J. A. Henning, M. S. Towsend. *J. Hazard. Mater.* **48**, 181–190 (1996).
9. J. L. Gardea-Torresdey, K. J. Tiemman, J. H. Gonzalez, I. Cano-Aguilera, J. A. Henning, M. S. Towsend. *J. Hazard. Mater.* **49** (2–3), 205–216 (1996).
10. J. L. Gardea-Torresdey, K. J. Tiemann, J. H. Gonzalez, O. Rodríguez. *J. Hazard. Mater.* **56**, 169–179 (1997).
11. D. Langmuir. *Aqueous Environmental Geochemistry*, Prentice-Hall, USA (1997).
12. A. Esposito, F. Pagnanelli, F. Veglio. *Chem. Eng. Sci.* **57**, 307–313 (2002).
13. J. E. Ferguson. *The Heavy Metals: Chemistry, Environmental Impact and Health Effects*, Pergamon Press, UK (1990).
14. T. L. Brown and H. E. LeMay. *Chemistry, the Central Science*, 2nd ed., Prentice-Hall, USA (1981).
15. D. C. Sharma and C. F. Forster. *Process Biochem.* **30** (4), 293–298 (1995).
16. I. A. H. Schneider, J. Rubio, R. W. Smith. *Int. J. Miner. Process.* **62**, 111–120 (2001).
17. M. Iqbal, A. Saeed, N. Akhtar. *Bioresource Technol*. **81**, 151–153 (2002).
18. K. J. Tiemann, J. L. Gardea-Torresdey, G. Gamez, K. Dokken, I. Cano-Aguilera, M. W. Renner, L. R. Furenlid, *Environ. Sci. Technol*. **34** (4), 693–698 (2000).
19. M. M. Davila-Jimenez, M. P. Elizalde-Gonzalez, W. Geyer, J. Mattusch, R. Wennrich. *Colloids Surf. A* **219**, 243–252 (2003).
20. Y. Orhan and H. Buyukgungor. *Water Sci. Technol*. **28 (**2), 247–255 (1993).
21. D. C. Sharma and C. F. Forster. *Water Res*. **27**, 1201–1208 (1993).
22. D. R. Crist, R. H. Crist, J. R. Martin, J. R. Watson. *FEMS Microbiol. Rev.* **14**, 309–314 (1994).
23. L. R. Drake and G. D. Rayson. *Anal. Chem.* **68** (1), 22A–7A (1996).
24. J. L. Gardea-Torresdey, K. J. Tiemann, J. G. Parsons. *Microchem. J.* **69** (2), 35–44 (2001).

25. J. L. Gardea-Torresdey, K. J. Tiemann, J. G. Parsons, G. Gamez, M. Jose-Yacaman. *Adv. Environ. Res*. **6** (3), 313–323 (2002).
26. J. G. Parsons, J. L. Gardea-Torresdey, K. J. Tiemann, G. Gamez. *Anal. Chim. Acta* **478** (1), 139–145 (2003).
27. M. Spinti, H. Zhuang, E. Trujillo. *Water Environ. Res*. **67** (6), 943–952 (1995).
28. G. de la Rosa, J. L. Gardea-Torresdey, J. R. Peralta-Videa. *J. Hazard. Mater.* **97** (1–3), 207–218 (2003).
29. P. A. Brown, S. A. Gill, S. J. Allen. *Water Res*. **34** (16), 3907–3916 (2000).
30. T. W. Goodwin and E. I. Mercer. *Introduction to Plant Biochemistry*, Pergamon Press, UK (1975).
31. S. Al-Asheh and Z. Duvnjak. *J. Hazard. Mater.* **56**, 35–51 (1997).
32. P. Nobel. *Physicochemical and Environmental Plant Physiology*, Academic Press, New York (1991).
33. J. H. Tobin, D. G. Cooper, R. J. Neufeld. *Enzyme Microb. Technol.* 591–595 (1990).
34. J. L. Gardea-Torresdey, L. Tang, J. M. Salvador. *J. Hazard. Mater.* **48** (1–3), 191–206 (1996).
35. K. J. Tiemann, G. Gamez, K. Dokken, J. G. Parsons J. L. Gardea-Torresdey. *Microchem. J*. **71** (2–3), 287–293 (2002).
36. K. J. Tiemann, A. E. Rascon, G. Gamez, J. G. Parsons, T. Baig, I. Cano-Aguilera, J. L. Gardea-Torresdey. *Microchem. J.* **71** (2–3), 133–141 (2002).
37. A. Kapoor and T. Viraraghavan. *Bioresource Technol*. **61**, 221–227 (1997).
38. J. L. Gardea-Torresdey, K. Dokken, K. J. Tiemann, J. G. Parsons, J. Ramos, N. E. Pingitore, G. Gamez. *Microchem. J.* **71** (2–3), 157–166 (2002).
39. I. Villaescusa, N. Fiol, F. Cristiani, C. Floris, S. Lai, V. M. Nurchi. *Polyhedron* **21** (14–15), 1363–1367 (2002).
40. H. Xia and G. D. Rayson. *Adv. Environ. Res*. **7** (1), 157–167 (2002).
41. R. P. de Carvalho, K. J. Guedes, M. V. B. Pinheiro, K. Krambrock. *Hydrometallurgy* **59** (2), 3407–412 (2001).
42. K. Xia, W. Bleam, A. Helmke. *Geochim. Cosmochim. Acta* **61** (11), 2223–2235 (1997).
43. J. G. Parsons, M. V. Aldrich, J. L. Gardea-Torresdey. *Appl. Spectrosc. Rev.* **37** (2), 187–222 (2002).
44. J. L. Gardea-Torresdey, K. J. Tiemann, V. Armendariz, L. Bess-Oberto, R. R. Chianelli, J. Rios, J. G. Parsons, G. Gamez. *J. Hazard. Mater.* **80** (1–3), 175–188 (2000).
45. B. K. Teo and D. C. Joy. *EXAFS Spectrospcopy, Techniques and Applications*, Plenum Press, New York (1981).
46. J. L. Gardea-Torresdey, M. Hejazi, K. J. Tiemann, J. G. Parsons, M. Duarte-Gardea, J. Henning. *J. Hazard. Mater.* **91** (1–3), 95–112 (2002).
47. J. L. Gardea-Torresdey, K. J. Tiemann, J. G. Parsons, I. Herrera, M. Jose-Yacaman. *Microchem. J.* **71** (2–3), 193–204 (2002).
48. K. Xia, W. Bleam, P. A. Helmke. *Geochim. Cosmochim. Acta* **61** (11), 2211–2221 (1997).
49. G. V. Korshin, A. I. Frenkel, E. A. Stern. *Environ. Sci. Technol*. **32** (18), 2699–2705 (1998).
50. J. G. Parsons, J. L. Gardea-Torresdey, K. J. Tiemann, J. H. Gonzalez, J. R. Peralta-Videa, E. Gomez, I. Herrera. *Microchem. J.* **71** (2–3), 175–183 (2002).
51. J. G. Parsons, M. Hejazi, K. J. Tiemann, J. Henning, J. L. Gardea-Torresdey. *Microchem. J*. **71** (2–3), 211–219 (2002).
52. J. Klein and H. Ziehr. *J. Biotechnol*. **16**, 1–16 (1990).
53. R. E. Hinchee, J. L. Means, D. R. Burris. *Bioremediation of Inorganics*, Battelle Press, USA (1995).
54. R. S. Bai and T. E. Abraham. *Bioresource Technol.* **87** (1), 17–26 (2003).
55. M. Ajmal, K. R. Ali, R. H. J. Ahmad. *J. Hazard. Mater.* **B79**, 117–131 (2000).
56. A. Saeed and M. Iqbal. *Water Res.* **37**, 3742–3480 (2003).
57. T. Srinath, T. Verma, P. W. Ramteke, S. K. Garg. *Chemosphere* **48**, 427–435 (2002).

58. F. Pagnanelli, M. Trifoni, F. Beolchini, A. Esposito, L. Toro, F. Veglio. *Process Biochem.* **37**, 115–124 (2001).
59. M. Yakup Arica, G. Bayramoglu, A. Denizli, S. Bektas. *Microchem. J.* **72** (1), 63–76 (2002).
60. M. Yakup Arica, C. Arpa, A. Ergene, G. Bayramoglu, Ö. Genç. *Carbohyd. Polym.* **52** (2), 167–174 (2003).
61. D. S. Kim. *Bioresource Technol.* **87** (3), 355–357 (2003).
62. K. Yew-Hoong Gin, Y. Tang, M. A. Aziz. *Water Res.* **36** (5), 1313–1323 (2002).
63. G. C. Donmez, Z. Aksu, A. Öztürk, T. Kutsal. *Process Biochem.* **34 (**9), 885–892 (1999).
64. B. Volesky, T. A. Davis, R. H. S. F. Vieira. *Water Res.* **34** (17), 4270–4278 (2000).
65. B. Volesky, J. Weber, J. M. Park. *Water Res.* **37** (2), 297–306 (2003).
66. J. L. Gardea-Torresdey, K. J. Tiemann, G. Gamez, K. Dokken, I. Cano-Aguilera, M. W. Renner, L. R. Furelid. *Environ. Sci. Technol.* **34**, 4392–4396 (2000).
67. I. Herrera, J. L. Gardea-Torresdey, K. J. Tiemann, J. R. Peralta-Videa, V. Armendariz. *J. Hazard. Subst. Res*. **4**, 1–16 (2003).
68. A. V. Pethkar, S. K. Kulkarni, K. M. Paknikar. *Bioresource Technol.* **80** (3), 211–215 (2001).
69. J. Cordery, A. J. Wills, K. Atkinson, B. A. Wills. *Miner. Eng.* **7** (8), 1003–1015 (1994).
70. A. C. Texier, Y. Andrès, C. Faur-Brasquet, P. LeCloirec. *Chemosphere* **47** (3), 333–342 (2002).
71. M. Tsezos and J. P. Bell. *Water Res.* **23** (5), 561–568 (1989).
72. W. C. Steen and S. W. Karickhoff. *Chemosphere* **10** (1), 27–32 (1981).
73. Y. Fu and T. Viraraghavan. *Bioresource Technol*. **79**, 251–262 (2001).
74. J. K. Polman and C. R. Breckenridge. *Text. Chem. Color.* **28** (4), 31–35 (1996).
75. A. K. Mittal and S. K. Gupta. *Water Sci. Technol.* **34** (10), 81–87 (1996).
76. J. L. Gardea-Torresdey, J. H. Gonzalez, K. J. Tiemann, O. Rodriguez, G. Gamez. *J. Hazard. Mater*. **57** (1–3), 29–39 (1998).
77. I. Cano-Rodriguez, J. A. Perez-Garcia, M. Gutierrez-Valtierra, J. L. Gardea-Torresdey. *Rev. Mex. Ing. Quim.* **1–3**, 97–103 (2002)
78. Y. Nuhoglu and E. Oguz. *Process Biochem*. **38**, 1627–1631 (2003).
79. Y. S. Ho, D. A. Wase, D. C. Forster. *Water Res*. **29** (5), 1327–1332 (1995).
80. G. de la Rosa, J. L. Gardea-Torresdey, J. R. Peralta-Videa, I. Herrera, C. Contreras. *Bioresource Technol*. **90** (1), 11–17 (2003).
81. N. Meunier, J. F. Blais, R. D. Tyagi. *Hydrometallurgy* **67** (1–3), 19–30 (2002).
82. S. K. Lister and M. A. Line. *Bioresource Technol*. **79** (1), 35–39 (2001).
83. J. L. Gardea-Torresdey, K. J. Tiemann, G. Gamez, K. Dokken. *J. Hazard. Mater.* **69** (1), 41–51 (1999).
84. M. A. Hashim, H. N. Tan, K. H. Chu. *Sep. Purif. Technol.* **19** (1–2), 39–42 (2000).
85. N. Akhtar, A. Saeed, M. Iqbal. *Bioresource Technol.* **88** (2), 163–165 (2003).
86. K. J. Tiemann, J. L. Gardea-Torresdey, G. Gamez, K. Dokken, S. Sias. *Environ. Sci. Technol.* **33** (1), 150–154 (1999).