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Chapter

Advances in Metal Recovery from Wastewaters Using Selected Biosorbent Materials and Constructed Wetland Systems

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Abstract

An expanding global population not only increases the amounts of municipal solid waste and wastewater generated but also raises demand for a wide range of raw materials used to manufacture goods. Extraction of these raw materials and many subsequent manufacturing processes contribute significantly to the presence of a variety of metals in wastewaters and leachates. Metal-rich wastewaters not only result in short- and long-term environmental and associated health concerns but also have potential economic value if the metals can be recovered. In this chapter, we review the effectiveness of biochar, microbial and lignin biosorbents as well as constructed wetland systems to remove soluble metals from wastewaters. The wide variation in adsorptive capacity of these biosorbent materials reflects the heterogeneous nature of the source materials used for their production. Physical and chemical modifications of biochars and lignins generally improve their adsorptive capacities which remain highly variable. Constructed wetlands are attractive because of their passive nature with low-energy and low-maintenance requirements, although their long-term capacity to treat metal-rich wastewaters is as yet largely undetermined. Future perspectives focus on increasing the selectivity of adsorbents to remove complex matrices of metals from wastewaters and on increasing their adsorption/desorption capacities.

Keywords: wastewater, biosorbent materials, biosorption, biochar, lignin, microbial adsorption, constructed wetlands

1. Introduction

Metals such as lead (Pb), nickel (Ni), silver (Ag), aluminium (Al), cadmium (Cd), zinc (Zn), chromium (Cr), copper (Cu), vanadium (V), platinum (Pt), mercury (Hg) and titanium (Ti) are found in wastewaters associated with many industrial processes. Such processes include milling, etching, electroplating, conversion-coating, electrolysis and waste-to-energy facilities to mention but a few. Certain pigment manufacturing processes utilise Cr and Cd, while Cu and arsenate are utilised during wood processing. The petroleum industry utilises significant amounts of catalytic material which includes V and Ni, while mining

operations produce a variety of extractive residues and leachates covering a very wide range of metals [1, 2]. Such industrial processes contribute significantly to the presence of metals in wastewaters. In addition, municipal solid waste contains significant quantities of metals such as silicon (Si), calcium (Ca), iron (Fe), Al, sodium (Na), magnesium (Mg), Zn, Cu and Pb [3] and can result in a highly toxic landfill leachate whether deposited as untreated waste or as incinerated ash residue.

Public interest in metal contamination of wastewater has some of its origins in the use of Pb as a gasoline additive in the United States which sparked a general interest in heavy metals as potential hazards in the minds of the public [4]. In addition the general low levels at which metals demonstrate toxicity is another key issue. In nature, heavy metals occur mainly as insoluble forms in natural mineral deposits occurring as silicates, carbonates, oxides or sulphides, which in general weather slowly. However not all are slow weathering, and as an example rainwater may solubilise rocks containing magnesium oxides as magnesium bicarbonate due to the carbon dioxide content of rainwater, whereas Fe may also dissolve but precipitates as insoluble ferric hydrate [4]. Many heavy metals precipitate in a similar way to Fe and thus are rarely present at neutral pH. With an increased awareness of metals as a component of wastewater and leachates and the often low level at which toxicity is demonstrated, there has been a keen interest in both their environmental and health-related consequences.

As all humans on the planet need drinking water, there is a vested interest in ensuring that it is of the best quality possible. The source of most raw water used for potable consumption is abstracted from surface waters (i.e. lakes and rivers), and these in turn are impacted by industrial, municipal as well as agricultural wastewater discharges. Most developed countries have drinking water quality standards. In Europe these are guided by the European Drinking Water Directive [5], in the United States the US Environmental Protection Agency (USEPA) utilise the Safe Drinking Water Act [6] and in Australia the Australian Drinking Water Guidelines are used [7]. Other countries use World Health Organisation (WHO) guidelines [8]. All of these guidelines specify maximum metal concentrations considered safe for human consumption, a selection of which are included in **Table 1**. It is critical therefore that

Parameter	Drinking water regulations ($\mu\text{g L}^{-1}$)			
	EU	United States	Australia	WHO
Al	200	N.S.	200	N.S.
As	10	10	7	10
Ba	N.S.	2000	700	1300
Cd	5	5	2	3
Cr	50	100	50	50
Cu	2000	1300	2000	2000
Hg	1	2	1	6
Ni	20	N.S.	20	70
Pb	10	15	10	10

N.S.—not specified.

Table 1.

Selection of specified maximum metal concentrations ($\mu\text{g L}^{-1}$) for drinking water in the EU [5], the United States [6], Australia [7] and the WHO [8].

Metal remediation technique	Basis of process
Precipitation, coagulation and flocculation	Precipitation was one of the earliest methodologies to treat metal wastewater. Lime precipitation (or indeed on occasion limestone) is often a first treatment used to remove metals particularly from acidic metal-containing wastewaters. Precipitation with lime, containing predominately calcium oxides and hydroxides, is one of the cheapest and simplest techniques with precipitation of the metal species such as Zn, Cu, Fe, Mn, Co and Ni as hydroxides. Incomplete precipitation can occur for other metals such as Cd, Pb and Hg, and in such cases soda ash can be employed based on its carbonate ion to precipitate Pb, while sodium sulphide has been used for Cd and Hg [19]. However these may give rise to the production of relatively large quantities of toxic sludge and incomplete removal [9, 20, 21]. Other agents such as alum, ferric chloride and a variety of polymers can also be used to flocculate and precipitate metals [22, 23]
Electrodeposition	Many industrial processes contain acid solutions saturated with metals, such as Cu, which may be ideal for the use of electrochemical techniques such as electrodeposition of the metal onto the cathode surface. Since the electron is the main reagent of the reduction reaction, the electrochemical process can be considered a clean technology and environmentally attractive [24]
Ion exchange	Traditionally developed to recover uranium (U), ion-exchange methods have widespread applicability for metal recovery with the use of a variety of resins to remove solubilised heavy metals from a variety of sludges [25]
Solvent extraction	Here specific organic solvents can be utilised to extract metal ions as an organic solvent soluble form. This is then recovered by acid treating the organic solution causing the metal to be recovered in a concentrated form [26]
Cementation	Cementation is a precipitation process whereby ions are reduced to zero charge at a solid metallic interface. A key example is where Cu ions in solution from ore leachate are precipitated in the presence of Fe. As the Fe oxidises, the Cu reduces with the Cu recovered on the surface of the Fe. This process can be used for several metals such as Zn or Cd [12]
Reverse osmosis	This technology pressurises water to enable it to pass from an area of high to low solute density through a semipermeable membrane which has a defined pore structure and size. This is the reverse direction to which natural osmosis occurs and is thus termed reverse osmosis. The semipermeable membrane captures the solutes as the water passes through. This technology is applied widely for desalination but can also have a role to play in metal recovery from wastewaters [27]
Ultrafiltration	Ultrafiltration is a membrane-based technology which utilises pressure to separate material through semipermeable membranes. High-molecular-weight materials are retained, while water and low-molecular-weight materials permeate the membranes. The retentate characteristics are a function of the molecular weight and exclusion size of the membranes. The technique combines complexation and ultrafiltration where soluble metal-binding polymers are added to complex the metals which then become concentrated and bind to the polymeric membrane material [17, 18]. Metal-binding ligands include carboxymethyl or diethylaminoethyl celluloses, chitosan, polyvinyl alcohols and polyacrylic acid [18, 28]
Adsorption processes	A range of adsorbent materials have been used to remove metal species from waste waters. Such materials include mineral organic materials, activated carbon, zeolites, wastes, biomass or natural or synthetic polymeric materials [29, 30]. Certain applications can be termed sorption flotation depending on the technology roll out [11, 31]. A small number of applications have emerged where microorganisms rather than polymeric materials have been utilised with adsorption to natural polymeric materials associated with the surface of microorganisms [2, 20]

Table 2.
Common technologies utilised to remove metals from wastewater streams.

wastewater treatment technologies have the capacity to remove or reduce effluent metal concentrations prior to discharge to receiving waters, such as rivers and lakes.

Within the range of treatment methods, there are a variety of technologies based on physiochemical methodologies. These include chemical precipitation [9], coagulation-flocculation [10], flotation [11], cementation [12] and electrocoagulation [13]. Adsorption onto zeolites, clay and resin ion exchange [14, 15] and membrane filtration techniques such as ultrafiltration, nanofiltration and reverse osmosis [16–18] have also been used (**Table 2**). Adsorption approaches have largely focused on the use of zeolites.

There is increased interest in the removal of metals from wastewater, not only because of expansion in industrial sectors which produce metal waste streams but also from mining activity, which is subject to rigorous regulation. In addition there is the added incentive to recover metals from such streams that may have unexpected economic value. Clearly a range of current technologies exist for metal removal from waste streams; however many of these require significant costs and the use of high-end technologies. Other cheaper adsorption options have been based, in large measure, around the use of activated charcoal and ion-exchange resins; however, in recent years there has been a developing focus on the potential use of biosorbent materials for metal removal from waste streams. These biosorbents possess a number of useful advantages in that they are, in most cases, naturally occurring, cheap, readily available in large quantities and can generally be modified to act as effective adsorbents for a range of metals from wastewater. The following sections of this chapter focus specifically on recent research in the application of some selected biosorbents including biochars, lignins and microbes and on constructed wetland systems in the removal of metals from wastewaters.

2. Bioremediation of metals from leachates

2.1 Biochars

2.1.1 Nature, sources and production of biochar

Biochar is a low-cost carbonaceous material derived from the thermal conversion of various biomasses using techniques such as gasification [32], pyrolysis [33–36], hydrothermal carbonisation [37] and torrefaction [38], at temperatures ranging from 300 to 900°C and in oxygen-limiting environments. High pyrolysis temperatures in the carbonisation of biomass (>500°C) lead to high surface areas, microporosity and a biochar that is highly hydrophobic in nature [33, 37]. Low pyrolysis temperatures (<500 °C) lead to partial carbonization and the presence of more oxygen-containing functional groups, lower surface areas and a biochar with more affinity for binding inorganic species from solution [33, 37]. Depending on the different types of thermal conversion approach, biochars can be designed to display a range of properties which make these materials suitable for pollutant removal scenarios. In particular, these properties include variable surface area, microporosity, surface charge and pH, polarity, adsorption and ion-exchange capacity [36]. A selection of typical biochar feedstocks and the associated compositions of their respective biochars, after formation, are outlined in **Table 3**. Typically biochars have been produced from woody-type wastes [32, 33], manures [37, 38], agricultural wastes [36] and energy crops such as alfalfa [34] and miscanthus [39]. Biochars derived from wood or crop wastes typically tend to show higher surface areas, whereas animal waste and activated sludge-derived biochars tend to exhibit lower surface areas.

Feedstock	Proximate analysis (%)			Ultimate analysis (%)				Reference
	Volatile matter (%)	Fixed carbon (%)	Ash content (%)	C	H	N	O	
Oak sawdust	69.2	16.5	0.81	52.3	5.7	0.06	41.9	[32]
Pine sawdust	83.1	16.8	0.10	51.0	6.0	0.10	42.9	[33]
Alfalfa	78.9	15.8	5.3	49.9	6.3	2.80	40.8	[34]
Bamboo	81.6	17.5	0.9	52.0	5.1	0.40	42.5	[35]
Corn straw			60.2	35.9	1.6	0.43	1.9	[36]
Poultry litter			37.7	49.8	4.4		3.2	[37]
Pig manure	19.1		46.5	44.1	2.5	2.1		[38]
Giant miscanthus	65.3	15.6	11.7	46.2	6.0	—	45.9	[39]

Table 3.
 Typical biochar feedstocks and associated composition.

2.1.2 Modification and activation of biochars

Following production of biochars, a physical or chemical activation process can be used to enhance the material surface area and pore fraction or simply to form surface functional groups, all of which can enhance the material's ability to function as an adsorbent for metal uptake. Specific physical activation methods are mostly based around the use of steam [40, 41], while chemical activation can be accomplished with the use of either base/oxidant [42] or acid/oxidant [43] combinations post pyrolysis or with the incorporation of metals pre-pyrolysis [44]. Typical activation methods are outlined in **Table 4**, and almost all of these methods have resulted in enhanced metal uptake from solution.

2.1.3 Application of biochars for metal recovery

Thus far much of the work on the use of modified and unmodified biochars has been aimed at the recovery of many of the transition and heavy metals such as arsenic (As) [45], Cr [46, 47, 52], Cu [37, 41, 51], Pb [49, 53, 56], Cd [40, 48], Zn [36], Ni [50], Hg [54] and U [57] from selected waste streams. Examples of the relative uptake of these metals by selected biochars can be seen in **Table 5**. The influence of solution pH on metal uptake levels varies significantly with many of the metals exhibiting maximal uptake in the range pH 4–8. The surface charge on the adsorbent and the solution pH are important. At low pHs, it is likely that the biochar surface is protonated and may present a suitable binding opportunity for metals in their anionic or negatively charged form. Increasing the solution pH can lead to a reduction in protonation of the biochar surface and a greater opportunity for the metal in its more cationic state to bind to the biochar.

Many of the metals, at strongly acidic conditions, will exist in their cationic states, but once the solution pH rises to between pH 5 and pH 8, many of these metals can be precipitated as hydroxide species and as such become unavailable for adsorption. Hence acid pHs tend to favour adsorption onto biochar materials. At pH 2 and less, there appears to exist significant competition for adsorption

sites between the M^{n+} form of the cation and H^+ in solution. As the pH rises to between pH 2 and 5, H^+ concentration decreases, leading to less competition with the M^{n+} form of the cation for adsorption sites on the biochar. Metal uptake tends to move significantly towards its maximum uptake level in this latter pH range. Beyond pH 5 the cationic form of the metal starts to shift towards a hydroxylated species in solution. Once moving towards pH 7, it can be difficult to determine whether adsorption or simply precipitation is taking place onto the biochar. The variations in metal form and biochar surface charge arising from variation in solution pH may potentially be of significant benefit in the regeneration of biochars.

Modification of some of these biochars by the broad methods outlined in **Tables 4** and **5** can, in many instances, lead to an enhancement of metal uptake levels. For example, adsorption of hexavalent chromium from aqueous solution was shown to rise significantly, with the presence of an increased number of amino groups being suggested to significantly enhance metal uptake onto a polyethyleneimine modified rice biochar [52]. Other scientific explanations for increased uptake of selected metals following modification of specific biochars, as outlined in **Tables 4** and **5**, include how a modification of peanut shell led to an increased specific surface area [53]; how treatment of corn straw biochar with sodium sulphide yielded more oxygen-containing functional groups on the surface [54]; how larger pore sizes, pore volumes, and more functional groups could be achieved with the treatment of wheat straw biochar with graphene oxide [55]; and how higher contents of surface carboxylate groups and ultimately negative surface charge on the modified biochar could be achieved with nitric acid treatment of cow manure biochar [57].

2.2 Microbial

There have been many studies on the effects of metals on soils and water in the natural environment and particularly on the microflora that interact with these metals [59, 60]. Such studies have revealed that soil and natural water streams contain a range of microorganisms with the capability of metal transformation. Such effects can be exploited not only in soil remediation but also in utilising such microorganisms as tools for remediation of wastewaters contaminated with metals. There are currently several categories of interaction that can be observed between microbial populations and metal species as summarised in **Table 6**.

Feedstock	Modifying agent	Nature of modification	Stage			Reference
Poultry manure	Steam	Physical	Post-pyrolysis	Cd^{2+}	+	[40]
Pine sawdust	Steam	Physical	Post-pyrolysis	Cu^{2+}	=	[41]
Municipal sludge	Bases	Chemical	Post-pyrolysis	As(V)	+	[42]
Peanut hull/hydrochar	Acid/oxidant	Chemical	Post-hydrothermal treatment	Pb^{2+}	+	[43]
Pine wood/ $MnCl_2$	Metals	Chemical	Pre-hydrolysis			[44]

Table 4.
Biochar activation methods.

Metal	Feedstock/modifier	Optimum pH range	Sorption capacity (mg g ⁻¹)	Reference
<i>Unmodified biochars</i>				
As(III)	Rice husk	8.0	19.3	[45]
Cr(III)	Peanut stalk	4.0	25.0	[46]
Cr(VI)	Sugar beet tailing	2.0	123.0	[47]
Cd(II)	Dairy manure	—	31.9	[48]
Pb(II)	Sludge	5.0	30.9	[49]
Cu(II)	Hardwood	5.0	6.8	[36]
Zn(II)	Corn straw	5.0	11.0	[36]
Ni(II)	Almond shell	6.0	20.0	[50]
Cu(II)	Pig manure	5–6	75.49	[51]
<i>Modified biochars</i>				
Cd(II)	Poultry manure/steam	—		[40]
As(III)	Rice husk/Fe	—	30.7	[45]
Cr(VI)	Rice husk/ polyethyleneimine	2.0–7.0	436.0	[52]
Ni(II)	Peanut/KOH	6.0–7.0	87.1	[53]
Hg(II)	Corn straw/Na ₂ S	4.0–6.0	5.7	[54]
Hg(II)	Wheat straw/graphene oxide	6.8–7.0	0.85	[55]
As(V)	Pine wood/Mn	8.0	6.5	[56]
U(VI)	Cow manure/HNO ₃	4.5	355.6	[57]
Cu(II)	Pine sawdust/H ₃ PO ₄	—	30.0	[58]

Table 5.
 Typical metal adsorption levels for unmodified and modified biochars.

Fungal and bacterial species that can grow and metabolise in the presence of metal species have been demonstrated to possess a variety of mechanisms of resistance that in many cases have a genetic basis [67–69]. The nature of the microbial species and the mechanism used are often dependent on the metal species present, and several mechanisms have been identified [67]. These include exclusion of the metal species by production of an extracellular matrix that acts as a barrier to entry of the metal. Such material known as extracellular polysaccharide substance (EPS) binds metal species and can have biotechnological applications [2]. Other techniques involve active metal efflux which is often associated with microbial mobile genetic elements [70], sequestration of metals, enzymatic detoxification exemplified by Hg resistance mechanisms and reduction of target sensitivity of the microorganism [67]. Understanding such mechanisms offers insights into the methodologies that have evolved in biological systems over millions of years and may offer new biotechnical approaches that can be exploited for metal remediation.

2.2.1 Microbial adsorption mechanisms

Microbial EPS material is often associated with the formation of stress-responsive structures on the surface of microbial cells during biofilm formation, and thus its production can be adaptive or protective in nature [2]. EPS can exist in many forms and can be genera specific in its chemical composition. In general

Type of microbe-metal interaction	Reference
Enzymatic transformation of the metal species such as the use of thiosulphate reductase to transform thiosulphate to sulphite for precipitation of metals such as Cd or Zn as metal sulphide species	[61, 62]
Accumulation of metal intercellularly. Examples include Ni accumulation as its phosphide and carbide crystal in <i>Pseudomonas aeruginosa</i>	[63]
Cell appendage adhesion such as metal binding to cell fimbriae as with the <i>E. coli</i> FimH adhesion binding to Pb, cobalt (Co) and Cr	[64]
Bioadsorption of metal species to microbial surface polymers. Many microbes produce surface polymeric materials as stress responses in the environment to resist change as protection against environmental stresses. Many of these extracellular polysaccharide substances are highly charged materials that bind metal species	[2, 29]
Biobleaching activities where metal species may be solubilised as a result of acid production by the interacting microbial species. Examples include leaching by sulphur-oxidising bacteria through production of sulphuric acid followed by precipitation of insoluble sulphides by sulphate-reducing microorganisms in acid environments. Citric acid produced by <i>Aspergillus niger</i> has also been utilised in alkaline environments to leach metals from alkaline wastes and soil	[65, 66]

Table 6.
Interaction between microbial populations and metal species.

EPS consists of repeating monosaccharide units forming hetero- or homopolymers linked in glycosidic linkage which in turn are linked to a lipid anchor. The complex composition and branching of the EPS with many phosphate, amino sugars and hexuronic acid residues [2, 71] give the EPS structure an anionic charge which can be utilised to protect the microbe from metal toxicity. Key chemical groups on microbial surfaces include carboxyl groups associated with microbial peptidoglycan, phosphate groups on surface material, uronic acid and charged amino acid groups [2].

There have been many studies of the utility of microbial cells in metal binding [72] although few actual processes have yet been developed. Cyanobacteria and algae have been extensively studied to bind a variety of toxic metals in natural water systems in polluted environments [73–76]. The rationale for their use is that many cyanobacterial and algal species are normal inhabitants of these water courses, and hence their presence would be less environmentally intrusive. Biosorption of a variety of metals has been studied including antimony (Sb), Ni, Cd, Cu, Pb, Co, Mn, As and Zn [2]. A rotating biological reactor containing microbial biofilms has previously demonstrated that metals can be accumulated in a process environment [77], and while this is as yet one of the few processes that have been developed, the potential to utilise microbial biomass is evident. Immobilised photosynthetic bacteria have been utilised to remediate swimming pool muds in Fukushima following the radioactive leak as a result of a Japanese tsunami [78] demonstrating the potential practicality of utilising microbes for metal remediation, in this case radioactive nuclides.

Table 7 outlines a number of microbes which have been tested for their metal biosorbent capabilities. An uptake of 277.5 mg Pb(II) g⁻¹ from aqueous solution at an optimum pH of 6.8 was measured in a study using the exopolysaccharides from *Paenibacillus peoriae* strain TS7 [79]. Another study which used the biosorbent *Anabaena doliolum* *Ind1* has outlined the presence of a range of surface groups including carboxyl, carbonyl, hydroxyl, amides and sulphate groups as being key binding sites for metals such as Cd(II) [80]. In a study which examined equilibrium and kinetic and thermodynamics of aqueous Al biosorption by *Streptomyces rimosus* biomass, the presence of methyl, hydroxyl, amine, carboxyl, thiol and phosphate groups was identified as significant binding sites [81], while fatty acid, amide, lipids

Strains	Source	Heavy metal	Optimum pH	Uptake level (mg g ⁻¹)	Reference
<i>Paenibacillus peoriae</i> strain TS7	Aqueous solution	Pb(II)	6.8	277.5	[79]
<i>Anabaena doliolum</i> Ind1	Contaminated soil coal mine	Cd(II)	7.0	92% (2 ppm)	[80]
<i>Streptomyces rimosus</i>	Antibiotic manufacturer	Al(III)	4.0	11.7	[81]
<i>Providencia vermicola</i> strain SJ2A	Soil (battery manufacturing site)	Pb(II)	—	155.1	[82]
<i>Rhizobium radiobacter</i> strain VBCK1062	Contaminated soil fertiliser/chemical industry	As(V)	—	0.068	[83]
<i>Rhodococcus opacus</i>	Water streams	Al(III)	5.0	41.6	[84]

Table 7. Microbes used for extracellular polysaccharide substance (EPS)-assisted heavy metal removal from selected wastewaters.

and protein moieties were identified as significant contributors to the adsorption of Pb(II) on *Providencia vermicola* strain SJ2A [82]. A study to measure the biosorption of Al(III) from waste streams using a *Rhodococcus opacus* strain reported a removal rate of 41.6 mg g⁻¹ and indicated that the presence of amine, alkyl, carbonyl and phosphate surface functionalities were significant in its removal [84]. There are several potential advantages of utilising microbial biosorption. They can be classed as environmentally safe and do not generate toxic by-products, while in addition both live and dead cells can be used. On the downside however, mild desorption must be used to recover metals, while the efficiency of biosorption may be low and dependent on sensitive physicochemical parameters. In addition metals may affect the viability of adsorbing strains and limit reuse and cycling [85].

2.3 Lignins

2.3.1 Sources and production of lignin

Lignin is a natural biopolymer which makes up typically 15–30% of wood and grass biomass and provides structural rigidity to many plant cell walls. Its structure depends largely on the plant type, age and growth location [86]. Wood-based lignins in particular have been used for adsorption of air pollutants, organics and heavy metals due to their physicochemical properties, low cost, abundant availability and extent of active adsorption sites [87]. Separation and isolation of lignin from cellulose is generally quite difficult due to condensation and oxidation reactions that occur during the separation process which generally consist of either chemical (e.g. alkaline pulping or acid hydrolysis) or mechanical separation processes (e.g. ball milling). In industry, significant quantities of lignin (approximately 70 million tonnes in 2017) are produced as a by-product of the 'kraft' paper manufacturing process. In this process woodchips are treated with sodium hydroxide (NaOH) and sodium sulphide (Na₂S) to separate lignin from the cellulose fibres of wood which results in a black-coloured lignin-rich liquor. Several efforts to extract lignin from the liquor and use it as an adsorbent of inorganic pollutants, including metals, have been made with varying degrees of success [88, 89].

2.3.2 Unmodified lignin as an adsorbent

Lignin polymers are hydrophobic in nature containing carboxyl, hydroxyl and phenolic surface groups, which give them an affinity for metal ion adsorption. Their specific surface area is relatively low, typically around 100–200 m² g⁻¹ [90]. Similar to biochars, the absorption research focus to date has been on heavy metals such as Cu, Cd, Cr, Pb and Zn, with typical adsorption rates using unmodified lignin-based adsorbents between 4.2 mg Cu g⁻¹ using straw-based lignin and 137 mg Cd g⁻¹ using lignin from kraft liquor (Table 8). The pH of the solution significantly influences metal uptake as described in the previous section on biochars, with generally higher adsorption rates found at pH 5–6.

Unmodified lignins tend to have relatively low aqueous metal adsorption capacity and in addition have poor selectivity for certain metals [94]. Because of this, modification and activation is frequently carried out on lignins to improve their metal adsorption properties.

2.3.3 Modification of lignins to enhance adsorption

Lignins can be chemically modified to improve their physicochemical properties, in particular their adsorption capacity, hydrophobicity and hydrophilicity as well as their overall stability. The modifications are usually carried out with oxygen-, nitrogen- or sulphur-containing functional groups which react mostly with the primary phenolic hydroxyl groups. For metal adsorption, the principal functional groups are divided into three categories [94]. The first category is oxygen-containing functional groups where acid treatment increases the naturally occurring fraction of oxygen groups as well as the hydrophobicity of the lignins. This process can significantly increase the adsorption rates for metals such as Cd and Pb ([95], Table 9) provided the pH is also controlled. In general, oxidised lignins have been shown to exhibit stronger adsorption capabilities than unmodified lignins due to the higher amounts of carboxyl groups present [96]. The second category is nitrogen-containing functional groups such as amines and triazoles, which have a high affinity for soluble metals and can be grafted onto the lignin by a Mannich reaction [97]. It has been shown that nitrogen-modified lignin increased the adsorption capacity for Pb(II) by over four times that of the original lignin [98].

Lignin type	Maximum metal adsorption capacity (mg g ⁻¹)					Reference	
	Cu(II)	Cd(II)	Cr(III)	Pb(II)	Zn(II)		pH
Wheat straw	4.2					6.0	[90]
Wheat straw	26.0					6.0	[91]
Kraft liquor (eucalyptus pulping)	87.1	137.1				4.5	[89]
Beech wood		6.7		8.2		5.0	[92]
Poplar wood		7.5		9.0		5.0	[92]
Kraft liquor from paper mill			18.0			5.0	[88]
Kraft liquor from paper mill					73	5.0	[93]

Table 8.
Typical metal adsorption capacities of unmodified lignins.

Functional group type	Lignin source	Maximum metal adsorption capacity (mg g ⁻¹)					Reference
		Cu(II)	Cd(II)	Cr(III)	Pb(II)	pH	
Oxygen-containing	Wheat straw		35.9		155.4	5.0	[95]
	Wheat straw	399.0				5.5	[99]
	Sugar cane bagasse				107.5	6.0	[100]
	Sugar cane bagasse		67.7			5.0	[100]
	Lignosulfonate	59.9	48.8		194.5	6.0	[101]
	Lignosulfonate			41.8		5.0	[101]
Nitrogen-containing	Cedar wood powder		129.3		370.8	5.2	[102]
	Industrial black liquor	72.5			55.4	6.5	[103]
	Alkaline black liquor				60.5	6.0	[99]
Sulphur-containing	Industrial black liquor				64.9	5.0	[104]
	Alkaline black liquor	175.9			103.4	6.0	[105]
	Bamboo		72.4			6.0	[106]
	Industrial black liquor				188.0	5.0	[107]

Table 9.
 Typical metal adsorption capacities of modified lignin.

The third category is sulphur-containing functional groups which have a strong affinity to metal ions such as Cd, Cu, Pb, Hg and others and are therefore used to enhance the adsorption properties of lignin (**Table 9**).

2.3.4 Activation of lignins to enhance adsorption

Lignin is one of a number of source materials used to manufacture activated carbons, which are commonly used in the water industry for removal of dissolved organic and inorganic pollutants. Activated carbons normally come in two types, granular activated carbon (GAC) and powdered activated carbon (PAC). GAC is normally used as a tertiary filter in water treatment processes and typically comprises particles of size 0.5–1.5 mm. The operation of a GAC filter is similar to that of a sand filter where GAC can be regenerated once it reaches a particular saturation ratio. PAC on the other hand comprises smaller particles, typically <0.2 mm, which are added to the water as an adsorbent. PAC tends to have very high adsorption rates due to its high specific surface area, but unlike GAC, it is very difficult to regenerate because of the difficulty in recovering the PAC powder from the water. Lignin-derived activated carbons can have very high adsorption rates because of their high micropore volume of up to 1 cm³ g⁻¹ and large specific surface area in the range 500–2000 m² g⁻¹ [108, 109]. Preparation of lignin-based activated carbon can be a two-step physical process comprising carbonation and activation or a one-step chemical process. In the two-step physical process, carbonation is achieved by pyrolysing the lignin in an inert atmosphere at temperatures in the range 600–900°C,

which results in the formation of a char. Activation then follows by further heating to higher temperatures of 700–1200°C during which the porosity is developed using agents such as CO₂, N₂, air or steam. This activation step increases the surface area and pore volume by removing internal carbon mass and volatile organic residues. Chemical activation on the other hand normally uses chemical agents such as NaOH and KOH to impregnate the lignin which is then pyrolysed at temperatures of 500–900°C in an inert atmosphere. In this process carbonisation and activation occur simultaneously resulting in activated carbon with an open porous structure and high specific surface area [110].

Typical adsorption rates of heavy metals from water, using wood-based activated carbons, range from 5.7 mg Cu g⁻¹ using rubberwood sawdust to 255 mg Zn g⁻¹ using oakwood (**Table 10**) and are influenced by the pH of the solution. For example, in a study to measure Cu(II) adsorption onto activated carbon-derived from rubberwood sawdust, optimum adsorption was measured at pH 6; however, at pH < 5, uptake decreased because of competition between H⁺ protons and free Cu(II) ions to the fixation sites [111]. Similarly, optimum adsorption of Cu, Ni and Zn onto a wood-based activated carbon powder was observed at pH 6, decreasing at pH < 6, while metal precipitation was observed at pH > 6 [112].

Unlike unmodified lignins, modified and activated lignins demonstrate a high adsorption capacity for metals and are considered a promising biotechnology for their adsorption from wastewater. Although abundantly available, one of the difficulties with lignin is its heterogeneity and therefore its ability to consistently produce suitable adsorbents. Lignin quality is very much dependent on its source as well as the processes used to isolate it, and these and other factors very much influence its metal adsorption capacity and selectivity.

2.4 Constructed wetlands

2.4.1 Constructed wetlands for wastewater treatment

The term constructed wetland (CW) refers to a technology designed to employ ecological processes found in natural wetland ecosystems. Constructed wetland systems utilise wetland plants, soils and associated microorganisms to remove contaminants from wastewater and are gaining popularity due to low operating

Activated carbon feedstock	Metal adsorption capacities of wood-based activated carbons (mg g ⁻¹)						Reference
	Cu(II)	Cd(II)	Cr(VI)	Pb(II)	Zn(II)	pH	
Rubber wood sawdust	5.7					6.0	[111]
<i>Moringa oleifera</i> wood	11.5				17.7	6.0	[112]
Wood apple shell		27.6				6.5	[113]
Rubber wood			44.1			2.0	[114]
Fir wood			180.3			3.0	[115]
<i>Acacia mangium</i> wood			37.2			2.0	[116]
Tamarind wood				134.2		6.5	[117]
Tamarind wood				43.9		6.0	[118]

Table 10.
Typical metal adsorption capacities of wood-based activated carbons.

costs, reduced energy requirements, low maintenance and enhanced environmental benefits [119]. Constructed wetlands are passive treatment systems and may be broadly categorised in terms of (i) hydrology (surface/subsurface flow), (ii) flow path (horizontal or vertical flow) and (iii) type of macrophytic growth (free floating, submerged or emergent plant growth) [120]. The two most commonly used types of CW are the free water surface (FWS) wetland and vegetated submerged bed (VSB) wetland, also termed horizontal subsurface flow wetlands. The FWS CW is a shallow wetland with a combination of emergent aquatic plants (bulrush, reeds and others), floating plants (duckweed, water hyacinth and others) and submergent aquatic plants (pondweed, widgeon grass and others). An FWS CW may have open-water areas dominated by submergent and floating plants and may contain raised habitat areas. The main treatment processes of FWS CWs include sedimentation, as well as biochemical and physical transformations. The VSB operates differently from the FWS wetland in that emergent plants are rooted in gravel through which the wastewater flows. This system is also shallow, and the gravel size is sufficiently large to facilitate long-term subsurface flow without clogging. Roots and tubers (rhizomes) of the plants grow into the pore spaces of the gravel which are mostly anoxic due to permanent saturation, although local aerobic zones exist around the plant rhizomes which create an area of complex biochemical activity.

Wetland characteristics such as the soil medium, vegetation community and microbial populations influence processes such as deposition and filtration [121], while other processes such as oxidation, reduction, adsorption and precipitation further remove contaminants [122]. Wetland vegetation has a series of roles in wetland systems including transpiration, water baffling, sediment retention, provision of habitats to microorganisms and enhancing the residence time of the wetland system [123, 124].

2.4.2 Use of constructed wetlands for metal removal

The application of constructed wetlands as passive remediation systems for low pH effluent is well documented [119]. Indeed application of wetland technology has demonstrated potential for treatment of a wide range of pollutants associated with mining and mine processing where remediation is undertaken using only naturally available energy sources such as microbial metabolic energy, photosynthesis and topographical gradient [125]. CWs are capable of biosorption, metal sulphide redox transformations and microspecies plant interactions when treating metal-rich waters [126, 127]. More recently the potential for wetland ecosystems and CWs to buffer high pH effluents has received attention [119, 128].

CWs can be effective in high Al removal rates (>90%) due to formation of insoluble compounds through hydrolysis and/or oxidation which leads to the formation of a variety of oxides [128–131]. For example, immobilisation and attenuation of V by sorption to readily extractable oxides and carbonate phases in soils were previously measured [128]. High Al removal was also reported in VSB wetlands [129–131], and this was also attributed to the formation of insoluble compounds through hydrolysis and/or oxidation leading to the formation of a variety of oxides.

A selection of typical heavy metal uptake rates from wastewater using CWs and their primary modes of removal are shown in **Table 11**.

In a study to measure removal of heavy metals from industrial wastewater, it was reported that with the exception of Ni, the sediment concentrations for all metals decreased as the distance between the inlet and outlet increased. In addition some of the macrophytes had a higher uptake of metals than others, in particular *Typha latifolia* (cattail), which demonstrated a high uptake of all metals, in particular Ni. The average proportion of metal uptake by the macrophytes was 79% (roots 56%, aerial 24%) compared with 21% for the sediment [132].

Removal medium	Metal concentrations in sediments, roots and aerial tissues (mg kg ⁻¹)						Reference
	Cu	Cd	Cr	Pb	Fe	Ni	
Sediment	1.5–2.7	0.7–1.8	0.4– 1.3	1.0–2.9	1.0–1.7	2.2–2.9	
Root tissue	3.9–5.6	2.3–5.2	1.4– 2.3	3.8–7.2	2.7–5.7	4.3–7.6	
Aerial tissue	1.3–2.7	0.9–2.5	0.4– 1.2	1.5–3.2	1.0–2.8	1.8–4.0	[132]
Total	6.7– 11.0	3.9–9.5	2.2– 4.8	6.3–13.3	4.7– 10.2	8.3– 14.5	
Overall removal efficiency	48%	92%	89%	50%	74%	41%	
Aerial tissue	6.98	0.01	0.16	0.17	—	1.33	[133]
Aerial tissue	288	0.05	—	0.09	—	—	[134]
Aerial tissue	—	4.4– 13.5	—	36–108	—	75–143	[135]
Aerial tissue	7.0	—	12.7	—	—	20.3	[136]

Table 11.

Typical metal uptake rates and primary modes of removal using constructed wetlands.

3. Conclusions and future direction

One of the consequences of a rapidly growing global population is the increasing generation of municipal and industrial wastewaters, and leachates commensurate with corresponding increases in metal emissions. Metal-rich wastewaters can result in short- and long-term environmental damage with toxicity often demonstrated at low concentrations. Metal recovery from wastewaters is therefore becoming a significant issue not only because of its resulting environmental damage and associated health impacts but also because of its potential economic value.

In this chapter we review the effectiveness of biochar, microbial and lignin biosorbents as well as constructed wetland systems to remove soluble metals from wastewaters. There exists a wide variation in the adsorptive capacities of the various unmodified biosorbent materials reflecting the heterogeneity of the source materials used for their production. In a manner similar to biochars and lignins, metal removal using selected microbes yields a range of uptake levels, with high Pb removal rates using the strains *Paenibacillus peoriae* strain T57 and *Providencia vermicola* strain SJ2A. Physical (e.g. steam, high temperature) and chemical (e.g. acids/bases) modifications of biochars bring about improvements in metal uptake levels, and interestingly, modification of lignins produces noticeably higher metal adsorption rates with many of the metal uptake levels in the range 50–400 mg g⁻¹ depending on the lignin source, particular type of modification and specific metal adsorbed. Modification of lignins leads to a significant increase in surface functionality by increasing the number of oxygen-, nitrogen- and sulphur-containing surface groups, while wood-based activated carbons also have a high affinity for many of the metals of interest, with uptake rates in many cases similar to those of modified lignins. While parameters such as contact time, adsorbent dosage, temperature and ionic strength play an important role in biosorption efficiency, the influence of solution chemistry and pH in particular also plays a highly significant role in the effective binding of a metal species to biosorbent materials. The solution pH also plays a key role in determining the oxidation state,

ionic nature and solubility of the metal species. However the pH at which maximum adsorption occurs may also simultaneously precipitate metals from solution, and it is important that reported metal adsorption rates in any experimental work do not also (and erroneously) include precipitated metals. Many of the studies presented in this chapter have reported maximum metal biosorption rates at pH 4–7, but some are as low as pH 2 and others as high as pH 8.

Constructed wetlands differ from biosorbents in that they are biosystems which remove metals and other contaminants by sedimentation as well as physical and biochemical transformations. Many of the metals in the wastewater are removed by the macrophytic system which if harvested can be permanently removed without leaching back into the system by natural plant decay. The specific removal rates in CW systems are much lower than those of corresponding biosorbents; however with sufficient hydraulic retention time and appropriate loading rates, the overall removal efficiencies can be relatively high. Because of their passive nature, low-energy and low-maintenance requirements as well as their perceived amenity benefits, CWs are considered a promising technology for removal of metals from wastewater. There is however scope for further investigation into CWs treating metal-rich wastewaters such as (i) their long-term capacity to treat and retain the adsorbed metals from wastewaters which have a matrix of metals and (ii) assessing the influence of wastewater characteristics such as suspended solids, pH and predominance of metal types on CW removal efficiencies.

While application of an abundant supply of biosorbent materials to remove metals from wastewater is gaining increasing attention due to their potential for metal recovery and pollution mitigation, there are nevertheless a number of shortcomings to be addressed before their widespread use can be implemented. Some of the most commonly identified improvements are to increase the selectivity of biosorbents to treat wastewaters which have a matrix of metals and to improve their consistency, mechanical stability and adsorption capacity, making them less sensitive to pH changes and high ionic concentrations. In addition there is a need to develop the desorption potential and regeneration capacity of biosorbents in order to increase their technology readiness level. There is a need also to improve the long-term mechanical stability of biosorbents which generally deteriorates after a number of cycles. Possible ways to achieve this might be to immobilise the biosorbents onto inert materials such as sand, glass or fibres or perhaps use an entrapment technique in polymeric matrices producing alginate or polyacrylamide beads.

There are a range of potential biological materials that could be utilised and developed as strategies to remove metals from waste streams. Their further use will depend on developing engineering and technological solutions for their full deployment. Hand in hand with the removal of metals, there is also an interest in strategic deployment of such techniques to enhance specificity of metal binding; this interest stems from the need to recover metals of particular interest such as rare earth metals, valuable metals or radioisotopes.

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Conflict of interest

The authors declare no conflict of interest.

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