

Heavy Metals Remediation of Water Using Plants and Lignocellulosic Agrowastes

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I. Introduction

Metals in the environment arise from natural sources or directly or indirectly from human activities such as rapid industrialization, urbanization, and anthropogenic sources, threatening the environment and human health (Nriagu 1979). Mining and metallurgical activities produce wastewaters that can be considered as the major source of heavy metal contamination of natural waters (Schalcscha and Ahumada 1998; Reddad et al. 2002a). In the United States alone, more than 50,000 metal-contaminated sites await remediation, many of them Superfund sites (Ensley 2000). They are potential hazards to aquatic, animal, and human life because of their toxicity and bioaccumulative and nonbiodegradable nature (Zuane 1990). Nonessential metals such as Hg, Cd, Cr, Pb, As, and Sb are toxic in their chemically combined forms as well as the elemental form (Manahan 1993). Acute metal poisoning in humans causes severe dysfunction in the renal, reproductive, and nervous systems, and chronic exposures even at low concentrations in the

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environment can prove to be harmful to human health (Wyatt et al. 1998). In addition, heavy metals that are discharged from a wide variety of industries such as electroplating, metal finishing, leather tanning, chrome preparation, production of batteries, phosphate fertilizers, pigments, stabilizers, and alloys to the aquatic environment have adverse impacts on aquatic species because they are conserved pollutants that are not subject to bacterial attack or other breakdown and remain as permanent additions to the marine environment (MacCarthy et al. 1995; El-Nady and Atta 1996). They are dangerous to aquatic animals because they tend to bioaccumulate and cause physiological defects and histopathological manifestations in tissues, resulting in reduced reproduction (Gardner 1975; Cutter 1991; Joseph et al. 2002; Krishnani et al. 2003a). Once mobile in the environment in ionic form, they find their way into the human body through drinking water, food, and air. There is a reasonable chance of having a fair amount of toxic metals in the body if a person has eaten fish regularly, has amalgam fillings, has received vaccinations, has drunk contaminated water, or been involved in industrial or agricultural work or pharmaceutical manufacturing.

II. Heavy Metals as Health Hazard to the Aquatic Environment

Arsenic is both ubiquitous in the environment and potentially toxic to humans. It was ranked first on the Comprehensive Environmental Response, Compensation and Liability Act priority list of hazardous substances in the U.S. in 1999 and 2001. Arsenic can occur in water in organic or inorganic forms but the inorganic form is more common (Fuhrman et al. 2004). Inorganic As may exist in -3 , $+3$, and $+5$ oxidation states, with As(III) and As(V) being the dominant species in natural waters. There is evidence that As(III), once absorbed, may be oxidized to As(V) and/or methylated in humans. Methylation of inorganic arsenic in the human body is a detoxification process that occurs in the kidney and reduces its affinity for that tissue (Das et al. 1995). Arsenic is classified as a human carcinogen based on sufficient epidemiological evidence (USEPA 2002). Drinking water with high arsenic concentrations is of particular concern, because studies of chronic arsenic exposure have shown that even small amounts of arsenic in drinking water can cause cancer if ingested over a long period (Karim 2000). The high concentration of arsenic found in drinking water sources has raised concern in many parts of the world including the Bengal Delta (Bangladesh and West Bengal, India) (Nickson et al. 1998), the Red River Delta (Vietnam) (Berg et al. 2001), and the western U.S. (Reid 1994). Occurrence of arsenic in the groundwater of Bangladesh and West Bengal has been described as the greatest mass poisoning in human history (Smith et al. 2000; Rahman et al. 2005), with 36 million people exposed to elevated arsenic in their drinking water (Nordstrum 2002). Today, 97% of Bangladeshi drink well water, and unfortunately vast areas of Bangladesh contain groundwater with arsenic concentrations above the World Health

Organization (WHO 1993) and U.S. Environmental Protection Agency (USEPA 2001, 2002) water guidelines of $10\mu\text{g/L}$. However, some experts believe that an even tougher standard of $3\mu\text{g/L}$ should be adopted. The severity of chronic arsenic poisoning in Bangladesh suggests that other metals such as Mn, Pb, Ni, and Cr in groundwater maybe magnifying As toxicity (Frisbie et al. 1999, 2002), which raises serious concerns relating to environmental health issues caused by multimetal effects. Thus, the development of more efficient arsenic treatment technologies is still urgently required.

Certain organic metal compounds are much more harmful to living organisms than the elements themselves. Examples include methyl and ethyl mercury and tributyl tin used as pesticides. Contamination of aquatic ecosystems with mercury creates health concerns because consumption of fish is the primary means by which humans are exposed to the neurotoxic, methylated form of mercury (Hightower and Moore 2003). Reduction, methylation, and demethylation are important mechanisms of Hg speciation in both the water column and the benthic sediment (Kim et al. 2004). When mercury enters water, it is often transformed primarily by sulfate-reducing bacteria, by microorganisms at the water – sediment interface, or by bacteria associated with the fish gut into the toxic methylmercury, which bioaccumulates and concentrates in living organisms (Compeau and Bartha 1985; Bodaly et al. 1997; King et al. 2000). Field measurements found that almost all Hg (>90%) in fish muscle was in methylated forms (Bloom 1992). In 1932, sewage containing mercury was released into Minamata Bay in Japan. The mercury accumulated in sea creatures, leading eventually to mercury poisoning in man from the consumption of contaminated fish (Kudo and Miyahara 1991). In the U.S., some 60,000 babies per year are born with neurological damage caused by mercury poisoning of their mothers from consuming large amounts of fish from polluted locations during pregnancy (Schrope 2001). Pregnant women and women breastfeeding their children are advised never to eat this kind of fish.

Cadmium is biopersistent and may interfere with the ability of metallothionein to regulate zinc and copper concentrations in the body. Metallothionein is a protein that binds to excess essential metals to render them unavailable. When cadmium induces metallothionein activity, it binds to copper and zinc, disrupting homeostasis levels (Kennish 1992).

Antimony is a metal used in the compound antimony trioxide, a flame retardant; this is a suspected human carcinogen. Previous studies suggest that the severity of chronic arsenic poisoning in Bangladesh might be magnified by the presence of antimony in the drinking water (Gebel 1999). Most antimony compounds do not bioaccumulate in aquatic life.

Small amounts of nickel are needed by the human body to produce red blood cells. Nickel can accumulate in aquatic life, but its presence is not magnified along the food chain. Nickel is a probable human carcinogen. Similarly, selenium and zinc are also needed by humans and other animals

in small amounts. Selenium prevents the cytotoxic effects of arsenic (Biswas et al. 1999). Zinc promotes the repair of tissues damaged by arsenic (Engel et al. 1994). The apparent absence of these essential nutritive elements in drinking water and possibly in food may cause a magnification of As toxicity in Bangladesh water (Frisbie et al. 1999, 2002). However, these metals also accumulate in living tissues of fish and other organisms, causing greater health problems in humans over a lifetime of overexposure.

Because of size and charge similarities, lead can substitute for calcium and be included in bone. Children are especially susceptible to lead because developing skeletal systems require high calcium levels. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and mobilized in the body.

In the U.S., chromium is the second most common inorganic contaminant in waters after lead (Wielinga et al. 2001). Chromium usually exists in both trivalent and hexavalent oxidation states in soils and aqueous systems. The hexavalent form is of particular concern because of its great toxicity, resulting from its powerful oxidation properties. Based on chronic effects, the USEPA (Nkhalambayausi-Chirwa and Wang 2001) and the International Agency for Research on Cancer (IARC 1987) categorize Cr(VI) as a carcinogen, whereas the trivalent form of chromium Cr(III) is not classifiable as it is about 300 times less toxic than Cr(VI). Furthermore, it has limited hydroxide solubility, making it relatively immobile and less available for biological uptake. As a result, Cr(VI) toxicity could be reduced and then become less bioavailable when reduced to Cr(III). Because of these differences, the discharge of Cr(VI) to surface water is regulated at 50 µg/L by the USEPA while total chromium is regulated at 2000 µg/L.

Applications, sources of contamination, and potential health effects of heavy metals are given in Table 1. Various agencies have recommended safe levels for heavy metals for the protection of drinking water, fish, and other aquatic life, which are given in Table 2. Although the content of metals in aquatic the environment has been rising in recent years, there is still a lack of effective means for the removal of metals. The increased concern about metal poisoning and stricter regulations for metal pollution have accelerated many efforts in developing cost-effective methods for removing metals from contaminated water for preserving the quality of aquatic systems, streams, and groundwater. Contaminated waters are generally cleaned by currently used water treatment technologies involving chemical precipitation, adsorption, evaporation, electrochemical treatment, and the use of ion-exchange resins (Leppert 1990; Ouki et al. 1997; Yang and Lin 1998). However, these technologies have been found to be limited because they often involve high operational costs and are sometimes ineffective, especially when metals are present in solutions at very low concentrations. They may also be insufficient to satisfy strict regulatory requirements for chemical precipitation. Among these methods, adsorption is by far the most

Table 1. Applications, sources of contamination, and potential health effects of heavy metals.

Metal	Applications	Sources of contaminant in drinking water	Potential health effects
As	Pesticides, wood preservatives	Erosion of natural deposits, runoff from glass and electronics production wastes	Nausea, vomiting, damage to skin and blood vessels, circulatory problems, cancer
Hg	Batteries, lamps, thermometers, as amalgam in dentistry, pharmaceutical	Erosion of natural deposits, discharge from refineries and factories, runoff from landfills and croplands	Abdominal pain, headache, diarrhea, hemolysis, chest pain, kidney damage, neurotoxicological disorders
Pb	Batteries, petrol additives, alloys, pigments	Corrosion of household plumbing systems; erosion of natural deposits	Anemia, vomiting, loss of appetite, convulsions, damage of brain, liver and kidney, high blood pressure, delays in physical or mental development in children
Cd	Nickel cadmium battery, pigments anticorrosive agent, stabilizers for PVC	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints	Diarrhea, growth retardation, bone deformation, kidney and lung damage, testicular atrophy, anemia, injury of central nervous system and liver, hypertension, cancer
Cr	Metal alloys, paints, cement, paper, rubber	Discharge from steel and pulp mills; erosion of natural deposits	Nephritis, gastrointestinal ulceration, diseases in central nervous system, cancer, allergic dermatitis
Cu	Additives to control fungal growth, electrical pipes	Corrosion of household plumbing systems, erosion of natural deposits	Hypertension, uremia, anemia, coma, sporadic fever, gastrointestinal distress, liver or kidney damage
Sb	Flame retardant, battery, pigments ceramics, glass	Discharge from petroleum refineries, fire retardants, ceramic, electronics; solder	Nausea, vomiting, diarrhea; increase in blood cholesterol, decrease in blood sugar, suspected human carcinogens
Se	Photoelectric cells, TV cameras, glass industry	Discharge from petroleum refineries; erosion of natural deposits, discharge from mines	Hair or fingernail loss, numbness in fingers or toes, damage to kidney, nervous system and circulatory tissues, irritability

Table 2. General Water Quality Criteria Recommended by Tennessee Department of Environment and Conservation (Tennessee Water Quality Control Board), USEPA, and WHO.

Heavy metals	Tennessee Water Quality Standards ($\mu\text{g/l}$) ^a				USEPA ($\mu\text{g/l}$) ^b	WHO ($\mu\text{g/l}$) ^c
	Domestic Water Supply	For protection of fish and aquatic life	For general -use ground water	For recreation	Groundwater and drinking water standards	Groundwater and drinking water standards
As	10	340 ^d	50	10	10	10
Cd	5	2	5	—	5	3
Cr (Total)	100	16 ^e	100	—	100	50
Pb	5	65	50	—	0	10
Hg	2	1.4	2	0.05	2	—
Ni	100	470	—	610	100	20
Sb	6	—	—	5.6	6	5
Se	50	20	50	—	50	10
Cu	—	13	1,000	—	1,300	2,000
Zn	—	120	5,000	—	—	—
Mn	—	—	500	—	—	500

^aRules of Tennessee Department of Environment and Conservation (Tennessee Water Quality Control Board), January 2004 (revised).

^bUSEPA (1996) USEPA drinking water regulations and health advisories. EPA 822-B-96-002. USEPA, Washington, DC.

^cWHO (1997) Guidelines for Drinking Water Quality. Health Criteria and Other Supporting Information, 2nd ed, vol 1. World Health Organization, Geneva, Switzerland.

^dAs(III).

^eCr(VI).

versatile and widely used method for the removal of toxic metals (Mattson and Mark 1971; Cheremisinoff and Ellerbush 1979; Gupta et al. 2003; Gupta and Ali 2004). Activated carbon has been used very frequently for the removal of various metal ions from wastewater for more than three decades (Huang and Wu 1977; Lalwani et al. 1998), but the high cost of activated carbon restricts its large-scale use for the abatement of heavy metal pollution, and in recent years the search for an low-cost adsorbent has grown (Reddad et al. 2002a–d, 2003; Dupont et al. 2003; Dupont and Guillon 2003; Krishnani et al. 2004; Parimala et al. 2004).

III. Plant Remediation as Alternative to Chemical Technologies

With the high costs of site remediation, it is important that we continue to develop and refine innovative low-cost methods for cleaning the environment. Advances in groundwater and soil remediation continue to lead to a

better understanding of the many processes by which plants can have a positive impact on contamination in the environment. This realization has provided impetus to studies in an emerging field of interest, which employs certain plants possessing the natural ability to take up heavy metals for an inexpensive means of environmental cleanup. This method is referred to as plant-assisted remediation or phytoremediation, and it also has the benefit of contributing to site restoration when remedial action is ongoing. The action of plants can include enzymatic degradation, also called phytotransformation or phytodegradation, immobilization by chemical compounds produced by the plants (adsorption or phytostabilization), accumulation (phytoextraction or phytoaccumulation), volatilization (phytovolatilization), and the enhancement of bacterial activity (phytostimulation or plant-assisted bioremediation) (Lee and Charles 2004; Anton and Mathe-Gaspar 2005; Chaney et al. 1997; Davis et al. 2003; Krishnani et al. 2004). To date there are approximately 400 known metal hyperaccumulators in the world (Reeves and Baker 2000), and the number is increasing. However, the remediation potential of many of these plants is limited because of their slow growth and low biomass. A plant suitable for phytoremediation should possess high biomass with high tolerance and metal accumulation in the shoot tissues (Chaney et al. 1997; Eapen and D'Souza 2005). Many hyperaccumulator plants excrete organic acids such as citric, malic, malonic, and oxalic acids (Ma et al. 2001), phytosiderophores that act as metal chelators and decrease the rhizosphere pH, thus making metal cations bioavailable (Kinnerseely 1993).

The phytoremediation of heavy metals has been reviewed by previous researchers (Moffat 1995; Salt et al. 1996; Bailey et al. 1999; Eapen and D'Souza 2005; Chuah et al. 2005). However, they highlighted mainly plant genetic engineering and reported only maximum adsorption capacity of some selected sorbents with very little information on removal mechanisms. This review describes the current technologies prevalent for plant-assisted remediation using live and dead biomass from plentiful natural sources and lignocellulosic wastes, with the major emphasis on removal mechanisms.

A. Using Living Biomass

In recent years biosorption research, which focuses on using readily available biomass that can passively accumulate heavy metals, has received growing attention (Davis et al. 2003). This approach involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. This process can be applied as a cost-effective way of purifying industrial wastewater whereby drinking water quality can be attained. Marine brown algae have been the focus of numerous biosorption studies, and their excellent metal-binding capacity has been well documented (Ramelow et al. 1992; Holan et al. 1993; Leusch et al. 1995; Davis

et al. 2003). The main components of the brown algal cell wall are cellulose as the fibrous skeleton, alginate and fucoidan, which constitute the amorphous matrix, and extracellular mucilage (South and Whittick 1987). Of these compounds, alginate contains carboxyl groups and fucoidan has sulfate groups, both of which are known to form complexes with metals (Buffle 1988; Davis et al. 2003). Kuyucak and Volesky (1989) speculated that alginate may be one of the main compounds involved in brown algae metal accumulation, and Fourest and Volesky (1996) have confirmed the importance of the alginate carboxylic groups; after blocking the weakly acidic carboxylic groups with propylene oxide, metal binding was reduced by 80%–95%.

Arsenic uptake by plants is associated with the phosphate uptake mechanism, where presumably arsenate is taken up as a phosphate analogue (Mkandawire et al. 2004; Khattak et al. 1991; Meharg and Macnair 1990; Pickering et al. 2000). To date, there is only one report (Ma et al. 2001) of a terrestrial plant, the Fern *Pteris vittata*, that hyperaccumulates arsenic, and it has been suggested that it could be used for the phytoremediation of arsenic-contaminated sites. However, Caille et al. (2004) reported that *P. vittata* may be suitable for phytoremediation only in moderately contaminated soils. The ability of *Lepidium sativum*, a watercress, to take up large amounts of arsenic from substrates containing relatively low concentration of this element indicate the plant may have potential for phytoremediation (Robinson et al. 2003).

Hyperaccumulating plants have been identified for a number of metals (Chaney et al. 1997; Lombi et al. 2001; Leduce and Terry 2005); however, the phytoremediation efficiency of most metal hyperaccumulators is limited by their slow growth rate and low biomass. For example, *Thlaspi caerulescens* a Penny-cress, is a Cd and Zn hyperaccumulator, and successfully removed 43% Cd and 7% Zn from an industrially contaminated soil, but this required 391 d (Lombi et al. 2001). The use of microorganisms such as bacteria (Texier et al. 1999), fungi, and algae (Kratochvil and Volesky 2000; Schiewer and Wong 1999; Yang and Volesky 1999) in treating waste effluents containing toxic metal ions is today an attractive technique but not yet suitable for application on a large scale (Reddad et al. 2002b).

B. Using Nonliving Biomass

In addition to live plants, studies have demonstrated that nonviable plant biomass can effectively bind toxic metals and as such can be used to remove metals from solution (Seki et al. 1998). The unique ability of these plants to bind metals has been attributed to the presence of various functional groups that attract and sequester metal ions (Baig et al. 1999). This technology is attractive mainly because it is environmentally friendly and inexpensive. Baig et al. (1999) examined the binding of Pb(II), Cu(II), Ni(II), Cd(II), Zn(II), Cr(III), and Cr(VI) to the inactivated biomass of *Solanum*

elaegnifolium (silverleaf nightshade) and reported that all showed binding to the biomass with optimum binding occurring between pH 5.0 and 6.0. Previous studies have reported the binding of metals to some organic acids that contain carboxyl ligands (Korshin et al. 1998). Work done by Baig et al. (1999) suggested that to some extent carboxyl groups ($-\text{COOH}$) are responsible for the binding of metal ions, and at lower pHs the carboxyl groups retain their protons, reducing the probability of their binding to any positively charged ions, whereas at higher pHs (above 4.0), the carboxyl groups are deprotonated and, as such, are negatively charged ligands ($-\text{COO}^-$), which attract the positively charged metal ions resulting in binding.

Thus, metal ion binding to the biomass is in essence an ion-exchange mechanism that involves electrostatic interaction between the negatively charged groups in the cell walls and metallic cations (Wase and Forster 1997), which means that metal binding can be enhanced by increasing the number of carboxylate ligands in the biomass. Interestingly, cellulose, hemicellulose, and lignin, major constituents of most plant tissues, contain methyl esters that do not bind metal ions significantly. However, these methyl esters can be modified to carboxylate ligands by treating the biomass, thereby increasing the metal-binding ability of the biomass. Baig et al. (1999) also observed that the biomass binds more than 80% of Pb^{2+} at pH 3.0 and about 50% at pH 2.0, suggesting that besides carboxyl groups, other groups may also be involved in Pb(II) binding. Conversely, the biomass binds more Cr(VI) at pH 2.0 compared to that bound at pH 5.0, for which two processes have been hypothesized (Baig et al. 1999). First, because Cr(VI) occurs as an oxoanion such as CrO_4^{-2} , HCrO_4^{-1} , or $\text{Cr}_2\text{O}_7^{-1}$, binding at higher pH where negatively charged carboxylate ions prevail is highly unlikely. Second, it has been reported that at lower pH, Cr(VI) is reduced to Cr(III) (Kratochvil et al. 1998). However, no significant difference in Cd(II) binding is observed upon modification, which suggests that probably other ligands are involved in the binding of Cd(II) to the biomass. Also as expected, the amount of Cr(VI) bound by the biomass is not enhanced by modification, because Cr(VI) exists as an oxoanion and therefore cannot bind to the negatively charged carboxylate ligands.

C. Using Lignocellulosic Agrowastes

Life on earth can exist only because of the cycling of matter, which is therefore of utmost importance to all living systems. For humans, biomass in the form of lignocellulosics provides a means of harnessing and storing solar energy and hence represents an important energy and material resource. But, before this renewable Carbon source can be used, its conversion to applicable form is necessary. As such, recycling of organic matter has assumed great significance from the point of view of resource utilization and pollution abatement. Among the chemical constituents in plant

biomass, cellulose, hemicellulose, and lignin occupy the major portion (Mani et al. 1998). The number of glucosidic bonds available for enzymatic action depends to a large extent on the degree of swelling of cellulose, which can be achieved by physical or chemical methods. Mild pretreatment of lignocellulosics with steam, acid, or alkali helps loosen the crystalline structures of cellulose.

Agricultural countries generate considerable amounts of lignocellulosic agrowastes and by-products such as sugar-cane bagasse, rice straw, rice husks, ground nut husks, crop wastes, peanut hulls, and animal manure. Many of these fibrous by-products are generally used as an ingredient of formulated feed (Miltner et al. 1983) and fertilizer to enhance the natural productivity of ponds, especially in freshwater aquaculture systems (Hepher and Pruginin 1981). These materials have the advantage of being readily available and could provide value-added products that otherwise would be considered as a waste. Today, the world's industry is utilizing less than 10% of the biomass of raw materials from plantations (Pauli and Gravitis 1997). In the U.S., approximately 350 million t of agricultural residues (AR) are currently disposed of every year, and many types of these abundant residues from tropical plantations are waiting for effective utilization. AR are the most abundant renewable organic resources of energy and production of a diversity of chemicals, including ethanol production (Ikeuchi et al. 1999), activated carbon (Namasivayan and Kadirvelu 1999; Bailey et al. 1999; Bansode et al. 2003), and ion exchangers (Simkovic and Laszlo 1997). Agricultural wastes have been reported to be efficient in removing toxic metals from aqueous solutions (Low et al. 2000; Cimino et al. 2000; Ho and McKay 2000; Vaughan et al. 2001). Many other applications for these residues are being developed. Development of new economically feasible ecofriendly products from agricultural wastes/by-products and natural plants for the treatment of shrimp culture water is the objective of continued research of the Central Institute of Brackishwater Aquaculture, Chennai (Krishnani et al. 2002, 2003b, 2004, 2006).

Lignocellulosic residues are composed mainly of cellulose, hemicellulose, and lignin. Lignin is the main component, which adds to the lack of efficacy of these materials, the result of mainly covalent bonds between lignin and carbohydrates. Lignin shields the carbohydrate (cellulose) from any kind of microbial attack. Hence, for incorporation in the aquatic system, the lignocellulosics need prior processing to increase efficacy to the maximum possible extent and to render them manually more efficient. The differences in the chemical composition of the lignocellulosics also affect their degradation in aquatic environments. Another factor that plays a significant role during decomposition is the C/N ratio. In the past few years, continuous efforts have been made to process the lignocelluloses through physical, chemical, and biological treatment. These treatments increase the accessibility for degradation due to partial removal of hemicellulose

(Woodford 1984). These wastes have potential manurial values in different farming practices, including freshwater aquaculture (Ayyappan et al. 1992; Barik et al. 2002), and have been used as substrates for a periphyton food source in aquaculture (Bombero-Tuburan et al. 1993; Azim et al. 2002; Keshawanath et al. 2001).

Numerous by-products of agroindustrial production have been studied for potential use as inexpensive biosorbents (Laszlo and Dintzis 1994; Marshall and Champagne 1995; Basso et al. 2002). One of these low-cost sorbents particularly suited to biosorption is bagasse, a complex native lignocellulosic fibrous waste remaining after extraction of juice from sugar cane. This by-product amounts to 25%–30% of the cane weight and contains about 50% cellulose, 27.9% hemicellulose, 9.8% lignin, and 11.3% cell contents (Kewalramani et al. 1988). Sugar-cane mills produce more bagasse than can be utilized as a fuel source for sugar processing; few commercial uses for the excess bagasse have been developed, and its accumulation presents a waste problem for the sugar industry. It is reported that about 8 million t dry bagasse was produced in India in 2001 (Khan et al. 2004). One potential use of bagasse is as a feedstuff for shrimp (Freeman et al. 1992), as this is an attractive agricultural by-product for a pond supplement due to its low cost and general availability without any adverse impact on water quality in shrimp-growing latitudes (Visscher et al. 1991).

Among available conventional processes used to remove Cr(VI), the most commonly used are precipitation as chromium hydroxide or ion exchange using macroporous resins (Jianlong et al. 2000). However, these methods suffer from disadvantages due to their relatively high operational costs. Conversely, in recent years, a promising alternative method for removal of Cr(VI) uses the sorption by lignocellulosic solid wastes such as bagasse (Krishnani et al. 2004), sugar-beet pulp (Reddad et al. 2003), wheat bran (Dupont and Guillon 2003), and sawdust (Raji and Anirudhan 1998). Bagasse has been found to be effective in removing chromium from coastal waters by ion-exchange and adsorption mechanisms (Krishnani et al. 2004). Krishnani et al. (2004) and Parimala et al. (2004) studied the efficacy of five different types of materials prepared from bagasse and coconut husk for detoxification of Cr(VI) from coastal waters, which is the source of brackish-water aquaculture. They found that acid-treated materials are the most effective materials for detoxification of Cr(VI) in the acidic medium, which can be attributed to the reduction of Cr(VI) into Cr(III), whereas the removal of Cr(VI) in treatments with other material prepared from bagasse and coconut husk in an alkaline medium has been attributed to the reduction by increase in the native microbial community in the coastal waters. Furthermore, bagasse is a biodegradable substrate that harbors a higher periphytic biomass than nondegradable materials, possibly because biodegradable substrates provide a better surface structure to which periphytic species can attach, or they may leach nutrients beneficial for the growth of periphyton, which has more than one role in aquaculture

(Azim et al. 2002; Keshavanath et al. 2001). It improves fish and shrimp production and water quality, thus enhancing the efficiency of aquaculture systems.

Sugar-beet pulp is a low-cost, unconventional sorbent that exhibits a large capacity to bind metals (Dronnet et al. 1997; Gerente et al. 2000). Actually, about 14×10^6 t sugar-beet pulp are produced every year in Western Europe, where it is used mainly as animal feed (Micard et al. 1997). Sugar-beet pulp, a common waste from the sugar-refining industry, was used for the removal of metal ions from aqueous solutions by Reddad et al. (2002a); they found that it has great potential for the removal of heavy metals from aqueous solutions with the affinity order $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$. They identified the predominant ion-exchange mechanism involving numerous carboxylic groups of the galactouronic acid residues in the pectins.

Previous studies (Gerente et al. 2000; Reddad et al. 2002c,d) have revealed that the lignocellulosic substrate has lignin and cellulose as its major constituents. Lignins bear functional groups such as alcohols, ketones, and carboxylic groups that may be involved in complexation reactions with metallic cations. The removal of Cr(III) and Cr(VI) from aqueous solutions using sugar-beet pulp as a biosorbent substrate was performed by Reddad et al. (2003) under various experimental conditions. They found that Cr(VI) removal was largely involved in a reduction mechanism with the appearance of Cr(III) ions in the solution and that the carboxylic groups of the biosorbent are the main reduction sites of the Cr(VI) species. They also found that Cr(III) ions are adsorbed onto the biosorbent by an ion-exchange mechanism with Ca^{2+} cations neutralizing the carboxyl groups of the material. The influence of solution pH greatly affected the adsorption efficiency of Cr(VI), and the optimum removal resulting from the reduction mechanism was achieved at acidic pH values (Reddad et al. 2003).

Studies conducted by Gerente et al. (2000) on the removal of Cu^{2+} , Pb^{2+} , and Ni^{2+} using sugar-beet pulp revealed that a key part of the mode of fixation is attributed to ion exchange. They found that the movements of Na and K ions are in the same order of magnitude and seem to be independent of the Cu^{2+} concentration, and thus their role in copper removal would be low. On the other hand, the release into solution of Ca^{2+} is correlated with the fixation of Cu^{2+} . As far as lead is concerned, adsorption seems to play an important role in fixation, and 25% would be fixed by adsorption (Gerente et al. 2000). In contrast, nickel seems to be fixed completely by ion exchange, and as for copper, the major part of fixation is attributed to ion exchange, only 5% being adsorbed.

Lignocellulosic substrates (LCS) such as rice hull (RH), sugar-cane bagasse (BG), and wheat straw are now regarded as abundant, inexpensive, and readily available natural resources for the chemical and paper indus-

tries. Dupont and Guillon (2003) studied the adsorption mechanism of Cr(VI) onto the LCS and showed that the adsorption reaction consumes a large amount of protons that go with reduction of Cr(VI) into Cr(III). The oxidation of lignin moieties takes place concurrently with chromium reduction and leads to the formation of hydroxyl and carboxyl groups. The latter contribute to an increase in the number of ion-exchange sites for the reduced chromium. They reported maximum adsorption capacity for Cr(VI) of about 35 mg/g in an acidic medium. Also, they used X-ray photo electron spectroscopy (XPS) to characterize the surface chemistry of LCS and Cr speciation adsorbed onto the LCS. Sorption capacity of the LCS could be related to the abundance of lignin and fatty acid moieties, which allow the reduction of hexavalent chromium into the trivalent form as well as fixation of Cr(III) on carboxylic moieties. The increase of carboxyl groups was estimated by XPS, and potentiometric titrations can be easily related to the increase in the retention capacity of LCS.

Lignocellulosic substrates isolated from wheat straw and bran exhibited high complexing capacities (Gauthier et al. 2002). A large difference in composition was observed between bran and straw LCS due to a much higher contribution of alkyl moieties in the former. These moieties correspond to fatty acids esterified to the lignocellulosic macromolecular structure, and such carboxyl groups play an important role in metal complexation and hence in applications for metal removal from industrial effluents.

Reddad et al. (2002b) conducted studies on the Ni(II)- and Cu(II)-binding properties of native and modified sugar beet and found that the chemical modifications applied to the native material resulted in an improvement of the cation exchange capacities. Because of the loss of all methoxy groups from the carboxyl moieties, base-extracted pulp and saponified pulp exhibited the highest Ni(II) and Cu(II) ion uptake among the materials tested.

IV. Adsorption Capacities of Sorbents

The reported capacities of various sorbents such as live and dead biomass from natural sources and lignocellulosic wastes are given in Table 3, and adsorption capacities of various other sorbents such as activated carbon, chitosan, lignin, clay, xanthate, peat moss, and bark are given in Table 4. These data show that sorbents prepared from lignocellulosic wastes are comparable to ordinary adsorbents and sorbents from other natural sources except chitosan, which have comparatively high adsorption capacity. However, lignocelluloses have an edge on other sorbents because of their great availability, very low cost, and simple operational process. In general, a sorbent can be assumed as low cost if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry (Bailey et al. 1999).

Table 3. Adsorption capacities (mg/g) for various biomass and lignocellulosic materials in the literature.

Type	Material	Source	Cd	Cr(VI)	Pb	Zn	Cu	Ni	As(V)
Dead biomass	<i>Chlorella minutissima</i>	Roy et al. (1993)	11.14	162.23	9.74	—	—	—	—
	<i>Solanum elaeagnifolium</i>	Baig et al. (1999)	18.94	2.16	20.6	6.96	13.14	6.5	—
	<i>Penicillium chrysogenum</i>	Niu et al. (1993)	—	—	116	—	—	—	—
	<i>Streptomyces griseus</i>	Matis and Zouboulis (1994)	28	—	—	—	—	—	—
Living biomass	Seaweed	Leusch et al. (1995)	215	—	344	—	—	—	—
Lignocellulosic substrates	Sugar-beet pulp	Reddad et al. (2003)	—	10 ^a	—	—	—	—	—
	Sugar-beet pulp	Reddad et al. (2002d)	24.4	—	73.76	17.78	21.16	11.85	—
	Wheat bran	Dupont et al. (2003)	—	35	—	—	—	—	—
	Sugar-beet pulp	Gerente et al. 2000	—	—	60	—	30	12	—
	Rice husk	Wong et al. (2003)	—	—	108	—	29	—	—
	Rice husk	Tarley et al. (2004)	4	—	45	—	—	—	—
	Rice husk	Roy et al. (1993)	21.36	164.31	11.4	—	—	—	615.1
	Rice husk	Lee et al. (1999)	—	—	—	—	—	—	18.98
	Sawdust	Sharma and Forster (1994)	—	39.7	—	—	—	—	—
	Bagasse	Sharma and Forster (1994)	—	13.4	—	—	—	—	—
	Sugar-beet pulp	Sharma and Forster (1994)	—	17.2	—	—	—	—	—
	Coconut husk fibers	Tan et al. (1993)	—	29	—	—	—	—	—
	Palm pressed fibers	Tan et al. (1993)	—	15	—	—	—	—	—

^aCr(III).

Table 4. Adsorption capacities (mg/g) for various other sorbents in the literature.

Type	Material	Source	Hg	Cd	Cr(VI)	Pb	Zn	Cu	Ni
Lignin	Lignin	Srivastava et al. (1994)	—	—	—	1,865	95	—	—
	Sulfuric acid lignin	Masri et al. (1974)	150	—	—	—	—	—	—
Xanthate	Cellulose xanthate	Bricka and Hill (1989)	0.64	19.88	19.67	—	—	—	—
Alginate	Sodium alginate	Jang et al. (1995)	—	—	—	—	—	138.3	—
Chitosan	Composite chitosan	Boddu et al. (2003)	—	153.8	—	—	—	—	—
	Chitosan from lobster shells	Peniche-Covas et al. (1992)	430	—	—	—	—	—	—
Bark	Chitin	Masri et al. (1974)	100	—	—	—	—	—	—
	Chitosan	Manuel et al. (1995)	—	—	78	—	—	—	—
Activated carbon	Black oak	Masri et al. (1974)	400	25.9	—	153.3	—	—	—
	Douglas-fir	Masri et al. (1974)	100	—	—	—	—	—	—
	<i>Pinus sylvestris</i>	Alves et al. (1993)	—	—	19.5	—	—	—	—
Peat moss	Filtrosorb 400	Huang and Wu (1977)	—	—	125.5	—	—	—	—
	Coconut shell	Alaerts et al. (1989)	—	—	20	—	—	—	—
Clays	Wallastonite	Tummavuori and Aho (1980a,b)	16.2	5.058	4.63	20.038	—	—	—
	Heat-treated bentonite	Yadava et al. (1991)	—	—	—	0.217	—	—	—
Zeolite	Zeolite	Pradas et al. (1994)	—	16.5	—	—	—	—	—
	Bagasse	Leppert (1990)	150.4	84.3	26.0	155.4	—	—	—
Fly ash	Bagasse	Gupta et al. (2003)	—	1.4	—	—	—	—	1.2
	Bagasse	Gupta and Ali 2004	—	—	20	30	—	—	—

V. Langmuir or Freundlich Isotherms Versus NICA–Donnan Model

Although numerous authors have reported on screening of biosorptive properties of different biomass types (Volesky and Holan 1995), most biosorption data are interpreted using simple Langmuir or Freundlich isotherms that can only reflect the influence of metal concentration on the uptake of that one particular metal. Few studies have focused on different conditions (e.g., metal concentrations, pH, ionic strength), whereas the Donnan model has been used to interpret ionic strength effects in poly-electrolytes (Marinsky 1987). For biosorption, ionic strength effects have only recently been taken into account using the Donnan model (Schiewer and Volesky 1997; Schiewer 1999; Bouanda et al. 2002). It has long been recognized that the binding of most divalent metals increases with increasing pH (Ferguson and Bubela 1974; Tsezos and Volesky 1981; Ramelow et al. 1992; Holan et al. 1993), and this is explained as an effect of decreasing competition with protons for the same binding sites (Greene et al. 1987; Crist et al. 1994). The Donnan model has been used successfully to determine the effect of ionic strength on biosorption by *Sargassus* seaweed biomass (Schiewer 1999). The binding of protons and metal ions is reduced with increasing ionic strength because Na^+ , H^+ and Mg^{2+} compete for electrostatic binding, all acting as counterions for the negatively charged binding sites in the biomass.

Currently, various kinds of unconventional substrates generated from agricultural and forest by-products are also being tested to evaluate their efficiency in the removal of toxic metal ions. Dupont et al. (2003) demonstrated the value of natural organic matter in the retention of heavy metal ions and has extracted a lignocellulosic substrate from wheat bran, which is able to fix these three metal ions efficiently in this order: $\text{H}^+ \approx$ copper \approx lead and cadmium ions. Greater affinity of H^+ ions has also been observed by Ravat et al. (2000) with a lignocellulosic substrate, and it is classic in the case of humic substances (Kinniburgh et al. 1996; Benedetti et al. 1995); this represents a very simple model of natural organic matter derived from lignin and cellulose. The total metal binding is composed of three contributions, the Donnan phase and the carboxylic- and phenolic-type sites. Whatever the pH, indeed, the implication of lignin and cellulose in the retention and transport of metal ions is now more and more assumed (Guillon et al. 2001). Metal ion binding to natural organic matter is assumed to occur through specific interactions between cations and surface functional groups and by nonspecific binding to any residual negative charge. Proton binding involves two major contributions from weak and high-affinity site types; the former can be identified with carboxyl sites and the latter with the phenol sites. Dupont et al. (2003) described the acid–base properties of LCS using NICA–Donnan formalism, where electrostatic interactions are taken into account. The affinity of metal ions or high-

affinity sites increases in the order $Cd < Pb \approx Cu \approx H$. The same sequence is observed for the low-affinity site except that H^+ has a greater affinity than Cu^{2+} and Pb^{2+} .

Summary

Toxic heavy metals and metalloids are constantly released into the environment, and their removal is a very difficult task because of the high cost of treatment methods. Various methods exist for the removal of toxic metal ions from aqueous solutions. Among these are adsorption using activated carbon, by far the most versatile and widely used method for the removal of toxic metals; however, it is relatively expensive and less feasible to use in developing countries. Furthermore, activated carbon loaded with toxicants is generally incinerated or disposed of on land, thereby causing environmental pollution through different routes. There is an urgent need to develop low-cost, effective, and sustainable methods for their removal or detoxification. The use of lignocellulosic agrowastes is a very useful approach, because of their high adsorption properties, which results from their ion-exchange capabilities. Agricultural wastes can be made into good sorbents for the removal of many metals, which would add to their value, help reduce the cost of waste disposal, and provide a potentially cheap alternative to existing commercial carbons. Although the abundance and very low cost of lignocellulosic wastes from agricultural operations are real advantages that render them suitable alternatives for the remediation of heavy metals, further successful studies on these materials are essential to demonstrate the efficacy of this technology.

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