Innovative use of silvichemical biomass and its derivatives for heavy metal sorption from wastewater

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Abstract: Biosorption is a process of metabolism-independent, passive, physico-chemical binding of metal ions involving non-living biomass, which offers advantages over conventional methods because of cost-effectiveness, especially for dilute metal solutions, and minimal environmental impact. This paper reviews heavy metal biosorption using silvichemical-based biomass materials. It discusses the use of a wide range of silvichemical biomasses and their derivatives for heavy metal removal from single and multi-metal systems. The structures and properties of silvichemical biomasses as well as methods of biosorbent pretreatment and immobilisation are evaluated. Metal biosorption mechanisms and binding sites, selective biosorption and biosorbent reuse and regeneration are also addressed.

Keywords: silvichemical biomass; heavy metal; biosorption; wastewater treatment; ion exchange.


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Geoff H. Covey obtained BSc Chemical Engineering from the University of Surrey. Two years pigment research at Laporte. PhD University of Melbourne. Nine years process development and plant technical at Australian Paper Manufacturers, developed commercial chemical recovery process. Four years research at Associated Pulp and Paper Mills. Eight years academic staff at the University of Melbourne with research in fluoride processing, pulp and paper and engineering economic analysis. Formed Covey Consulting in 1989, now Chairman, work for many clients on research, design, process improvement and business analysis.
Introduction

Heavy metal is a general collective term applying to the group of metals with an atomic density greater than 5 g/cm\(^3\). Although being only a loosely defined term, it is widely recognised and usually applied to elements such as Cd, Cr, Cu, Hg, Ni, Pb and Zn, which are commonly associated with pollution problems (Alloway and Ayres, 1997). An alternative (and theoretically more acceptable) name for this group of elements is trace metals, but this is not as widely used. Depending on the level of threshold concentration, some of the trace metals are both essential and toxic elements, and can act as either nutrients or poisons (Gadd, 1992). Unlike most other toxic pollutants, metals can accumulate throughout the food chain owing to their non-biodegradability, and thus have detrimental effects on all living species (Zouboulis et al., 1999; Bakkaloglu et al., 1998; Ferraz and Teixeira, 1999). As a result, many water quality guidelines have been laid out stipulating levels that metal constituents must not exceed (Table 1).

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.003</td>
<td>0.01</td>
<td>0.26</td>
</tr>
<tr>
<td>Cu</td>
<td>2.0</td>
<td>0.2</td>
<td>2.10</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05</td>
<td>0.1</td>
<td>1.70</td>
</tr>
<tr>
<td>Ni</td>
<td>0.02</td>
<td>0.2</td>
<td>2.40</td>
</tr>
<tr>
<td>Pb</td>
<td>0.01</td>
<td>2.0</td>
<td>0.43</td>
</tr>
<tr>
<td>Zn</td>
<td>3.0</td>
<td>2.0</td>
<td>1.50</td>
</tr>
</tbody>
</table>

The increased use of heavy metals in the process industries and mining activities have resulted in the generation of large quantities of toxic liquid wastes that contain high levels of heavy metals and pose environmental disposal problems (Leusch et al., 1995; Cho et al., 1999). Current metal removal technologies include precipitation, adsorption using silica gel, zeolites and activated carbon, ion exchange on resins, electrolysis and membrane separation, many of which are firmly established, well understood and represent significant capital investment by industry (Kapoor and Viraraphavan, 1995; Gallagher et al., 1997). However, these technologies are inefficient, technically complicated or costly in meeting the increasingly stringent discharge standards (Table 1), especially when dealing with dilute heavy-metal solutions (1–100 ppm) (Brown et al., 2000).
Chemical precipitation is relatively inexpensive, but it generates a large volume of waste sludge and becomes less effective for dilute metal solutions. Electrolysis does not need extra chemical reagents, thus no sludge is produced. However, the economics of this method depend heavily on the energy price and the amount of electricity consumed per volume of metal solution treated. Reverse osmosis, electrodialysis and other membrane process tend to be utilised in more specialised applications owing to their process complexity, and are hindered by the flow rate of the treated solutions and the presence of contaminants. Ion exchange is more effective, but high capital expenditure is usually required for such a system (Gadd, 1990; Kapoor and Viraraphavan, 1995; Volesky and Holan, 1995; Gaballah and Kilbertus, 1998; Sanchez et al., 1999).

Environmental biotechnology is broadly defined as the development, use and regulation of biological systems for remediation of contaminated environments. Biosorption is a form of adsorption process, in that it too is concerned with the removal of metal ions from the liquid phase onto a solid, only here biomass is used as the adsorbent. It is believed that some of these materials are actually economically competitive with existing non-biomass based treatments (Brower et al., 1997). This is true particularly if the biomass is produced as a waste product from another industrial process such as fermentation or the pulp and paper industry. Industrial waste by-products that require little processing or pretreatment and have abundant local availability will be of distinct advantage over conventional sources of adsorbents. They could be potentially applied for metal bearing solutions either as a cost-effective replacement or a refining secondary stage to conventional treatment processes (e.g., precipitation).

Among the different types of biomaterials tested so far, which include microorganisms as well as higher organisms, plant based natural polymers have been identified as a promising class of low-cost adsorbents for heavy-metal binding. This paper presents a review on the use of silvichemical biomass, a group of chemical products derived from the wood and bark of the tree, and its derivatives, either in their natural forms or as industrial waste by-products, for the removal of heavy metals from industrial waste streams. Various aspects including the structures and properties of biosorbent materials, biosorbent pretreatment and immobilisation, reuse and regeneration, biosorption mechanisms and selective sorption in multi-metal systems are discussed.

### 2 Structures and properties of silvichemical biomass

Trees are composed of a complex mixture of organic compounds and can be separated into three structural units: leaves, bark and wood. The wood component of the harvested log consists of two distinct fractions – the cell wall or cellular component and the extraneous contents or extractives. Extractives are distinguished from the other components of the tree in that they are not an essential part of wood structure. Bark is more complex anatomically than wood, and is generally divided into fibre, cork and amorphous dust when being mechanically disintegrated (Browning, 1963).

The major chemical components in the fibrous or structural portion of wood and bark include the high molecular weight polymers of lignin and polysaccharides (cellulose and hemicellulose) (Table 2). The extractive contents of wood and bark are made up of a number of organic compounds that are soluble in neutral organic solvents
and cold water, and the bark is generally a richer source of extractives than wood in terms of both quantity and complexity. The most important extractive components are the monomeric and polymeric phenolics such as flavonoid compounds, tannin and phenolic acids (Hillis, 1962; Browning, 1963).

### Table 2 Structural components of wood and bark (wt %)

<table>
<thead>
<tr>
<th></th>
<th>Hemicelluloses</th>
<th>Celluloses</th>
<th>Lignin</th>
<th>Extracts</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>21.2–33.3</td>
<td>42.1–50.8</td>
<td>21.4–27.5</td>
<td>2.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Bark</td>
<td>22.3–27.1</td>
<td>24.4–37.8</td>
<td>17.1–27.0</td>
<td>16.3–23.1</td>
<td>4.6–5.5</td>
</tr>
</tbody>
</table>


Cellulose is the primary structural component responsible for much of the mechanical strength of the cell wall and amounts to roughly one-half of the wood weight (Table 2). It is a linear macromolecule consisting of anhydroglucose units joined through 1,4-glucosidic bonds. The degree of polymerisation, i.e., the number of sugar units in a cellulose chain, for the purest form of cellulose – cotton lint, is estimated to be around 1750–3350 (Browning, 1963). Cellulose is insoluble in most solvents including strong alkali. It is difficult to isolate cellulose from wood in pure form because it is intimately associated with the other constituents of the cell wall (Rowell, 1984). Cellulose can be modified by substitution reactions to form a large number of cellulose derivatives such as cellulose ester, ether, xantha, graft copolymers and block copolymers (Browning, 1963). As discussed later, some of the cellulose graft copolymers with ion exchange capacity have been applied for selective removal of heavy metals from aqueous solutions.

Wood lignin is an amorphous aromatic polymer consisting of an irregular array of variously bonded hydroxy- and methoxy-substituted phenylpropanol units (Figure 1). It accounts for ~28% of wood tissue and is insoluble in common organic solvents (Rowell, 1984; Browning, 1963). Lignin serves as a joining matrix for the polysaccharide components in the cell wall, both chemically and physically, thereby resulting in a tissue of high strength and durability. The principal objective of chemical pulping processes is to dissolve the undesirable lignin when preparing high-grade cellulose fibres for the pulp and paper industry. As a result, a large amount of dissolved lignin exists in the spent pulping liquors. Lignin can also be recovered from sugar cane bagasse, which is available in large quantities as a residue from sugar mills. These combined resources of lignin in the form of waste by-products are most commonly used as an energy source, but they can also be used as a phenol resin replacement, barrier and landscaping material, or soil modifier (Piccolo et al., 1997; Goto and Suyama, 2000; Berube and Kahmark, 2001). The application of paper mill residues to coal-mine spoils to raise the pH and reduce heavy metal concentration in the acidic runoff from the spoils has also been reported (Berube and Kahmark, 2001).
Tannins are water-soluble polyphenols with molecular weights between 500 and 3000 g/mol. They are the third most abundant natural polymers produced by vascular plant tissue, after polysaccharides and lignin; leaves and barks are especially high in tannin and may contain up to 40% tannin by dry weight (Kraus et al., 2003). Significant amounts of tannins are also found in various agricultural wastes including peanut skins, nutshells, coconut husks and waste tea and coffee (Bailey et al., 1999). Depending upon its structure, tannin is further classified into hydrolysable and condensed tannins. The former contains a central core of polyhydric alcohol, such as glucose, and hydroxyl groups, which are esterified either partially or wholly by gallic acid (gallotannins) or hexahydroxydiphenic acid (ellagitannins). Important examples of gallotannin include Chinese tannin or tannic acid (Figure 2(a)) and Turkish tannin (Cruz et al., 2000). Upon hydrolysis, hydrolysable tannins commonly decompose into glucose, gallic acid and ellagic acid (Browning, 1963). The condensed tannins are structurally more complex than hydrolysable tannins and are mainly the polymers of flavanols joined by C–C bonds (Figure 2(b)). Detailed description of the chemistry and structure of different tannins is available in the literature (Hillis, 1962; Kraus et al., 2003; Chung et al., 1998).
Both lignins and tannins contain a large number of hydroxyl, carboxylic and other functional groups capable of forming complexes with metal ions and other macromolecules such as proteins (Browning, 1963; Gauthier et al., 2003; Neumann et al., 1995). Condensed tannin and its monomeric unit flavonoids, for example, are known to readily precipitate many metal ions by complex formation. These reactions are believed to involve either the ortho-dihydroxyl groups on the flavonoid B-ring or a phenol group and a carbonyl group (Figure 3) (Nest et al., 2004; Slabbert, 1992). Slabbert (1992) studied the complexation of divalent and trivalent metals with wattle tannin and established the order of complex stability as: Fe(III) > Al(III) > Cu(II) > Pb(II) > Zn(II) > Ni(II) > Mg(II) > Ca(II).
Many industrial applications of tannin and tannin-containing materials have been developed based on the metal-complexing ability of tannins. These include anticorrosive primers for steel and non-ferrous metals, agents for precipitation and recovery of certain metal ions, production of dyestuffs and inks when complexed with iron, chromium or copper and modifiers of rheological properties of minerals and clays, and as a pharmaceutical product for use in prevention and treatment of diarrhoea in livestock (Krisper et al., 1992; McDonald et al., 1996). Tannins have been used in wood preservation treatments to fix fungicidal Cu(II) ions and gravimetric analyses of metals. In addition, one of the methods commonly used for tannin analysis relies on tannin – metal complex reaction in alkaline solution (Slabbert, 1992; Nest et al., 2004; Hagerman and Butler, 1978).

An important class of silvichemical-derived biomass is humic substances that are components of the natural organic matters present in soil, peat, sediments and natural waters. Together with water, cellulose and lignin, humic substances constitute the principal components of peat, the first stage of coal formation. Peat formation results from incomplete biodegradation and accumulation of organic tissues such as decayed lignin or tannin in the waterlogged, anaerobic environment of marshes, bogs and swamps. This process takes up to 10,000 years to complete, and is followed by the transformation of peat into lignite and then into coal as a result of increasing pressure and temperature beneath the earth’s surface for ca. 40 million years (Brown et al., 2000; Crum and Planisek, 1988).

Humic substances consist of a complex mixture of dark-coloured, predominantly aromatic and polar molecules with their molecular weight ranging from a few hundreds to over 300,000. They are commonly classified into humic acid, fulvic acid and humin according to their solubilities in acid and alkaline solutions. Humic acids are the components that are soluble in dilute alkaline solutions but precipitate upon acidification, humin is the fraction that is insoluble in both acid and base, and fulvic acids are those that are soluble over a wide pH range. The molecular weights of the three fractions appear to follow the order of humin > humic acid > fulvic acid, although their chemical structures are still not well known. Humic acids are believed to form in the initial stage of humification, which then further degrade into fulvic acids, and humin is considered the ultimate product of the humification process (Boggs et al., 1985; Rosa et al., 2003). The principal functional groups in humic substances are carboxyl, phenolic hydroxyl, alcoholic hydroxyl, carbonyl, etc. (Table 3), rendering the macromolecules weakly acidic in solution (Boggs et al., 1985).

**Table 3** Functional groups in typical humic and fulvic acids

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Humic acids (meq/g)</th>
<th>Fulvic acids (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxyl</td>
<td>3.6</td>
<td>8.2</td>
</tr>
<tr>
<td>Phenolic hydroxyl</td>
<td>3.9</td>
<td>3.0</td>
</tr>
<tr>
<td>Alcoholic hydroxyl</td>
<td>2.6</td>
<td>6.1</td>
</tr>
<tr>
<td>Methoxyl</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Quinonoid and ketonic C=O</td>
<td>2.9</td>
<td>2.7</td>
</tr>
</tbody>
</table>

*Source*: Boggs et al. (1985)
A similar characteristic of humic substances to that of tannins and lignins is their ability to form soluble and insoluble complexes with metal ions, which is of particular interest since metal–humic substance interactions may have a large impact on the mobility of these metals in natural waters, and hence their bioavailability and toxicity. Extensive research on metal ion binding to humic substances has been carried out over the past decades. General reviews on this subject are given in the literature (Boggs et al., 1985; Kingery et al., 2001; Johns and Bryan, 1998; Vaughan et al., 1993; Lund, 1990; Livens, 1991, Sposito, 1986, Aiken et al., 1985).

3 Metal sorption by silvichemical biosorbents

A number of studies have been carried out to investigate the potential of silvichemical biomasses as agents for metal removal from industrial effluents. Tannin components in tree bark were used to synthesise biodegradable polyurethane foams for the biosorption of heavy metal ions and protein (Nakashima et al., 1996). Cellulose based ion exchange resins have been demonstrated to be effective in removing different dyes as well as heavy metals including Fe(III), Co(II), Cu(II), Zn(II), Cr(III), Pb(II) and V(IV) (Kabay et al., 1999; Waly et al., 1998; Beker et al., 1999). Biologically decayed wood and lignin were investigated for wastewater purification from heavy metals such as Cu(II) and Cr(III). The sorption capacities of wood, damaged by brown and white rot fungi, were approximately two to three times higher than those of undamaged woods owing to a higher level of lignification on the accessible sorbent surface (Kokorevics et al., 1999; Gravitis et al., 2001). Zhuang et al. (2003) developed a new remediation technology using lignin derivatives from pulping processes and ferric chloride as flocculating agent for the treatment of mercury contaminated water and soils. Clean effluent was obtained under optimised dosing and pH conditions, with a residual mercury level of <1 µg/l. The solid lignin-ferric adsorbent was also able to stabilise leachable mercury in contaminated soil.

Previous work has established the ability of coal, humic acid and peat to adsorb heavy metals from polluted waters (Brown et al., 2000; Gardea-Torresdey et al., 2004a, Xu et al., 2001). Effective removal of a number of bivalent metals by humic acids prepared from coals was achieved in continuous flow tests (Madronova et al., 2001). Ringqvist and Oborn (2002) reported that Carex peat could remove up to 80% and 95% of Zn(II) and Cu(II), respectively, from solution at high pH level (8.0). Burns et al. (1999) examined the efficiency of a range of Australian coals to adsorb heavy metals frequently found in industrial waste streams. Of the five coals of varying ranks tested, the lowest-ranked brown coal was found to be the most efficient adsorbent at low pH, with 50% Cr(III) removal achieved at a pH of 2.8. This was attributed to a high density of surface functional groups on lower-ranked coal. More detailed reviews on metal sorption studies using peat are provided by Brown et al. (2000) and Bailey et al. (1999).

Lignocellulosic wastes from wood and pulp and paper industries such as tree bark, leaves, sawdust, cork, wood powder and paper mill sludge were tested for removal of various heavy metals and recovery of uranium. Many of these demonstrated a potential for commercial exploitation (Seki et al., 1997; Cho et al., 1999; Joshi et al., 2003). Seki et al. (1997) reported that coniferous barks could effectively remove common heavy metals from dilute aqueous solutions. Batch and continuous column tests using
Innovative use of silvichemical biomass and its derivatives

P. jezoensis bark showed an adsorption capacity of 10–16 mg Cd (II)/g adsorbent, depending on the pH and the initial Cd concentration in solution. Cho et al. (1999) compared the chromium adsorption ability of leaves from 34 coniferous species with a commercial activated carbon. The deciduous conifer species (e.g., Ginkgo, Larix) generally exhibited higher affinity for Cr(III) and Cr(VI) than activated carbon in dilute chromium solution. Joshi et al. (2003) tested different bio-waste materials (waste carrot pulp, tea-leaves, microbial waste and paper mill sludge) and activated carbon for their metal sorption efficiencies in batch experiments. It appeared that paper mill sludge was more efficient than other types of sorbent materials in removing Pb (II), and, when combined with microbial bio-waste from the fermentation industry, was effective in simultaneous removal of Pb(II), Zn(II) and Ni(II) from multi-metal solutions. Ulmanu et al. (2003) examined the biosorption of Cu(II) and Cd(II) using cellulose pulp waste and other sorbents such as active carbon, kaolin, bentonite and diatomite. The maximum sorption capacities of metals on cellulosic waste were found to be 5.0 mg/g and 5.8 mg/g for Cu(II) and Cd(II), respectively, which were comparable to those of the other materials, despite a lower specific surface area for the cellulosic waste biomass.

Activated carbon is traditionally produced from controlled chemical and physical activation processes of carbonaceous material, normally wood, coal, peat and wastes of vegetable origin (e.g., coconut shells). This activation results in a porous material with a large surface area (500–1500 m²/g) and a high affinity for organic compounds and other types of contaminants. Khalili et al. (2000) reported the production of activated carbon from paper mill sludge. After ZnCl₂ activation at various ZnCl₂ to sludge ratios, paper mill sludge could be successfully and economically converted into micro- and mesoporous activated carbons with surface areas above 1000 m²/g. Efficient removal of phenol, 2,4,5-trichlorophenol and Cr(VI) was also achieved with an activated carbon prepared from H₃PO₄-activated lignin from Kraft black liquors (Gonzalez-Serrano et al., 2004). Raji et al. (1997) demonstrated that activated carbon derived from sawdust (wood processing waste) was capable of binding up to 262 mg/g Pb (II), 190 mg/g Hg(II) and 182 mg/g Cd(II) from aqueous solutions at 30°C. Based on the thermodynamic parameters calculated from the Langmuir isotherm model, the nature of adsorption was also determined.

The potential of ellagic acid, a major hydrolysis product of ellagitannins, as an agent for heavy metal removal from industrial effluents was recognised in early investigations (Sioumis, 1993; Zhang and Chen, 1988; O’Connor et al., 1998, O’Connor et al., 1999). Ellagic acid is available in large quantities as a waste by-product, generated from the pulp and paper and tanning industries. It is known to form insoluble metal deposits in the piping system during neutral sulphite/soda pulping processes using Eucalyptus wood, and cause precipitation in tanning solutions (Yu, 2000). Yu and coworkers (Yu et al., 2000, 2001a, 2001b) evaluated the performance of an ellagic acid adsorbent obtained from pulp mill waste in a series of metal sorption tests. The results showed that the ellagic acid waste biosorbent had high adsorption capacity and affinity for the metals tested (i.e., Cu(II), Cr(III) and Zn(II)), which compared favourably with various types of microbial and lignocellulosic materials, as well as commercial adsorbents such as activated carbon and ion exchange resins. Table 4 shows the favourable comparison of the Cu(II) binding capacity of ellagic acid relative to those of other silvichemical biosorbents.
Table 4  Copper adsorption capacity of a purified ellagic waste in comparison to other adsorbent materials

<table>
<thead>
<tr>
<th>Adsorbent type</th>
<th>Adsorption capacity (meq/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ellagic acid waste from pulp mill</td>
<td>5.4–6.2</td>
<td>Yu et al. (2001a)</td>
</tr>
<tr>
<td>Commercial ellagic acid</td>
<td>3.0</td>
<td>Yu et al. (2001a)</td>
</tr>
<tr>
<td>Microbial biomass</td>
<td>0.05–4.7</td>
<td>Volesky and Holan (1995)</td>
</tr>
<tr>
<td>Tannin</td>
<td>0.3–1.1</td>
<td>Liao et al. (2004b) and Goto and Suyama (2000)</td>
</tr>
<tr>
<td>Lignin</td>
<td>0.05–2.2</td>
<td>Gravitis et al. (2001) and Goto and Suyama (2000)</td>
</tr>
<tr>
<td>Coniferous barks</td>
<td>0.16–0.30</td>
<td>Seki et al. (1997), Vaquez et al. (1994) and Al-Asheh and Duvnjak (1998)</td>
</tr>
<tr>
<td>Pine bark</td>
<td>0.04–0.32</td>
<td>Seki et al. (1997), Vaquez et al. (1994) and Al-Asheh and Duvnjak (1998)</td>
</tr>
<tr>
<td>Peat moss</td>
<td>0.5–5.0</td>
<td>Volesky and Holan (1995) and Gardea-Torresdey et al. (2004a) and Madronova et al. (2001)</td>
</tr>
<tr>
<td>Humic acid/humin</td>
<td>0.57–1.18</td>
<td>Gardea-Torresdey et al. (2004a) and Madronova et al. (2001)</td>
</tr>
<tr>
<td>Coconut coir</td>
<td>7.14</td>
<td>McKay et al. (1999)</td>
</tr>
<tr>
<td>Cellulose pulp waste</td>
<td>0.16</td>
<td>Ulmanu et al. (2003)</td>
</tr>
<tr>
<td>Paper mill sludge</td>
<td>0.42–4.4</td>
<td>Gardea-Torresdey et al. (2004a) and Calace et al. (2002)</td>
</tr>
<tr>
<td>Sawdust</td>
<td>0.3</td>
<td>Gardea-Torresdey et al. (2004a)</td>
</tr>
<tr>
<td>Cork</td>
<td>0.63</td>
<td>Chubar et al. (2004a)</td>
</tr>
<tr>
<td>Bio-degraded wood</td>
<td>0.17–0.20</td>
<td>Gravitis et al. (2001)</td>
</tr>
<tr>
<td>Tree leaves (Z. noltii)</td>
<td>1.5</td>
<td>Sebe et al. (2004)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>0.18–0.20</td>
<td>Seki et al. (1997), Vaquez et al. (1994) and Al-Asheh and Duvnjak, 1998</td>
</tr>
<tr>
<td>Commercial ion exchange resins</td>
<td>0.35–5.0</td>
<td>Volesky and Holan (1995)</td>
</tr>
</tbody>
</table>

4 Biosorbent modifications

After screening and identifying the promising types of silvichemical biomass for metal sorption, one strategy to enhance the applicability of biosorption over alternative metal removal techniques is biosorbent modification by various pretreatment and immobilisation techniques, with the general aims of:

- increased biosorption capacity
- higher mechanical strength and stability
- effective biomass/liquid separation.
Principal techniques applied for the modification of silvichemical biosorbents include:

- activation with alkalis, acids, oxidising agents or microorganisms
- grafting with active functional groups on the silvichemical backbone
- entrapment in a polymeric matrix
- cross-linking with organic molecules.

More than one of the above techniques are often used simultaneously, i.e., cross-linking together with activation, grafting or entrapment, to obtain the optimal biosorbent performance, as each of them have their advantages and disadvantages. Some of these have been summarised by Volesky (2001).

The major objectives of biosorbent activation are to have controlled chemical- or biological-breakdown of silvichemical macromolecules to increase the number of reactive sites accessible, thereby increasing the metal binding capacity, and the extraction of soluble organic components (Gaballah and Kilbertus, 1998). The organic compounds in the lignocellulosic biomass, if not extracted, can cause augmented chemical or biological oxygen demand in treated effluent, which may have an impact on aquatic life (Reddy et al., 1997). Gaballah and Kilbertus (1998) described the acid treatment of Indian bark by HCl. It was observed that the modified bark was more efficient than the raw bark in removing lead cations with a 27% increase in uptake capacity (90 mg/g), and the modified bark did not introduce any colouration of the metal solution, as was the case for the raw bark. Chubar et al. (2004b) found that pretreatment of a cork biomass with sodium hypochlorite containing 7% active chlorine was the most efficient of all physico-chemical activation methods tested, leading to an increase of 70–80% in copper binding capacity. Similarly, Yamaguchi et al. (1991) investigated the effect of pretreatment with sulphonation, trichloroacetic acid and resorcinolation on heavy metal sorption on tannin resin. Activation by trichloroacetic acid was found to be the most effective method as a result of ring severance of the flavonoid skeleton of the tannin molecules. On the other hand, chemical activation involving concentrated acids (e.g., sulphuric, nitric and phosphoric acids) can sometimes have negative effects on metal binding because of mechanical deterioration and leaching of the sorbent (Tele de Vasconcelos and Gonzalez Beca, 1997).

Another technique commonly used to enhance the metal uptake of biomass is graft copolymerisation of vinyl monomers of various chemical structures on the macromolecule backbone, where radical sites are generated either by a chemical initiator or radiation. Graft copolymers may also provide new properties such as hydrophilic character, improved elasticity, heat resistance and dye absorption (Gulu et al., 2003). The majority of recent biosorption studies involving grafting have been devoted to cellulose and lignin copolymer systems (Gurdag et al., 2001; Waly et al., 1998; Gulu et al., 2003; Parajuli et al., 2005).

Biosorption is most effectively applied in scaled-up industrial application via a fixed-bed reactor configuration. For this purpose, immobilisation of biomass material by cross-linking and/or entrapment is necessary to avoid disintegration of free biomass owing to its low density and mechanical strength (Gupta et al., 2002; Volesky, 2001). Cross-linking with organic molecules has been employed to improve the physical properties of biosorbent such as particle strength, hardness, density and swelling characteristics. Common chemical cross-linking agents include formaldehyde,
glutaraldehyde, sulphone and divinylsulphone (Gupta et al., 2002; Tobin, 2001). Cross-linking of *E. triticornis* and *Pinus sylvestris* sawdusts and *Pinus radiata* D. Don bark with ~37% formaldehyde in acidic media resulted in the stabilisation of the extractable compounds of wood, although the metal uptake capacities of the modified biomass were not always enhanced (Taty-Costodes et al., 2003; Rao et al., 1998; Freer et al., 1989). Tannin-based resins have also been developed by formaldehyde cross-linking for heavy metal removal and the recovery of rare earth elements from radioactive liquid wastes (Hamaguchi et al., 1998; Zhan et al., 2001; Yamaguchi et al., 1992).

Natural and synthetic polymers such as gelatin, collagen, polyvinyl alcohol and silica gel have been utilised as entrapment matrices for the production of biosorbent gel beads (Sun et al., 2004; Goto and Suyama, 2000; Liao et al., 2004c; Rosa et al., 2003). High chemical and thermal stabilities of a tannin biosorbent were achieved by entrapping hydrolysable tannins on bovine collagen fibres, with which tannins are usually associated in traditional leather making (Liao et al., 2004b, 2004c). The adsorption capacity of this collagen-immobilised tannin for gold ion [Au (III)] was found to be as high as 1500 mg/g at 323 K (Liao et al., 2004c). Silica gel was used as immobilising agent for humin owing to its low price, simple preparation protocol, relative non-toxicity and high reusability and stability. Silica-immobilised humin exhibited an average metal binding capacity of 160 µmol metal/g for Cr(III), Cu(II) and Pb(II), which is higher than those of other biosorbents such as rice hull and a fungal biomass (Rosa et al., 2003).

5 Determination of biosorption mechanisms and binding sites

5.1 Biosorption mechanisms

Numerous studies on biosorption have found that ion exchange is the principal mechanism. The attachment of metal ions to the functional groups of silvichemical biomass is often accompanied by the release of hydrogen ions into solution, as evidenced by decreasing pH of solution during the uptake of heavy metals onto biomass (Yu et al., 2001a; Reddy et al., 1997) (also see Figure 3). However, in many cases, the mechanism appears to be a complex phenomenon that also involves adsorption (physisorption and chemisorption), complexation, sequestration, chelation or microprecipitation owing to the complex structure of biomass and the metal chemistry (Tobin et al., 1984; Volesky and Holan, 1995; Kratochvil and Volesky, 1998). For example, the mechanisms of metal adsorption on tannin are proposed to be ion exchange coupled with physical adsorption according to the enthalpy changes of adsorption (heat of adsorption) determined from thermodynamic analysis (Yamaguchi et al., 1992; Liao et al., 2004a).

5.2 Determination of binding sites

Information on the main binding sites participating in ion exchange and/or other metal uptake processes may be gained using chemical modification and spectroscopic techniques (Gardea-Torresdey et al., 2004a). Various esterification tests of lignocellulosic materials (sawdust, cork and corncob) have been used to identify the major sites of ion exchange to be weakly acidic carboxyl groups forming constituents of plant cell walls
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(Chubar et al., 2004a; Marchetti et al., 2000; Clave et al., 2003). These esterification treatments are divided into two sets: (i) to increase the number of carboxyl groups by esterification with cyclic anhydrides such as maleic anhydride and succinic anhydride (Figure 4(a)) (Clave et al., 2003; Marchetti et al., 2000), or (ii) to block carboxyl groups by Fisher esterification, whereby the biomass is reacted with an excess of methanol in a solution of dilute HCl (Figure 4(b)) (Chubar et al., 2004a, 2004b).

Figure 4 Types of esterification reactions used to assess the role of carboxyl groups in metal binding

![Image of esterification reactions]

Source: Clave et al. (2003) and Chubar et al. (2004b)

The contribution by other functional groups such as phenolic, hydroxyl and amino groups is also recognised (Reddy et al., 1997; Sebe et al., 2004; Parajuli et al., 2005; Taty-Costodes et al., 2003; Gravitis et al., 2001). Kokorevics et al. (1999) and Gravitis et al. (2001) found that modification of hydrolysed lignin with additional amino groups enhanced its adsorption activity towards Cu (II) and Cr (III). So, the authors indicated that biosorption by lignin proceeds mainly by ion exchange reactions between the metal ions and amino groups present on the biomass surface.

In addition to chemical modification, infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) are used to assess the nature of metal-binding sites of biomass (Gardea-Torresdey et al., 2004a; Clave et al., 2003; Sebe et al., 2004, Taty-Costodes et al., 2003). Clave et al. (2003) investigated the removal of Cu(II) from aqueous solutions by the crude and modified non-wood lignocellulosic material, corncobs. IR and XPS analysis of Cu (II)-equilibrated corncobs showed that carboxylic groups introduced to the surface of the corncobs via esterification with succinic and maleic anhydrides played an important role in increased copper retention in comparison to that of unmodified corncobs. Gardea-Torresdey (2000, 2004a, 2004b) and Parsons et al. (2002) demonstrated that XAS is a powerful tool for evaluation of metal-binding mechanisms of different biomaterials. The XAS spectrum provides information on the oxidation state of adsorbed metals and the metal – ligand coordination environment such as bond identity, the interatomic distances and the coordination number. The molecular geometry of unknown complexes can also be determined through comparison with known model compounds.
6 Selective sorption in multi-metal systems

Most biosorption studies are concerned with single metal solutions, which is rarely the case for industrial wastewaters. Mutual interference between metal ions should not be overlooked when assessing the performance and industrial potential of biosorption. The presence of coions generally reduces the uptake of the target metals because of the direct competition between different metal ions and protons for the same binding sites (Yu et al., 2000; Modak and Natarajan, 1995). Selectivity is of interest if recovery of metals is sought from a mixture of metal ions, which is true for many of the practical cases of wastewater treatment. This could be applied in conditions where a difference in the metal-binding affinity was apparent. Selectivity is generally a problem with biosorption systems (Gadd, 1989), but favourable selectivity in silvichemical biosorbents may be achieved depending on the pH conditions and the chemical nature of the binding sites and metals present (Shukla et al., 2002).

Selective binding of metals is particularly sensitive to the chemical nature of binding sites. The stability of metal complexes of humic macromolecules is known to be affected by the size of the chelating rings (five-member rings form the most stable chelates) and substitution in the chelating molecule owing to steric hindrance (Boggs et al., 1985). The sorption of Cu(II), Ni(II) and Zn(II) on cork powder was studied by Chubar et al. (2004a). It was suggested that most of the Cu(II) and Ni(II) (~56–70% total capacity) were selectively adsorbed onto carboxylic acid groups, which were also the only binding sites responsible for Zn(II) uptake. Thus, selective separation may be achieved by modifying biomass with chemicals possessing suitable functional groups. Fischer and Lieser (1993) and Lieser and Gleitsmann (1982) demonstrated that cellulose exchangers with certain tailor-made chelating anchor groups exhibited high selectivity for trace U (VI) over other elements (Cr(III), Mn(II), Fe(III), Cu(II), etc.) in seawater. The selectivity for uranium by different anchor groups followed the order: amidoxime >> amidrazone >> hyphan ≈ oxatepene > carbonyl.

The stability of metal chelates is known to depend on the properties of metal ions such as charge, ionic radius, electronegativity, atomic number and ionisation potential (Langmuir, 1997, Giesy, 1983, Chaberek and Martell, 1959). The complex stability usually increases with increasing charge and/or decreasing radius of cations for a given ligand (Langmuir, 1997; Chaberek and Martell, 1959). It is also believed to be linearly proportional to the electronegativity and ionisation potentials of the metals. Irving and Williams (1948) correlated the relative stabilities of transition metal chelates with the atomic number of the metal ions. The authors reported increasingly stable complexes with atomic number between Mn (II) and Cu (II), i.e., Pd > Cu > Ni > Co > Zn > Cd > Fe > Mn > Mg. The Irving-Williams stability series is generally applicable irrespective of the nature of the ligands used. However, according to Pandey et al. (2000), the measured stability constants for metal-humic acid complexes indicated substantial deviation from the Irving-Williams series. Similar departures from this series were also reported for metal chelation on peat and fulvic acid (Giesy, 1983).

Yu (2000) investigated the effect of cations on sorption by means of a separation coefficient, \( \eta \), which was defined for multi-metal systems to describe the effectiveness of biosorption by a pulp mill ellagic acid waste in a separation process, similar to the one used in ion exchange processes:
where \( Q_M \) (mmol/g) and \( Q_C \) (mmol/g) are the amounts of the main metal and coion adsorbed, respectively. The extent of selective separation in multi-metal systems was found to depend strongly on solution pH. High selectivities (separation coefficients of 10–20) were obtained for Cu–Cr and Cr–Zn binary systems at pH 3.0 and 5.5, respectively; but the total metal uptake at these pH levels was relatively low. As the pH increased, the extent of separation decreased but the total metal uptake increased to be close to the capacities of corresponding single systems for Cu (II) and Cr (III). Hence, the optimum pH conditions for metal adsorption using the ellagic acid adsorbent for metal adsorption from a copper-chromium or chromium-zinc binary system would depend on whether selectivity or the total metal uptake was most important. Similar pH-dependent selectivity in mixed metal combinations was found for bark biomass and tannin resin. Jang et al. (2005) reported a binary selectivity index for hardwood bark to be: Pb(II) > Cu(II) > Zn(II), with a high separation coefficient between Pb and Zn(19.4–25.0) obtained at pH 5.0–6.0. Santana et al. (2002) evaluated the simultaneous adsorption of Ce, Cu(II), U(VI), Eu, Fe(III), Th and Nd by tannin resins. Selective sorption was achieved for uranium and thorium at pH 5, while maximum removal for the other elements was observed at pH 7 or higher. Table 5 summarises the metal selectivity sequences for some of the silvichemical biomasses reported in the literature.

**Table 5** Sequences of metal sorption by silvichemical biomass materials

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Metal sorption sequence</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp mill ellagic acid waste</td>
<td>Cu (II) &gt; Cr (III) &gt; Zn (II)</td>
<td>Yu (2000)</td>
</tr>
<tr>
<td>PMW + biowaste mixture</td>
<td>Pb (II) &gt; Zn (II) &gt; Ni (II)</td>
<td>Joshi et al. (2003)</td>
</tr>
<tr>
<td>A. nilotica bark</td>
<td>Cr (III) &gt; Ni (II) &gt; Cu (II) &gt; Ca (II) &gt; Pb (II)</td>
<td>Prasad et al. (2001)</td>
</tr>
<tr>
<td>Hardwood bark</td>
<td>Pb (II) &gt; Cu (II) &gt; Zn (II)</td>
<td>Jang et al. (2005)</td>
</tr>
<tr>
<td>Sawdust-based activated carbon</td>
<td>Pb (II) &gt; Hg (II) &gt; Cd (II)</td>
<td>Raji et al. (1997)</td>
</tr>
</tbody>
</table>
Table 5  Sequences of metal sorption by silvicultural biomass materials (continued)

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Metal sorption sequence</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose ion exchanger</td>
<td>Fe (III) ≈ Cu (II) ≈ Co (II) &gt; Zn (II)</td>
<td>Beker et al. (1999)</td>
</tr>
</tbody>
</table>

7 Regeneration and recovery

Industrial applications of biosorption depend on the ease of biomass regeneration for reuse in multiple cycles to increase the cost-effectiveness of the process. Biosorption is often reversible by simple physico-chemical treatments (because ion exchange mechanisms are involved), but different eluents have been found to interact differently with metal laden biomass, resulting in different extents of recovery (Gadd, 1990; Modak and Natarajan, 1995). The use of dilute acids, however, has been quite effective (Suhasini et al., 1999).

Calace et al. (2003) and Lister and Line (2001) suggested that mineral acids (e.g., HCl and H₂SO₄), carbonates (e.g., Na₂CO₃) and chelating agents (e.g., NTA and EDTA) could be used for regeneration of paper mill waste biomass loaded with metal ions. Freer et al. (1989) reported that desorption efficiencies of uranium from bark with 0.5 M sulphuric acid were 25% and 63% after 1 and 3 hours, but were lower with sodium carbonate solutions (0.5–2.0 M). Gaballah and Kilbertus (1998) tested the copper uptake efficiency of a modified pink bark for ten consecutive biosorption/desorption cycles. The authors found that the biomass retained most of its metal removal efficiency (~70%) from the second cycle when it was treated with 0.5 M HCl. Similar behaviour was observed for a purified elagic acid waste biosorbent regenerated with the same eluant (Yu, 2001b). Liao et al. (2004a) studied the desorption of Th (IV) from a tannin column. A high concentration factor of 62 was observed using 0.1 M HNO₃. In another study, Liao et al. (2004c) found that the Au (III) desorption efficiencies by 1.0 M Na₂CO₃, HCl, urea and thiourea for columns of immobilised tannin were not satisfactory, possibly because of the involvement of other biosorption mechanisms such as electrostatic attraction and chemical adsorption that resulted in high binding affinities of metal ions on charged components of biomass. Thus the choice of metal recovery method and reagent depends mainly, if not solely, on the mechanisms of metal accumulation.

The different sorption affinities of metal ions exhibited for a binding site can be exploited in the desorption cycle to selectively separate and recover the desired metal.
species from a loaded biosorbent using an appropriate elution scheme. For instance, divalent metal cations (Cu, Pb, Cd, etc.) can be desorbed from a paper mill waste biomass using 1.0 M HCl, whilst Ag (I) is displaced by HNO₃ and EDTA, which do not form precipitates with silver (Calace et al., 2003).

8 Conclusion

Purification of heavy metal contaminants from various industrial wastewaters poses a tremendous task for existing separation processes. Considering the high capital and regeneration costs of ion exchange resins and drawbacks of other traditional techniques, the use of biological systems for the removal of heavy metal ions from industrial effluents has the potential of achieving equivalent performance at a minimal cost and environmental impact. Research over the past decade has, to a certain extent, provided better understanding of passive metal biosorption and a wide range of innovative biosorbent materials has been identified. Unlike conventional ion exchange on resins, the ion exchange process of biosorption is often complicated by other physico-chemical interactions because of the presence of numerous chemical functionalities. Better knowledge of these mechanisms and the precise nature of the binding sites enables specification and control of the process parameters for metal removal, recovery and biosorbent regeneration, and consequently facilitates the expected commercial applications of biosorption and tailored modification of biosorbents for specific process demands.

Silvichemical biomass and its derivatives possess the potential to be effective biosorbent materials owing to their low cost and abundant availability as industrial and agricultural waste by-products. Previous studies showed a number of advantages for heavy metal removal from dilute aqueous solutions. These include high adsorption capacities and selectivities for a wide range of heavy metals and radionuclides, ease of biosorbent regeneration and metal recovery with minimal secondary solid wastes. It is biodegradable with no known tendency to promote undesirable chemical reactions. Future developments on biosorbent immobilisation techniques to convert biomass into reactors and enhance metal-binding capabilities and selectivities through molecular engineering will increase the attractiveness of biosorption technology using silvichemical biomass.

References


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