CELLULOSIC SUBSTRATES FOR REMOVAL OF POLLUTANTS FROM AQUEOUS SYSTEMS: A REVIEW. 1. METALS

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Recent years have seen explosive growth in research concerning the use of cellulosic materials, either in their as-recieved state or as modified products, for the removal of heavy metal ions from dilute aqueous solutions. Despite highly promising reports of progress in this area, important questions remain. For instance, it has not been clearly established whether knowledge about the composition and structure of the bioadsorbent raw material is equally important to its availability at its point of use. Various physical and chemical modifications of biomass have been shown to boost the ability of the cellulose-based material to bind various metal ions. Systems of data analysis and mechanistic models are described. There is a continuing need to explain the mechanisms of these approaches and to determine the most effective treatments. Finally, the article probes areas where more research is urgently needed. For example, life cycle analysis studies are needed, comparing the use of renewable biosorbents *vs.* conventional means of removing toxic metal ions from water.

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INTRODUCTION

This article reviews publications in which lignocellulosic materials have been used, either "as-received" or in modified form, to remove various heavy metals from dilute aqueous solution. There have been an impressive number of relevant publications in this field. The preparation of the present article was made easier by the existence of earlier reviews, some of which are listed in Table 1. As shown, certain reviews have dealt with the biosorption of metal ions in general, while others have focused on specific ionic species or classes of biomass. Some of the articles have reviewed chemical or thermochemical modifications of cellulosic raw materials to render them more effective for the collection and binding of various metal ions. Readers interested in certain metals, certain types of sorbents, or certain aspects of metal bioadsorption are encouraged to scan the columns of Table A (see Appendix), as well as chapters in Wase and Forster (1998). In addition, a book by Cooney (1998) describes engineering principles and strategies for implementation of absorbent-based water treatment systems. Kurniawann *et al*. (2006a) and Owlad *et al*. 2009) reviewed systems other than biosorption for removal of metals.

Table 1. Selective List of Relevant Review Articles and Chapters

Metal species considered	Cellulose-based substrates	Emphasis of the article	Citation information
Chromium	All options	Metal recovery	Agrawal *et al.* 2006
Heavy metals	Microbial & plant	Choice of sorbent	Ahluwalia & Goyal 2005b
Chromium	Agro-based	Bio-sorption	Alpana 2008
Rare earth metals	Microbial biomass	Capacities, models	Andrès *et al.* 2003
Heavy metals	Low-cost biomass	Activated carb., *etc.*	Babel & Kurniawan 2003
Heavy metals	Low-cost biomass	Lignin, chitosan	Bailey *et al.* 1999
Heavy metals	Fungal biomass	Sustainability	Bishnoi & Garima 2005
Heavy metals	Various	Bioaccumulation	Chojnacka 2009, 2010
Heavy metals	Rice husk	Low cost	Chuah *et al.* 2005
Heavy metals, *etc.*	Polysaccharide	Polym. modification	Crini 2005
Mined metals	Various methods	Recovery of metals	Cui & Zhang 2008
Heavy metals	Brown algae	Sorbent properties	Davis *et al.* 2003
Heavy metals	Agro-based	Low concentrations	Demirbas 2008
Various pollutants	Activated carbon	Low cost biomass	Dias *et al.* 2007
Various pollutants	Various sorbents	Drinking water	Dubey *et al.* 2009
Heavy metals	Biomass	Low cost sorption	Gadd 2009
Heavy metals	Chitosan	Adsorp. capacities	Gérente *et al.* 2007
Heavy metals	Various biomass	Sorp. rate models	Ho & McKay 1999
Heavy metals	Biosorbants	Mechanisms	Ho *et al.* 2000
Heavy metals	Fungal biomass	Performance	Kapoor & Viraraghavan 1995
Heavy metals	Biopolymers	Protein-based	Kostal *et al.* 2005
Heavy metals	Agricultural prods.	Compilation	Kumar 2006
Heavy metals	Various biomass	Biomass attributes	Kurniawan *et al.* 2006
Cadmium	Biosorbants	Thermo & kinetics	Lodeiro *et al.* 2006
Mined metals	Plant, microbial	Metal recovery	Madrid & Camara 1997
Heavy metals	Algae	Wastewater	Mehta & Gaur 2005
Heavy metals	Nonliving biomass	Each metal-ion pair	Modak & Natarajan 1995
Chromium(III, VI)	Carbons, low-cost	Strategies, theories	Mohan & Pittman 2006
Arsenic	Absorbents	Strategies, options	Mohan & Pittman 2007
Heavy metals	Modified cellulose	Activated carb., *etc.*	O'Connell *et al.* 2008
Heavy metals	Activated carbons	Low-cost sources	Pollard *et al.* 1992
Trace metals	Functionalized	Preconcentration	Pyrzynska & Trojanowicz 1999
Heavy metals	Dead macrophytes	Phytoremediation	Rai 2009
Heavy metals	Algae	Statistical review	Romera *et al.* 2006
Heavy metals	Fungal biomass	Functional groups	Sag 2001
Various pollutants	Sawdust	Mechan., factors	Shukla *et al.* 2002
Heavy metals	Agricultural waste	Compilation	Sud *et al.* 2008
Various pollutants	Lignin, act. carbon	-	Suhas *et al.* 2007
Heavy metals	Biosorbents	Metals recovery	Veglio & Beolcini 1997
Various pollutants	Bacterial	Binding mechan.	Vijayaraghavan & Yun 2008
Heavy metals	Biosorbents	Selec. of biomass	Volesky 1994
Heavy metals	Biosorbents	Sorption capacities	Volesky & Holan 1995
Heavy metals	Biosorbents	Implementation	Volesky 2001
Heavy metals	Modified plants	Modification	Wan Ngah & Hanafiah 2008b
Heavy metals	Fungal biomass	Yeast	Wang & Chen 2006
Heavy metals	Biosorbents	Ads. sites, trends	Wang & Chen 2009
Heavy metals	Silvichem biomass	Methods, immobil.	Yu *et al.* 2008
Metals	Ion exchange	Introductory text	Zagorodni 2007
Arsenic	Low-cost biomass	Drinking water	Zahra 2010

Table 2 displays the main organization of the present article. An attempt was made to gather metal sorption data from many individual studies, bearing in mind that conditions of sample preparation, treatment, and testing verried greatly among the published studies. A second main goal of this review article is to provide a fairly complete overview of several mathematical formulas that have been employed to fit metal adsorption data. By using Table 2, readers can select topics of highest interest within the article.

Table 2. Organization of the Present Article

Topic	Page
Introduction	2161
Guide to the tabulation of data	2164
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Biomass types and important factors	2166
Modification of biosorbents	2172
Sorption mechanism and ion exchange	2177
Sorption isotherms	2181
Applying isotherms to metal sorption data	2187
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Metals in soluble form have raised increasing concerns in recent years. Toxic effects of various metals have been described in detail by Chang (1996), and more recently by Babula *et al.* (2008) for less common metals. Metal-induced neurological disorders in particular are covered in a book edited by Zatta (2003). Progress has been achieved recently in understanding the attributes of metal ions that contribute to their toxicity (Yoon et al. 2008). Most metal ions become harmful when their concentration exceeds a certain threshold, which depends on the sensitivity of the consuming organism. At the same time, a majority of the same metal species can be considered as essential nutrients, and serious adverse health effects would result if they were completely eliminated from an environment or from a drinking water/food supply system. The most dangerous metals are those that tend to bioaccumulate, building up in the fatty tissues of animals in a food chain (Luoma 2008; Chojnacka 2009, 2010). Chromium(VI) is of particular concern in this regard, since the chromate ion (CrO_4^{2-}) is easily transportable across cell membranes. The species is readily reduced to the Cr(III) form, which tends to form insoluble complexes that cannot easily be expelled by the affected organism (Cabtingan *et al.* 2001; Srinath *et al.* 2002; Aravindhan *et al.* 2004b; Deng *et al.* 2006). Metal speciation and the analysis of metal ion species in water have been reviewed by Ali and About-Enien (2006).

Many of the published studies considered in this review article may have been motivated by a desire to find profitable uses of specific waste streams or under-utilized materials produced during industrial operations. When considered separately, almost every such study can be considered successful. However, there has been a need to answer some practical questions, such as those that follow:

- Are cellulosic materials universally effective at removing hazardous metal ions from aqueous solutions?

- Are there rules of thumb that can lead to the selection of suitable biomass for use in sorption of metal ions from solution?
- What are the most useful mathematical expressions that can be used to fit adsorption isotherm data?
- What mechanisms governing metal uptake have been well established? Where are there opportunities for progress in useful theories?
- Can the biosorption of metal ions be improved by mechanical treatments of the cellulosic material?
- What kinds of chemical extractions, derivatizations, or grafting can greatly improve the efficiency of metal ion uptake?
- Should one attempt to regenerate or incinerate cellulose-based biosorbent materials after they have been used to remove metals from water and thereby change the material's life-cycle?

Guide to the Tabulation of Data

As a first step in attempting to answer questions such as those listed above, an extensive literature search was performed, and information reported in the various articles are collected in Table A, which due to its size is placed in the Appendix to this article. Because Table A will be mentioned frequently during subsequent discussions, a description of its organization is provided here. Columns in Table A indicate the type of biomass, the type of modification (if any), the studied metal species, the adsorption capacity (listed both on a mass basis and a molar basis per unit mass), an abbreviated summary of key findings, and the author-year information, which can be used to find the full citation in the "Literature Cited" section. Going down the table, the entries are organized according to biomass type (first column) and then alphabetically by author name within each category. An exception is made when considering studies in which the biomass was so profoundly modified that the nature of the original biomass was judged to be unimportant in comparison. Thus, the various kinds of chemical modifications, as well as production of activated carbon products from cellulose-derived resources, are given unique groups with no regard for the biomass type that was used as the starting material. Starting at the top of the table, the biomass types are organized as follows: **Wood**: (hardwood, softwood, unspecified), wood fibers, bark, foliage, cones, nut shells; **Crop residuals**: husk, stalks; **Food residuals**: sugar cane bagasse, sugar beet pulp, other, seeds, fruit stone, fruit peel, tea leaves; straw and grasses; weeds and plants; **Aquatic plants**: fresh water, seaweed, loofa; **Microbiota,** *etc.*: algae, bacterial biomass, yeast; **Fungal biomass**, **Lignin-related**: isolated lignin, lignite and humic matter, peat moss, sludge and biogas residuals; **Chemically modified**: alkali-treated, oxidized, with adsorbed materials, derivatized (succinylated, citric acid-treated, carboxymethylated, aminated, other), grafted; **Activated carbons**; and **Ash**.

Criteria for Success

A wide range of criteria have been considered by different authors when judging the relative success of methods to remove heavy metal ions from water. Most authors list adsorptive capacity of the biosorbent among their top concerns. It has been pointed out, however, that one of the most advantageous applications of cellulose-derived sorbents is

in the treatment of very dilute solutions and in the reduction of aqueous metal concentrations to very low levels (Gaballah and Kilbertus 1998; Gupta *et al*. 2000; Amuda *et al*. 2007; Demirbas 2008). None of the reviewed works expressed the opinion that adsorbtion was not rapid enough for any envisioned usage, though the speed of uptake is mentioned by many authors. Rather, much attention has been paid to modeling the kinetics of metal uptake (see, for instance Table A), and the obtained rate expressions have been used in modeling water treatment systems based on both packed-bed operations and batch treatment (Ho and McKay 1999a; Ho *et al*. 2000b).

Far less attention has been paid to a number of other criteria that might be used to judge the success of a metal remediation strategy. One such criterion is the stability of partially or fully saturated biosorbent. A question remains as to whether the bioadsorbent will continue to hold onto adsorbed metal ions during long-term storage. Another issue that has received relatively little attention is the practical handling of the biomass, including its efficient collection from an aqueous mixture for proper disposal or regeneration without discharging into a surrounding waterbody (Kapoor and Viraraghavan 1998b). Some powdered biomass tends to become soft when placed into water. Its low density and fine particle size can make it difficult to separate from treated wastewater, and fixed bed reactors filled with biomass powders have a tendency to clog (Kapoor and Viraraghavan 1998b).

Using the cellulose-derived material as a support for a primary adsorbent

Another way to define successful use of cellulose-based matter in removal of heavy metals involves the concept of "support". In other words, the biomass may serve as a backbone structure upon which the main adsorbent material is attached. Zhu *et al*. (2009b) demonstrated such a concept in their use of zero-valent-iron (ZVI) nanoparticles supported on activated carbon. The combination was found to be effective for the removal of arsenic from water. The ZVI nanoparticles act as a strong reducing agent, having the potential to change the valence state of such metals as arsenic and chromium to less toxic forms. The cited article is a prime example of how it is possible to address such problems without needing to release a strong reducing agent directly into aqueous streams or groundwater, which would create an additional contribution to the pollutant load.

Life-cycle issues

It is important, for both environmental and economic reasons, to consider in detail what happens to an absorbent material after it has been employed to remove heavy metals from water. As evidenced by numerous entries in Table A, most cellulose-based sorbents can be "regenerated" by treatment with acid solution (see, *e.g.*, Chang *et al*. 1997), though some studies also evaluated the feasibility of using an alkaline solution or brine. In each case, the idea is to displace the metal ions back into a relatively concentrated solution, which either can be disposed of or further processed as a source of valuable metals or inorganic compounds (Cui and Zhang 2008). Another approach is to incinerate the metal-containing biomass, so that the metal content can be concentrated in the ash (Gaballah and Kilbertus 1998).

Relatively little attention has been paid by researchers to landfilling as an alternative fate for used sorbent material. Unlike the options considered in the previous paragraph, landfilling does not require the use of either chemical treatment or incineration of the contaminated sorbent. Treatments with acid or brine can have environmental consequences, even if the pH is subsequently neutralized. Energy may be required to dry sorbent material before it can be incinerated. Thus, as a potential end-of-use strategy for metal-containing biosorbent material, landfilling should be an option in future life-cycle analyses. Issues that need to be considered include the degree to which typical biosorbents will hold onto their metal content during long-term storage and the likely concentrations of metal ions in leachate from such operations. Considering the case where material in a landfill is subjected to rainfall, research results suggest that typical biosorbents will release relatively low concentrations of metals (Gaballah and Kilbertus 1998; Gupta *et al*. 2000; Amuda *et al*. 2007; Demirbas 2008). None of the cited studies, however, addressed what might happen as the biomaterial breaks down in the soil.

BIOMASS TYPES AND KEY FACTORS

Based on the reviewed literature, it appears that almost every possible category of biomass material has been evaluated for the uptake of heavy metal ions. As indicated in Table A, multiple respresentatives from many different classes of cellulose-derived materials have been evaluated and judged to be successful as biosorbents. Individual studies have generally tended to be narrow in scope, considering relatively few sorbents, relatively few heavy metal ions, and a limited range of aqueous conditions. Taken together, however, a voluminous collection of scientific work has been published, most of it within the last 20 years. In addition, effects of a great many chemical and thermochemical modifications of cellulosic materials have been used in an attempt to achieve higher adsorption capacities. The take-away message is that there is a large selection of suitable sorbent materials with which one can remove heavy metals from water.

Evaluation of First Hypothesis: The Type of Biomass is Important

The first question to consider is whether there are clear differences in metal uptake, depending on the type of untreated biomass support. Figures 1A and 1B display the amounts of lead and chromate ions that were taken up by unit mass of different classes of cellose-based materials under the conditions specified in the cited works. Each plotted "X" symbol in the figure corresponds to the results of an individual study. In general, the data taken from studies considered in this review show that the adsorbed amounts varied over very wide ranges, even within each class of sorbent. For instance in the case of "Wood, sawdust" (as represented by the left-most column), the results for Cr(VI) sorption (Fig. 1B) spanned a factor of about 300). Subsequent sections of this article will describe a variety of reasons that each might account for part of these differences. Note that the rectangular "boxes" in these figures indicate the 25%, 50%, and 75% levels based on the relative frequency of articles reporting different values. The "stems" in the diagram extend upwards and downwards to the highest and lowest reported values of metal sorption in each case.
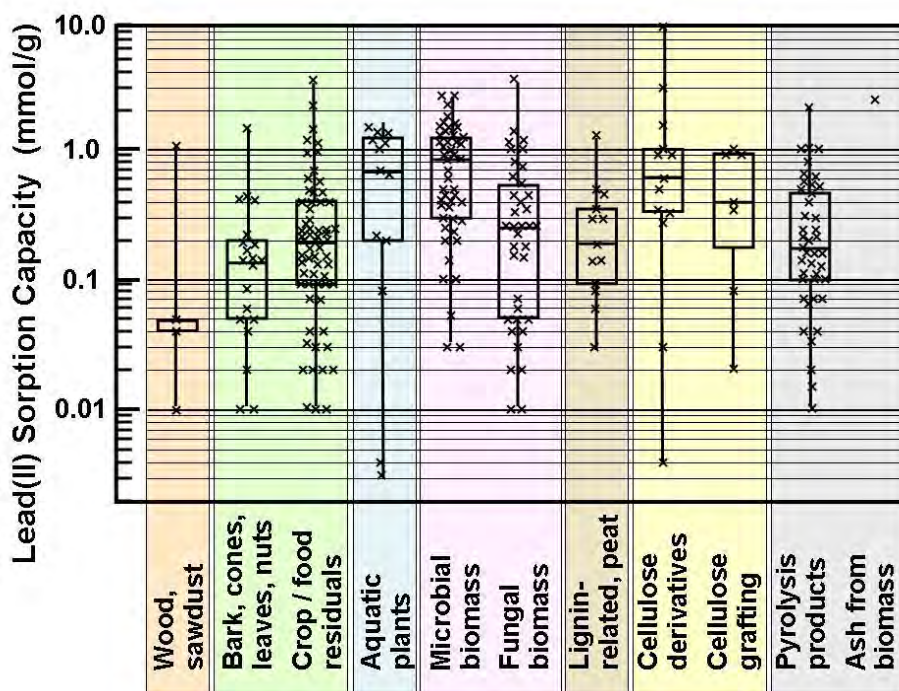
Figure 1A. Graphical summary of reported amounts of lead ion, Pb(II), adsorbed by diffent classes of cellulose-based matter according to the conditions specified in articles cited in Table A .
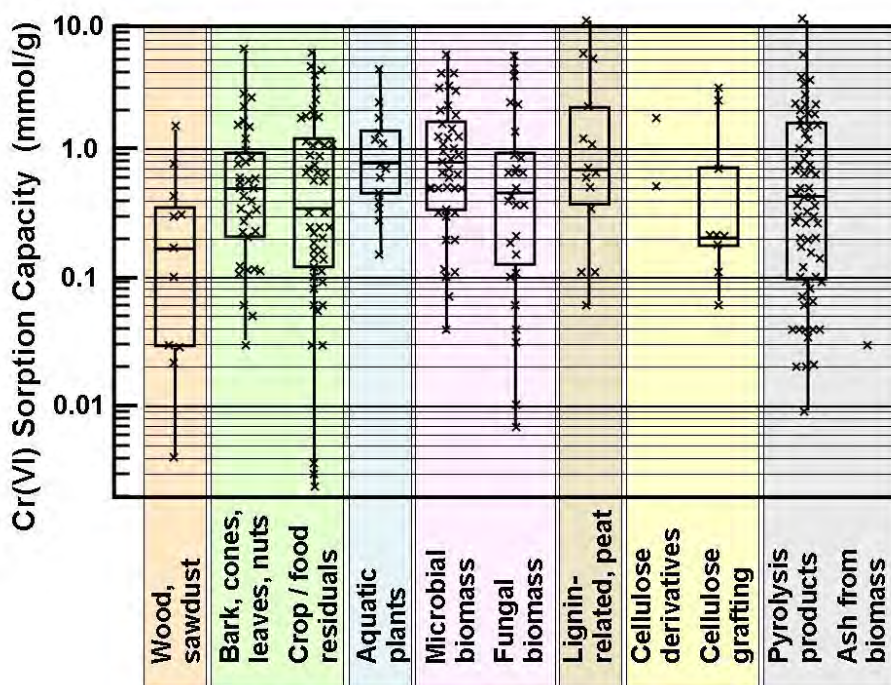

Figure 1B. Graphical summary of reported amounts of adsorbed Cr(VI) taken up by diffent classes of cellulose-based sorbents according to the conditions specified in articles cited in Table A. Note that Cr(VI) can be present as the CrO_4^{2-} (cromate) anion, depending on the pH.

Visual inspection of Fig. 1A and B suggests that certain biomass classes were somewhat more promising in terms of achieving relatively high levels of sorption of specific metal ions. Though there were important differences attributable to the metal species (especially when comparing adsorption of the chromate ion *vs*. cationic metal species), such differences appeared to be dominated by effects attributable to differences among the substrate samples, even when the nominal material was similar. As a class, average adsorptive capacities reported for "Wood" did not appear to be as high as those reported for such classes as "Bark, cones, leaves, and nuts," "Crop/food residuals," "Aquatic plants," "Lignin-related," and "Pyrolysis products."

Figure 2 addresses a related question: How did different metal ions generally compare against each other, with respect to their tendency to be taking up by a given class of cellulosic material? To make this comparison, seven kinds of metal ions were compared with respect to their sorption by the "crop/food residuals" types of biomass. Though later sections of this article will refer to studies providing evidence of significant "metal selectivity," such effects are not apparent when one looks at the assemblage of data plotted in Fig. 2.

One of the most fascinating aspects of these results is the finding that the chromate ion (data plotted farthest to the right) compared very well with the other ions, even though the chromate ion (CrO_4^{2-}) has a negative charge, which is the same net charge as that of typical cellulosic surfaces.
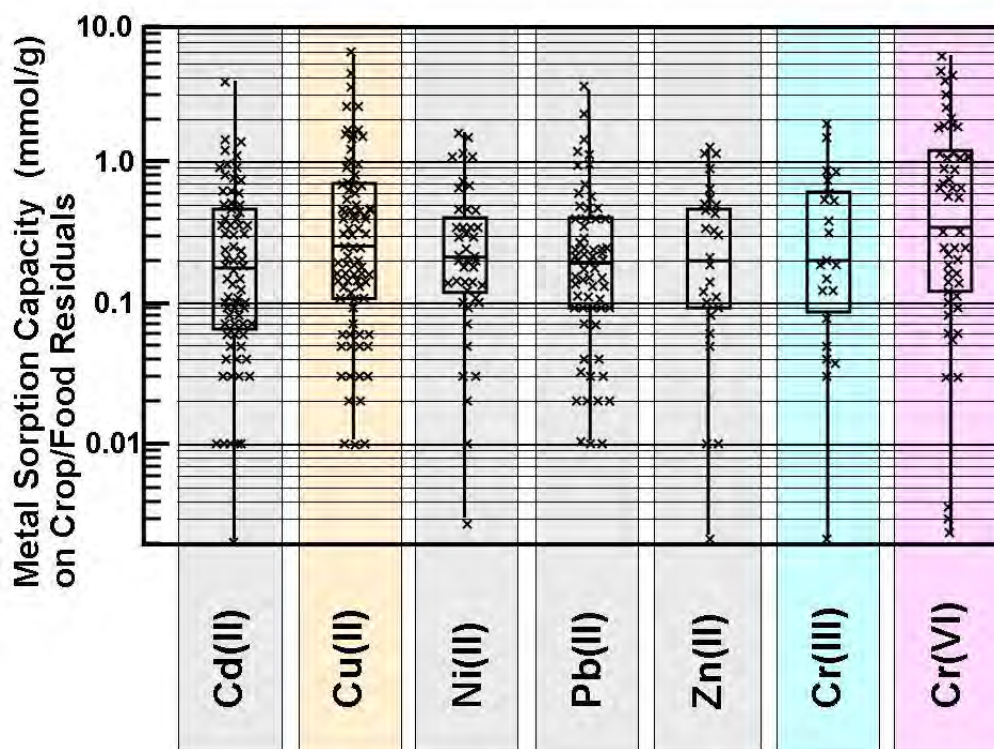

Figure 2. Graphical summary of reported amounts of seven types of metal ions taken up by one class of cellulose-based sorbents ("crop/food residuals) according to the conditions specified in articles cited in Table A

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Because the proportions of cellulose, hemicellulose, and lignins can differ to a great extent, not only among the biomass categories mentioned above, but also from species to species, it makes sense to compare the metal sorption efficiency of biomass samples showing large differences in compostion. Various authors have proposed that lignin-rich samples, such as composts, would be expected to have a high affinity for metals ions due to an expected high level of carboxylation (Harman *et al*. 2007). Indeed, various studies support this hypothesis (Srivastva *et al*. 1996; Lalvani *et al*. 1997; Dizhbite 1999; Crist *et al*. 2002, 2003; Acemioğlu *et al*. 2003; Babel and Kurniawan 2003; Basso *et al*. 2004; Demirbas 2004, 2005; Sciban and Klasnja 2004a,b; Celik and Demirbas 2005; Mohan *et al*. 2006; Harman *et al*. 2007; Guo *et al*. 2008; Quintana *et al*. 2008; Wu et al. 2008; Harmita et al. 2009). By contrast, there has been a notable lack of attention paid to hemicelluloses and extractive components of biomass in this regard; this is surprising, since these components of biomass are known generally to be rich in carboxylic acid groups (Sjöström 1993).

Cost and Availability

A possible lesson that can be drawn from Table A is that almost any biomass-derived product can be used for metal ions removal from solution. It is difficult, however, to claim that any one type of source material is consistently superior to others, though large differences have been observed between different types of biosorbents. That being the case, it is worth questioning whether it is sometimes adequate to make one's selection based only on cost and local availability. For instance, if one were able to obtain peanut shells, fungal biomass, and pine sawdust from local sources, what factors other than performance ought to guide one's choice?

In principle, transportation costs and associated usage of energy can be minimized by using locally-collected biomass as the basis for a biosorbent system. But the overall cost and energy expenditure will also depend on the performance of the material. One needs to consider that a higher-performing biosorbent may achieve one's objectives for metal removal with much less biosorbent material, thus reducing labor costs and operational costs. There may be savings related to safe disposal or regeneration of the spent material.

The ideal biosorbent should be very cheap, an unwanted byproduct that currently has to be hauled away and landfilled or burnt in heaps. On the other hand, the ideal biosorbent should have a huge appetite for a broad range of metal ions, binding them quickly, tightly, and dependably. One approach is just to test various readily available materials in "as-received" form. However, as will be shown in the course of this review, other investigators have employed a more proactive option, treating the biomass in various ways to improve its performance. Though the detailed prices of various biosorbents, both in their as-received and treated forms, lie beyond the scope of the present review article, it is expected that some of the collected data will permit subsequent investigators to make judicious choices among existing biosorbents and to develop additional variations to further enhance performance of biosorbents for different applications.

Cost

The words "low cost" have been used frequently, especially in review articles, by authors summarizing the main motivations prompting the use of biosorbent technology (Scheider *et al*. 1995; Gupta *et al*. 1998; Bailey *et al*. 1999; Brown *et al*. 2000; Gérente *et al*. 2000; Kumar *et al*. 2000; Marchetti *et al*. 2000a; Wartelle and Marshall 2000; Yu *et al*. 2000; Reddad *et al*. 2002b; Babel and Kurniawan 2003; Fiol *et al*. 2003; Ulmanu *et al*. 2003; Krishnani *et al*. 2004; Chuah *et al*. 2005; Horsfall and Spiff 2005b; Karthikeyan *et al*. 2005; Agarwal *et al*. 2006; Ali and Gupta 2006; Kumar 2006; Kumar and Bandyopadhyay 2006a; Kurniawan *et al*. 2006b; Lodeiro *et al*. 2006; Mohan and Pittman 2006; Parab *et al*. 2006a; Pino *et al*. 2006; Sarin and Pant 2006; Singh *et al*. 2006; Upendra and Manas 2006; Abdel-Ghani *et al*. 2007; Dubey and Krishna 2007; Garg *et al*. 2007; Ghodbane *et al*. 2007; Nouri *et al*. 2007; Soleimani and Kghazchi 2007; Zafar *et al*. 2007; Ahmady-Asbchin *et al*. 2008; Arief *et al*. 2008; Chakravarty *et al*. 2008; Demirbas 2008; Farinella *et al*. 2008; Igwe *et al*. 2008; Sud *et al*. 2008; Anandkumar and Mandal 2009; Gadd 2009; Rai 2009; Shukla *et al*. 2009; Wang and Chen 2009; Parab *et al*. 2010; Zahra 2010). Though Gupta *et al*. (2000) claimed that the operating costs involved in the usage of biosorbents for metal removal can be low relative to various alternative pollution abatement measures, there has been insufficient attention to operating costs, including the costs of transporting the sorbent material to the point of use, as well as costs associated with transportation to a site of final disposal, regeneration, or other beneficial use.

Gadd (2009) raised the following challenge to those attempting to make distinctions, other than cost, among alternative cellulose-derived sorbents: Because the composition of biomass does not vary a great deal between different species, it would seem pointless to spend a lot of effort testing many different representatives within a given class of biomass.

As an alternative, it was suggested that researchers should focus on biomass types that have distinct chemical differences from other types. Fungal biomass was mentioned as a key example, since it contains chitin within its cell walls (Ahluwalia and Goyal 2005b). The amino groups within chitin may have the potential to bind certain metal ion species in a different way from other kinds of biomass. Details about the use of fungal biomass for metal remediation have been reviewed (Sag 2001; Bishnoi and Garima 2005).

Local availability of large quantities

When the attributes of a needed commodity include "very low cost," and often "bulky," it can be a great advantage to minimize transportation costs. One promising low transportation strategy is to position one's bioremediation facility adjacent to a business that produces a suitable lignocellulosic waste stream. For example, substantial quantities of microbial biomass are produced during industrial-scale fermentation processes (Ahluwalia and Goyal 2005b). Likewise, there may be opportunities to accumulate such bypoducts as bark, sawdust, carcoal, or ash adjacent to a facility that produces wood products or paper pulp as a primary product.

Performace Factors

Having already noted that cellulosic biomass is mainly composed of cellulose, hemicellulosics, lignin, and some extractives – the next challenge is to try to account for the huge ranges of metal ion adsorptive capabilities, such as those that are indicated in Fig. 1. Indeed, while certain cellulose-based sorbents represented in the figure were not very effective on a unit mass basis, others can equal or exceed the sorption capability of commercial ion exchange resins (*e.g.* Chang and Hong 1994; Ariff et al. 1999; Chamarthy *et al.* 2001; Saliba *et al.* 2002b; Choi and Yun 2004; Bishnoi and Garima 2005; Cochrane *et al.* 2006; Arshad *et al.* 2007; Ziagova *et al.* 2007).

Surface area

Cellulosic materials of biological origin tend to be organized with systems of interconnecting pores, thus providing a relatively high surface area per unit mass. However in such cases, there may be questions about: (a) whether parts of that surface area are inaccessible to the metal ions in question, and (b) whether parts of that surface area are lacking in potential binding sites for the metal ions. The importance of maximizing the accessible surface area has been demonstrated by studies that considered effects of particle size of the sorbent (Bai and Abraham 2001). However, there has been a lack of detailed study to compare surface area parameters *vs.* metal uptake under well-defined conditions. Future research might use, for instance, the BET nitrogen adsorption method (Faur-Brasquet *et al.* 2002; Budinova *et al.* 2006; Demiral *et al.* 2008; Hanafiah and Ngah 2009) to quantify the surface area of sorbent materials. A solvent-replacement method and freeze-drying could be used to minimize collapse of submicroscopic pores as water is removed (Stone and Scallan 1996).

A shown in Figs. 1 and 2, the typical data for adsorption of specified metal ions on nominally similar biomass samples range over three orders of magnitude. Including all the factors to be considered in this article, such a wide spread of data would appear to be best explained by differences in accessible surface area. Indeed, the cited work of Stone and Scallan (1996) showed that the drying of cellulosic material has the potential to decrease the apparent surface area by at least a factor of 100. Stone and Scallan revealed that about half of the mesopores that collapsed during drying of cellulosic pulp failed to re-open when the same fibers were rehydrated under the conditions of testing. Future studies related to metal remediation could address this point by scrupulously avoiding inadvertent drying of fresh biomass material at any point before the start of experimentation. This approach has the potential to show whether or not "un-dried biomass," in contrast to more typically available samples of unknown drying history, might offer substantially higher metal uptake capacity.

Agitation

Another possibility that researchers have studied is whether the uptake of metal ions may be limited by the rate of diffusion of metal ions to surfaces. Some researchers have found that the amount of metals adsorbed increased with increasing agitation during batch testing (Ahalya *et al.* 2005; Basci *et al.* 2003). Though both of the cited studies observed higher adsorbed amounts associated with higher rates of agitation, the mechanism is not completely clear. Agitation can be expected to facilitate convective

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transport of metal ions to sorbent surfaces, and several studies indeed showed positive effects of agitation on the rate or extent of metal sorption (Basci *et al*. 2003; Ahalya *et al*. 2005; Shen and Duvnjak 2005b,c; Malkoc 2006; Martinez-Garcia *et al*. 2006b; Chaves *et al*. 2009; Garg *et al*. 2009).   Alternatively, the associated pressure pulses acting on suspended particles in a mixture might also create a pump-like action, creating intermittent flow into and out of pore spaces within cellulosic materials in suspension. Such questions have not been adequately resolved and will require further research.

Ion exchange capacity

        The issue of "binding sites," as mentioned previously, can be addressed by considering the ion exchange capacities of candidate sorbent materials (Gadd 2009). Strictly speaking, ion exchange capacity can be measured by determining how much of one type of ion desorbs from a unit mass of a given sorbent when the system is saturated with a specified metal ion.   The desorbed ion is usually either the proton, sodium, or an alkaline earth ion, such as calcium.   The term "ion exchange" usually implies that the researchers are considering non-specific, electrostatic mechanisms of metal binding. Though such approaches often can be used as a first approximation, later sections of this article will consider alternative approaches that can help to explain deviations from an anticipated 1:1 stoichiometry between the ion exchange capacity of a sorbent and the adsorption capacities of different metal ions, even those having the same valence.

        The major proportion of the ion exchange capacity of a biosorbent material usually can be attributed to surface-bound carboxylic acid groups.   In principle, the content of carboxylic acid groups can be estimated by titrating a mixture of the sorbent material in water between two levels of pH, such as 3 and 9, and comparing the result with a blank determination (Gill 1989; Herrington and Petzold 1992; TAPPI 1993; Lindgren *et al*. 2002).   An alternative method is required if one needs to determine carboxylic acid groups in the presence of other sources of acidity (*e.g*., Chai *et al*. 2003). The importance of carboxyl groups in sorbing metal ions has been demonstrated in many studies (Maranon and Sastre 1992b; Gloaguen and Morvan 1997; Jia and Thomas 2000; Kadirvelu *et al*. 2000; Merdy *et al*. 2002; Tiemann *et al*. 2002; Chubar *et al*. 2003; Davis *et al*. 2003; Pagnanellil *et al*. 2003; Karunasagar *et al*. 2005; Leyva-Ramos *et al*. 2005; Southichak *et al*. 2009b; Gurgel *et al*. 2008; Lodeiro *et al*. 2008; Bakir *et al*. 2009; Iqbal *et al*. 2009b; Jaramillo *et al*. 2009; Martin-Lara *et al*. 2008, 2009).

MODIFICATION OF BIOSORBENTS

        Once a decision has been made to use a certain type of biosorbent , perhaps due to favorable performance of the as-received material, the next decision may involve whether and how to modify that material to improve its efficiency. The following discussion will start with gross mechanical and thermal treatments, then proceed to chemical treatments. Of the latter, relatively superficial "rinsing" strategies will be considered first, then more pervasive treatments such as oxidation, polymer adsorption, and formation of chemical derivatives or graft polymers at the surface of cellulosic materials. Activated carbon, which is often prepared from cellulosic biomass, will be considered last.

Size Reduction

In principle, a more finely ground sample of a given cellulose-based material is expected to adsorb more metal ions from solution, under specified conditions, compared to coarser particles. Indeed, this statement has been proven in a few studies (Ajmal *et al*. 1998; Blazquez *et al*. 2005). A further question is whether the effort and expense of size reduction can be justified. Here the answer is less clear. The study by Ajmal *et al*. (1998) observed an increase in metal sorption capacity by only a factor of about 2 when the particle size of sawdust was decreased from 500 µm to 100 µm. In addition to the high energy requirements, especially if one aims to achieve particles much smaller than 1 mm, one can anticipate increased problems with the handling of very fine material, including greater difficulties in later separation from the water phase, clogging of filters, and even dust and fire hazards if and when the material is dried. Sawdust actually represents a favorable case, since the energy to reduce the particle size has already been expended, perhaps in the production of lumber. Unfortunately, there have been few studies dealing systematically to determine under what circumstances one can justify the energy and time needed to reduce the particle size of a selected biomass sample in preparation for its use as a metal sorbent.

Living *vs.* Dead Biomass

One of the likely consequences of mechanically or chemically treating a biomass sample (see next sections) is its conversion from living organisms into dead biomass. Several investigators have investigated whether a change from living to dead has a significant effect on the ability of the material to adsorb metals ions (Kapoor *et al*. 1999; Srinath *et al*. 2002; Chen *et al*. 2005; Methta and Guar 2005; Yan and Viraraghavan 2003). Mehta and Guar (2005) reviewed relevant studies and concluded that dead biomass samples typically outperform living biomass for the uptake of heavy metals. Only in some cases did the investigators find substantially higher uptake when utilizing live cells (Yan and Viraraghavan 2003; Chen *et al*. 2005). The ability of some cells to accumulate metals internally by active biological processes has been suggested (Chen *et al*. 2005), and interest in the use of living cells for biosorption has been predicted to increase (Wang and Chen 2009). Other researchers have found cases where metal sorption was actually increased after such processes as autoclaving (Kapoor *et al*. 1999; Srinath *et al*. 2002; Deepa *et al*. 2006). The explanation for the latter findings may be that killing the cells opens internal surfaces, making the material more accessible. Kapoor and Viraraghavan (1998a) found mixed results; pretreatment of live *Aspergillus niger* biomass with various reagents yielded the best results for uptake of lead, cadmium, and copper, but the best uptake of nickel ions was observed with dead cells.

As noted by Ahluawalia and Goyal (2005b), non-living biosorbants have many potential advantages, including insensitivity to growth conditions or toxins, easier handling, easier storage, and easier disposal. Also, as noted by Ozdemir *et al*. (2004) and Hasan *et al*. (2007), the growth of living cells may be inhibited in the presence of significant concentrations of the specific metal that one would like to remove from an aqueous system. Kurek and Majewska (2004) found that autoclaving of different strains of fungal biomass tended to minimize differences among them in terms of metal sorbency.

Heat Treatment

Rocha *et al*. (2006) observed that the drying conditions used to prepare algal biomass may impact its sorptive capacity. In general, drying tended to shrink the material and resulted in the closing of pores. Various authors have reported increases in metal sorption capacity in the case of heat-inactivated biomass samples (Kacar *et al*. 2002; Bayramoglu *et al*. 2003; Gurisik *et al*. 2004; Arica *et al*. 2005; Tunali *et al*. 2005).

Drying of biomass also has been reported by many researchers as having a positive effect on metal uptake (Rocha *et al*. 2006), and many of the articles cited in this work specified the use of dried biomass. However, there has been almost no systematic study of this important issue.

Alkaline Treatment

Treatment with alkaline solution has been shown to enhance metal uptake in a few cases (Azab and Peterson 1989; Luef *et al*. 1991; Fourest and Roux 1992; Addour *et al*. 1999; Kapoor *et al*. 1999; Mameri *et al*. 1999; Kumar *et al*. 2000; Reddad *et al*. 2002d; Spanelova *et al*. 2003; Min *et al*. 2004; Tuanli *et al*. 2005; Sciban *et al*. 2006b; Southichak *et al*. 2006a; Afkhami *et al*. 2007; Nasir *et al*. 2007; Gupta and Rastogi 2008b; Argun *et al*. 2009). The mechanism has not been confirmed in detail. It seems likely that saponification of various ester groups may be involved, increasing the number of carboxylate groups on the treated surfaces (Reddad *et al*. 2002e; Xuan *et al*. 2006; Li *et al*. 2007, 2008).

Oxidation

One kind of treatment that has been consistently shown to increase the ability of cellulose-derived substrates to adsorb cationic metal species is oxidation (Maekawa and Koshihima 1984; Jia and Thomas 2000; Rangel-Mendez and Streat 2002; Chen and Zeng 2003; El-Hendawy 2003; Park *et al*. 2003; Park and Kim 2004; Babel and Kurniawan 2004; Saito and Isogai 2005; de Mesquita *et al*. 2006; Kikuchi *et al*. 2006; Argun *et al*. 2008a; Chavez-Guerrero *et al*. 2008; Baccar *et al*. 2009; Berenquer *et al*. 2009; El-Hendawy 2009; Foglarova *et al*. 2009; Han *et al*. 2009; Jamillo *et al*. 2009; Klasson *et al*. 2009; Shukla *et al*. 2009). As already has been noted, oxidation of cellulose-derived material may result in increased numbers of carboxyl groups, which can dissociate to their negatively charged carboxylate form as the pH is increased in a range of 3 to 6.

In contrast to oxidation, chemical reduction may be useful for metal ion uptake, but only in isolated circumstances. Harry *et al*. (2008) observed enhanced adsorption on carbon cloth following electrochemical reduction, especially in the case of Cr(VI). Reduction would be expected to render the biomass-derived surfaces less negative in charge, thus favoring the adsorption of a negative species. Consistent with this finding, Aggarwal *et al*. (1999) found that oxidation of activated carbon samples suppressed the adsorption of the Cr(VI) chromate anion, though it favored the adsorption of the Cr(III) cation. However, other authors observed higher adsorption onto substrates that had been oxidized, even for the adsorption of Cr(VI) (Babel and Kurniawan 2004). Redox interactions during the adsorption of Cr(VI) and certain arsenic and mercury ions will be discussed in a later section.

Polymer Adsorption

Although polymer adsorption can be considered as a gentle treatment in the sense that no covalent reactions need to take place with the substrate, the effects on metal adsorption capacity can be profound. There has been a notable lack of research attention paid to adsorption of carboxyl-containing species onto biosorbents, for purposes of enhancing metal uptake.

Surprisingly, increases in adsorption of metal cations have been observed when using positively charged polyelectrolytes such as polyamines (Deng and Ting 2005b,c). Such systems are especially effective for adsorption of the chromate anion (Deng et al. 2006; Fang et al. 2007). Analogously, a cationic surfactant has been used to enhance the uptake of chromate ions onto fungal biomass (Mungasavalli et al. 2007). Chitosan, a positively charged polymer of natural origin, was likewise found to be effective for adsorption of Cr(VI) (Nomanbhay and Palanisamy 2005). The chitosan was loaded onto a charcoal support in the cited work. Tschabalala et al. (2004) observed, similarly, that a cationized cellulosic support was effective for removing phosphate, a negatively charged material, from aqueous solution. Gérente et al. (2007) have provided context from some of these findings in their review of research related to the use of chitosan for removal of heavy metals from aqueous solution.

Chemical Derivatization

Chemical derivatization of cellulosic material can be defined as the covalent attachment of various functional groups. This approach makes it possible for technologists to select chemical functionalities that may be expected to enhance metal uptake. From a scientific standpoint, derivatization also can be considered as a way to evaluate different hypotheses regarding which chemical groups, some of which may be present naturally, are likely to contribute to observed metal-binding effects.

Carboxylic acid derivatives

Earlier it was noted that carboxylic acid groups contribute directly to the ion exchange capacity of sorbent materials. Accordingly, many authors have reported favorable effects on metal uptake when using biosorbents that have been derivatized to increase their carboxylic acid content. Xie et al. (1996) describe the use of chloroacetic acid for this purpose. Other authors have achieved similar effects by reacting the cellulosic material with succinic anhydride (Marchetti et al. 2000a; Nada and Hassan 2006; Karnitz et al. 2007; Gurgel et al. 2008; Parab et al. 2008; Belhalfaoui et al. 2009; Chandlia et al. 2009; Garg et al. 2009). In general, such approaches have been shown to increase the adsorption capacity of a biosorbent for the target metal(s).

Multifunctonal carboxylic acid derivative

Esterification of a cellulose-based polymer with 1,2,3-propanetricarboxylic acid was found to yield strong binding of a wide range of heavy metals (Sugur and Babaoglu 2005). By such a reaction, there is potential to create adjacent carboxylic acid sites at the sorbent surface. Ideally, if one were to use just the right monomer, there is a theoretical possibility to approach the strong metal binding capabilities of a chelating agent. However, one needs to keep in mind that the most effective chelating agents require three

to six carboxylic acid groups in a specific arrangement that is best suited for coordinating with a given type of metal ion (Lawrance 2010).

Phosphate derivative

Alternatively, it has been shown that a phosphate group can be attached to the surface of activated carbon (Nada *et al.* 2002a; Puziy *et al.* 2002). The product was found to be stable and offering a good ion-exchange capability and ability to bind heavy metal ions.

Sulfur-containing derivatives

When the goal is to adsorb such metals as Hg, Ag, and As, it may make sense to prepare sulfur-containing derivatives. Such an approach has been demonstrated in several cases (Tashihiro and Shimura 1982; Igwe *et al.* 2008). Thus, Aoki *et al.* (1999a) derivatized cellulose with a variety of groups, including isothiouronium and mercapto groups and achieved higher adsorption of Ag(I) and Hg(II). Macias-Garcia *et al.* (2004) and Marshall *et al.* (2007) introduced sulfur groups – presumably sulfonate – by use of SO_2 gas during propration of activated carbon. Kim *et al.* (1999) observed a three-fold increase in the adsorption of lead after derivatizing algal biomass with xanthate groups.

Grafting

The term "grafting" will be used to represent a polymeric or oligomeric group that is attached to the cellulosic surface, usually by a covalent reaction involving the hydroxyl groups. Researchers have demonstrated the potential to create high-performing biosorbents by such treatments (Kubota and Shigehisa 1995; Yu *et al.* 2007), and the field has been reviewed by O'Connell *et al.* (2008). In particular, researchers have attached acrylamide-related chains to cellulosic surfaces (Aoki *et al.* 1996b; Raji and Anirudhan 1998; Bicak *et al.* 1999; Marchetti *et al.* 2000b; Shibi and Anirudhan 2002, 2005, 2006; Guclu *et al.* 2003; Choi *et al.* 2004; Unnithan *et al.* 2004; Chauhan *et al.* 2005a,b, 2006; Deng and Ting 2005a; Hashem 2006; Hashem *et al.* 2006a; Nada and El-Wakil 2006; Nada et al. 2007a; Sharma and Chauhan 2009; Sokker *et al.* 2009). The major increases in metal-binding capability that have been observed by many of these authors are consistent with the chelating effects that can be achieved by multifunctional carboxylic acids, as in the case of substrates that have been grafted with acrylic acid chains. In principle, grafting technologies enable the technologist to attach a wide range of highly specific functional groups to the substrate surface. As such, the approach can be compared to the use of the underlying biomaterial as a kind of support, rather than necessarily being a significant individual contributor to metal uptake.

Pyrolizing to Produce Activated Carbon Products

Very strong heating in the relative absence of oxygen is known to convert cellulosic materials into carbon. Careful control of the pyrolysis conditions, including the temperature and the composition of the surrounding gases, make it possible to achieve a very high accessible surface area per unit mass, in addition to providing significant control regarding the chemical sites at the carbon surface (Dias *et al.* 2007; Chen *et al.* 2008). For instance, the pore structure often can be enhanced by the use of steam during

preparation of the activated carbon (Budinova *et al*. 2006). Many authors have demonstrated the potential to remove metal ions from aqueous systems by the use of such products, and these are listed in the appropriate section of Table A. Because of the generally hydrophobic nature of many activated carbon products, some authors regard such products as being especially suitable for removal of organic pollutants from aqueous systems, whereas removal of metal ions might be considered as a secondary benefit (O'Connell *et al*. 2008).

Numerous strategies have been used to render activated carbon products more effective in the uptake of one or more kinds of metal ions, and these are likewise indicated in Table A (see the "Activated Carbon" section indicated in the first column, near to the back of the table, and see the "Modifications" as indicated in the second column). Many of these treatments have already been discussed in preceding paragraphs. In general, these modifications can be achieved by the following strategies: First, the gaseous conditions can be adjusted, *e.g.* by the addition of steam, controlled amounts of oxygen, and by controlling the temperature, *etc*. Second, the mixture fed into the pyrolysis operation can be treated, for instance, with such materials as phosphoric acid to achieve a higher proportion of carboxylic acid groups or phosphorous-containing groups on the resulting carbon surface. Finally, the resulting powder can be post-treated, *e.g.* with nitric acid, to oxidize the surface, thus increasing the number of carboxyl groups (see, *e.g.* Lyubchik *et al*. 2004).

Ash

Ash often is available as an under-utilized waste product of the combustion of lignocellulosic materials. Though the properties of the ash itself are seldom a prime consideration in its genesis, it still makes sense to consider its possible beneficial applications. Chonjacka and Michalak (2009) found, for instance, that ash from wood was three times as effective for the removal of metal ions, compared to bone ash. Other studies that have considered the use of ash for metal removal can be cited (Rao *et al*. 2002; Banarjee *et al*. 2004; Chaves *et al*. 2009; Chu and Hashim 2002; Gupta *et al*. 1998, 1999, 2003; Gupta and Ali 2000, 2004; Pehlivan et al. 2006; Srivastava *et al*. 2006a,b,c, 2007, 2008a, 2009a,b).

MECHANISMS OF INTERACTIONS WITH METAL SPECIES

Ion-Exchange

"Ion exchange" refers to a class of mechanisms in which adsorbing metal ions take the place of other species already associated with the sorbent surface. For instance, these entitities may be metal ions such as Na^+, Ca^{2+}, or the proton, *etc*. Let's suppose that a given biosorbent material has been prepared by equilibration in either NaOH solution or NaCl brine. In such cases, its reasonable to expect that acidic sites on the substrate will be mainly associated with Na ions. If the Cu^{2+} ion, for instance, is then introduced to the system, it may have a higher affinity for acidic sites in comparison to a monovalent cation. The resulting competition will lead to a net desorption of Na^+ from surface sites and a net uptake of Cu^{2+}.

Recent studies reviewed by Sag (2001) with fungal biomass in general and seaweed in particular have indicated a dominant role of ion exchange in metal binding. The classical ion-exchange concept, based on exchange-equilibrium constants and separation factors, can be applied. For a generalized ion-exchange reaction for dissolved species A being exchanged for a bound species B, with the underlined character representing the bound species,

$$bA^{a+} + a\underline{B}^{b+} \leftrightarrow b\underline{A}^{a+} + aB^{b+}$$ (1)

where the equilibrium constant K_{AB} and the separation factor γ_{AB} are given as follows, for the case of ideal behaviour of the exchanging species (1:1 ion exchange, activity = 1) in both of the phases:

$$K_{AB} = \frac{q_A^b C_{Bf}^a}{C_{Af}^b q_B^a} = \left(\frac{y_A^b x_B^a}{x_A^b y_B^a}\right)\frac{C_o^{b-a}}{Q^{a-b}}$$ (2)

$$\gamma_{AB} = \frac{y_A x_B}{x_A y_B}$$ (3)

For a binary ion-exchange system, the value of the equilibrium constant K_{AB} can be determined from the slope of the plot of q_A/q_B versus C_A/C_B. Biosorbents can also be prepared in different ionic forms, and the sorption analysis is often reduced to considering a series of simple binary ion-exchange systems. By eliminating q_B through substitutions, the following expression is obtained:

$$\frac{q_A}{Q} = \frac{1}{1 + \dfrac{C_B}{K_{AB}C_A}}$$ (4)

As q_A / Q represents the fraction of the binding sites occupied by A, this equation may be used to evaluate the decrease of the equilibrium uptake of the species A by the biosorbent caused by the presence of species B. Using simple dimensionless concentration fractions as variables, Eq. (4) can be re-written as follows:

$$y_A = \frac{1}{1 + \dfrac{x_B}{K_{AB}x_A}}$$ (5)

This equation is the most generalized description of the ion-exchange sorption equilibrium for binary systems (Kratochvil and Volesky 1998). Modeling multi-metal ion exchange in biosorption has been applied to the brown alga *Sargassum fluitans*, which contains the carboxyl groups of alginate and the sulfate groups of fucoidan. An ion-exchange-based two-site model has been developed (Schiewer and Volesky 1995) and

extended to describe multi-site and multi-ion system behavior (Schiewer and Volesky 1996).

Substantial published evidence supports the validity of the concept as just described, when it is applied to cellulosic-derived substrates. Desorption of displaced ionic species has been demonstrated during the uptake of a charge-equivalent amount of the heavy metal of interest. For instance calcium or magnesium ions may be released, depending on how the sorbent material has been prepared (Akthar *et al*. 1995; Diniz and Volesky 2005).

As an example, alkali-treated *A. niger* biomass was used to sequester silver ions from dilute as well as concentrated solutions (Akthar *et al*. 1995). The bound Ag^+ was fully desorbed by dilute HNO_3, and the biosorbent was regenerated by washing with Ca^{2+}/Mg^{2+} solution. The binding of Ag^+ was attended by a stoichiometric release of Ca^{2+} and Mg^{2+} ions together (the sum of the two released being equal to Ag^+ bound in molar terms, as expected on the basis of the univalency of the Ag^+ ion). This equivalence established the mechanism of Ag^+ sorption as being quantitatively due to exchange with ($Ca^{2+} + Mg^{2+}$) ions of the biosorbent.

Biosorption of the lanthanides, lanthanum (La^{3+}), europium (Eu^{3+}), and ytterbium (Yb^{3+}) from single component and multi-component batch systems using *Sargassum polycystum* Ca-loaded biomass was studied (Diniz and Volesky 2005). The ion exchange sorption mechanism was confirmed by the release of calcium ions from the biomass that matched the total number of metal and protons removed from the solution.

In other cases, the adsorption of metal ions is accompanied by dissociation of a stoichiometrically equivalent amount of protons. Metal (Pb, Cu, Zn, Cd, Ca) uptake by kraft lignin was also found to occur by displacement of protons or bound metals (Crist *et al*. 2002), as shown by the following equations, where *X* stands for a mono-valant bonding site on the substrate. Square brackets indicate concentrations in solution, while terms in parentheses represent the sorbate on the sorbent after ion exchange.

$$M^{2+} + \left(CaX_2\right) \leftrightarrow \left(MX_2\right) + Ca^{2+} \tag{6}$$

$$K_{ex} = [Ca^{2+}]\left(MX_2\right)/[M^{2+}]\left(CaX_2\right) \tag{7}$$

$$M^{2+} + 2\left(HX\right) \leftrightarrow \left(MX_2\right) + 2H^+ \tag{8}$$

$$K_{ex}^{H} = \left[H^+\right]^2\left(MX_2\right)/\left[M^{2+}\right]\left(HX\right)^2 \tag{9}$$

Crist *et al*. (2003) also conducted a detailed study with a kraft pine lignin powder. This material has acid functions that can act as ion exchange sites, which showed that uptake of divalent toxic metals was accompanied by a release of protons or existing metals from the lignin. A demonstrated stoichiometry of one mole Ca displaced for one mole of metal (Sr or Cd) sorbed was fully consistent with a chemical reaction of ion exchange and difficult to explain by frequently used adsorption models.

Adsorption of Hg(II), Cr(III), Cu(II), Cd(II), Ni(II), Ca(II), Sr(II), Zn(II), Co(II), Mn(II), Mg(II), K(I), and Na(I) by activated carbon made from pecan shells (Dastgheib and Rockstraw 2002a), showed that the Slips and Freundlich equations (see later) were satisfactory for explaining the experimental data. The ratio of equivalent metal ions adsorbed to protons released was calculated for the studied metal ions over a range of concentrations. In most cases, particularly at low concentrations, this ratio approached one, confirming that ion exchange of one proton with one equivalent metal ion was the dominant reaction mechanism.

Other studies have shown correlations between the number of weak-acid sites on the substrate in comparison to the amount of metal ions that can be adsorbed. The concept of ion exchange is also supported by the fact that a sufficiently high concentration of salt, acid, or base can cause a reversal of the process; this type of phenomenon will be discussed later in this article with respect to the regeneration of sorptive materials that have been used at least once in the sorption of heavy metals.

Figure 3 contrasts the ion exchange concept, as just described, with a site-specific concept. Ion exchange is mainly concerned with the stoichiometry of displacement of bound ions by dissolved ions, as displayed in the left-hand frame of the figure. For instance, adsorption of a trivalent metal ion is shown to occur from the displacement of three mono-valent species. By contrast, a complexation model (see later discussion) focuses on the underlying interactions of ions with surface sites. Thus, the right frame of Fig. 1 envisions the adsorption of a hydrated divalent ion, the simultaneous release of some of the waters of hydration, and the formation of a bi-dentate complex having moderate stability. Concepts related to such complexation are considered near the end of this article.
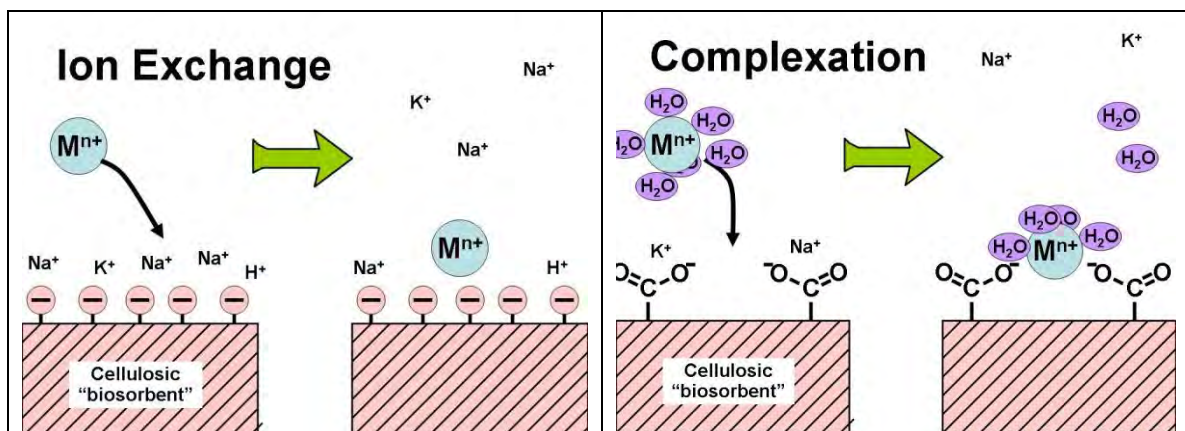

Fig. 3. Pictorial comparison of ion exchange concept (left frame) *vs.* metal adsorption involving chemical complexation (right frame)

To further understand implications of the foregoing observations, the next sections deal with mathematical, as well as theoretical fits between adsorption character-istics and solution concentrations, *i.e.* sorption isotherms.

SORPTION ISOTHERMS

When any sorption system reaches a state of equilibrium, there is a defined distribution of sorbate molecules at the solid-liquid interface and also in the bulk at a particular temperature. This provides an idea of the capacity of the sorbent for the sorbate. The maximum possible accumulation of the sorbate at the solid surface is a function of its concentration at a constant temperature, and it can be expressed by the following generalized relationship,

$$q_e = \mathrm{f}(C_e) \tag{10}$$

where q_e is the amount of sorbate sorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the sorbate (mg/L), and "f" can be equated to the phrase "is a function of". This type of relation is termed a 'sorption isotherm', which represents equilibrium between the concentration of a solute in solution and its concentration on the sorbent, at a given temperature. For assessing the maximum sorption capacity of a given biosorbent, the derivation of sorption isotherms is the most appropriate method. Further, the study of sorption isotherms is useful not only to evaluate to what extent a sorption system can be improved, but also to help predict conditions for working in open reactors and estimate optimal operating conditions.

The mathematical modeling of sorption is a very powerful tool for understanding the sorption process and essential for process design and optimization (Esposito *et al.* 2002). Several equilibrium-based models have been used to describe the metal transfer between the solution and solid phase during the sorption process (Vijayaraghavan *et al.* 2006a).

Langmuir Sorption Isotherm

The Langmuir model, which is one of the most widely used (see Table A), was initially proposed for the adsorption of a gas on the surface of a solid. Nevertheless, it has been extended to include the sorption of solute at a solid–liquid interface. The Langmuir model suggests that the sorption occurs on the surface of the solid that is made up of elementary sites, each of which can adsorb one sorbate molecule, *i.e.* monolayer sorption. It was also assumed that every sorption site is equivalent and the ability of sorbate to get bound there is independent of whether or not the neighbouring sites are occupied (Langmuir 1918).

The Langmuir model is given as follows (Langmuir 1918):

$$q_e = \frac{Q^o b C_e}{1 + b C_e} \tag{11}$$

Equation (11) can be linearized as follows:

$$C_e / q_e = 1 / Q^o b + C_e / Q^o \tag{12}$$

where q_e (mg/g) and C_e (mg/L) are the sorbed metal ions on the sorbent and the metal ion

concentration in the solution at equilibrium, respectively, b (L/mg) is the constant related to the affinity of binding sites, *i.e.* the affinity of sorbent for the sorbed species. Q^o (mg/g) is known as the Langmuir constant, which represents the monolayer sorption capacity, *i.e.* a practical limiting sorption capacity when the surface is fully covered with metal ions. Q^o assists in the comparison of sorption performances. In general, for good sorbents, high values of Q^o and low values of b are required (Kratochvil and Volesky 1998). Equation 11 also can be linearized to other forms. The final linearized form will be a function of the data distribution.

The affinity between adsorbate and adsorbent can be predicted using the Langmuir parameter b from the dimensionless separation factor R_L,

$$R_L = 1/(1 + bC_o) \tag{13}$$

where C_o is the initial metal ion concentration and b is the Langmuir isotherm constant. The adsorption process as a function of R_L may be described as follows: When R_L is greater than one, then the sorption reaction is unfavourable, and it is linear when R_L is equal to one. When R_L is between zero and one, the reaction is favourable, while the reaction is supposed to be irreversible when R_L is equal to zero. This can be summarized as follows:

$R_L > 1$ unfavorable
$R_L = 1$ linear
$0 < R_L < 1$ favorable
$R_L = 0$ irreversible

Freundlich Sorption Isotherm

The Freundlich isotherm model, which is also very widely used, describes the sorption of solute from liquid to solid surface and assumes that the stronger binding sites are occupied first and that the binding strength decreases with an increasing degree of site occupation. The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, and/or interactions between sorbed species, *i.e.* multilayer sorption (Freundlich 1907).

The Freundlich model can expressed by the following empirical equation:

$$q_e = K_F C_e^n \tag{14}$$

Equation (14) can be expressed in logarithmic terms to obtain the following form,

$$\log q_e = \log K_F + n \log C_e \tag{15}$$

where K_F (mg^{1-n}/g L^n) and n (dimensionless) represent the Freundlich constants characteristic of the system. K_F is indicative of the relative sorption capacity, whereas n is the measure of the nature and strength of the sorption process and the distribution of active sites. If $(n) < 1$, then the bond energies increase with the surface density. If $(n) > 1$, the bond energies decreases with the surface density. When $n = 1$, all surface sites are equivalent. Alternatively, it has been shown using mathematical calculation that n values

between 1 and 10 represent beneficial sorption. These parameters are empirical constants, and they depend on several factors (Bajpai *et al.* 2004; Febrianto *et al.* 2009).

Dubinin-Radushkevich (D-R) Sorption Isotherm

The Dubinin–Radushkevich isotherm model (Dubinin and Radushkevich 1947) is postulated within a sorption space close to the sorbent surface to evaluate the sorption free energy and to help determine the nature of bonding, *i.e.* either physisorption or chemisorption.

The D–R isotherm can be presented as follows,

$$\ln q_m = \ln X_m - K_{DR}F^2 \qquad (16)$$

where q_m is the amount of sorbate sorbed (mmol/g), X_m is the maximum sorption capacity of the sorbate retained (mmol/g), K_{DR} is the activity coefficient constant related to the sorption free energy of the transfer of the solute from the bulk solution to the solid sorbent ($mol^2 kJ^2$), and F is the Polanyi potential, which is given by the equation,

$$F = RT \ln(1 + \frac{1}{C_e}) \qquad (17)$$

where R is the universal gas constant (0.0834 kJ/mol/K) and T is the absolute temperature in Kelvin. C_e was defined earlier.

Assuming that the surface of the sorbent is heterogeneous and when choosing an approximation to a Langmuir isotherm model as a local isotherm for all sites that are energetically equivalent, the quantity K_{DR}, which is related to the mean free energy (E) of the transfer of 1 mol of solute from infinity to the surface of the sorbent, can be expressed by the equation:

$$E = \frac{1}{\sqrt{-2K_{DR}}} \qquad (18)$$

If the magnitude of E is between 8 and 16 kJ/mol, then the sorption process is supposed to proceed via chemisorption, while for values of $E < 8$ kJ/mol, the sorption process is of physical nature (Basar 2006; Hasany and Chaudhary 2001; Saeed *et al.* 1996; Tunali *et al.* 2006; Vijayaraghavan *et al.* 2006a).

Temkin Isotherm

The Temkin isotherm equation (Temkin and Pyzhev 1940) contains a factor that explicitly takes into account adsorbing species–adsorbate interactions. It assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate repulsions and that adsorption involves a uniform distribution of maximum binding energy. In addition, it assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been written in the following form,

$$q = \frac{RT}{b_{Te}} \ln(a_{Te} C_e) \qquad (19)$$

Equation 19 can also be represented as follows:

$$q = \frac{RT}{b_{Te}} \ln a_{Te} + \frac{RT}{b_{Te}} \ln C_e \qquad (20)$$

where, T is the absolute temperature in Kelvin, and R is the universal gas constant, 8.314 J/mol/K. The constant b_{Te} is related to the heat of adsorption (J/mol), and a_{Te} is the equilibrium binding constant (L/g) corresponding to the maximum binding energy.

Flory-Huggins Isotherm

Another two-parameter isotherm is the Flory-Huggins model, which can be represented as follows (Padmesh *et al.* 2006):

$$\log \frac{\theta}{C_o} = \log K_{FH} + n_{FH} \log(1 - \theta) \qquad (21)$$

The equilibrium constant, K_{FH} has been used to compute the Gibbs free energy (ΔG):

$$\Delta G = -RT \ln K_{FH} \qquad (22)$$

where $\theta = (1 - C_f/C_o)$ is the degree of surface coverage, K_{FH} is the Flory-Huggins equilibrium constant, and n_{FH} is the Flory-Huggins exponent.

Redlich–Peterson Isotherm

The R–P isotherm can be described as follows (Padmesh *et al.* 2006),

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta}} \qquad (23)$$

where K_{RP} is a first R–P isotherm constant (l/g), a_{RP} is a second R–P isotherm constant (L/mg), β is an exponent, the value of which lies between 0 and 1, and C_e is the equilibrium liquid phase concentration (mg/L).

If $\beta = 1$, then the Langmuir will be the preferable isotherm, while if $\beta = 0$, the Freundlich isotherm will be preferred. Although the two parameters in the Langmuir and Freundlich equations can be graphically determined, Redlich–Peterson constants are not computed by graphing, because there are three unknown parameters. However, the values of the three parameters in the equation can be obtained using non-linear regression analysis.

Toth Isotherm

The Toth isotherm is derived from the potential theory, and it is applicable for heterogeneous adsorption (Toth 1971). This model assumes a quasi-Gaussian energy distribution, where most sites have adsorption energies lower than the peak or maximum adsorption energy. The Toth isotherm is represented as follows (Padmesh *et al.* 2006),

$$q = \frac{q_{max} b_T C_f}{[1 + (b_T C_f)^{1/nT}]^{nT}} \tag{24}$$

where q_{max} is the maximum dye sorption (mg dye/g biomass), b_T is the Toth model constant, and n_T is the Toth model exponent.

Determining Isotherm Parameters

By linearization

The simplest approach to determining isotherm constants for two-parameter isotherms is to transform the isotherm variables so that the equation is converted to a linear form and then to apply linear regression (Ho *et al.* 2002). Although a linear analysis is not possible for a three-parameter isotherm, a trial and error procedure has previously been applied to a pseudo-linear form of the Redlich-Peterson isotherm to obtain values for the isotherm constants (McKay *et al.* 1984), and this involves varying the isotherm parameter, K_{RP}, to obtain the maximum value of the correlation coefficient for the regression.

By non-linear regression

Due to the inherent bias resulting from linearization, alternative isotherm parameter sets can be determined by non-linear regression (Ho *et al.* 2002). This provides a mathematically rigorous method for determining isotherm parameters using the original form of the isotherm equation (Seidel and Gelbin 1988; Seidel-Morgenstern and Guiochon 1993; Malek and Farooq 1996; Khan *et al.* 1996). Most commonly, algorithms based on the Levenberg-Marquardt or Gauss-Newton methods (Edgar and Himmelblau 1989; Hanna and Sandall 1995) are used.

The optimization procedure requires the selection of an error function in order to evaluate the fit of the isotherm to the experimental equilibrium data. The choice of error function can affect the parameters derived. Error functions based primarily on absolute deviation bias the fit towards high concentration data, and this weighting increases when the square of the deviation is used to penalize extreme errors.

This bias can be offset partly by dividing the deviation by the measured value in order to emphasize the significance of fractional deviations. In the cited study (Ho *et al.* 2002), five non-linear error functions were examined and in each case a set of isotherm parameters were determined by minimizing the respective error function across the concentration range studied. The error functions employed were as follows:

1. The Sum of the Squares of the Errors (ERRSQ):

$$\sum_{i=1}^{P} (q_{e,meas} - q_{ecalc})^2_i \tag{25}$$

2. A Composite Fractional Error Function (HYBRD):

$$\sum_{i=1}^{P} \left[\frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \right]_i \tag{26}$$

3. A Derivative of Marquardt's Percent Standard Deviation (MPSD):

$$\sum_{i=1}^{P} \left(\frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right)^2_i \tag{27}$$

4. The Average Relative Error (ARE):

$$\sum_{i=1}^{P} \left| \frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right|_i \tag{28}$$

5. The Sum of the Absolute Errors (EABS):

$$\sum_{i=1}^{P} \left| q_{e,meas} - q_{e,calc} \right|_i \tag{29}$$

As each of the error criteria is likely to produce a different set of isotherm parameters, an overall optimum parameter set is difficult to identify directly. Hence, in order to try to make a meaningful comparison between the parameter sets, a procedure of normalizing and combining the error results was adopted, producing a so-called 'sum of the normalized errors' for each parameter set for each isotherm.

The calculation method for the 'sum of the normalized errors' was as follows:

(a) select one isotherm and one error function and determine the isotherm parameters that minimize that error function for that isotherm to produce the isotherm parameter set for that error function;

(b) determine the values for all the other error functions for that isotherm parameter set;

(c) calculate all other parameter sets and all their associated error function values for that isotherm;

(d) select each error measure in turn and ratio the value of that error measure for a given parameter set to the largest value of that error from all the parameter sets for that isotherm; and

(e) sum all these normalised errors for each parameter set.

The parameter set thus providing the smallest normalised error sum can be considered to be optimal for that isotherm, provided that:

- There is no bias in the data sampling – *i.e.* the experimental data are evenly distributed, providing an approximately equal number of points in each concentration range; and
- There is no bias in the type of error methods selected.

APPLYING ISOTHERM EQUATIONS TO METAL SORPTION DATA

The following subsections describe a number of cases in which authors have provided justification for different types of isotherm models for the analysis of metal sorption onto cellulosic materials under different experimental conditions.

Langmuir Isotherm

As has been noted, the use of the Langmuir adsorption isotherm implies an assumption of uniform, non-interacting adsorption sites. When one considers the impure nature of typical biomass-derived sorbents, it is remarkable how large a proportion of the publications considered in this review reported that good fits were achieved by means of the Langmuir equation (see Table A). Possible ways to explain the goodness of fit, in so many of the listed cases, are as follows:

- Many studies tend to be dominated by effects due to one kind of chemical group, *e.g.* a certain kind of carboxylate group present on that type of modified biomass.
- In addition, it is likely that in many cases the adsorption experiments were performed at sufficiently high ionic strength such that the adsorption of a metal ion at one site did not have an appreciable influence on the adsorption of the next metal ion at an adjacent site. The likely range of influence can be roughly estimated based on the Debye-Hückel reciprocal length parameter (Hiemenz and Rajagopalan 1997).

Multifunctional Langmuir Adsorption Models

Aksu *et al*. (1997, 1999) studied adsorption onto *Chlorella vulgaris* for Fe(III), Cr(VI) and Cu(II) as single-component systems, as well as Fe(III)–Cr(VI) and Cu(II)–Cr(VI) binaries. They concluded that single-component isotherms could be modeled by either the Freundlich or Langmuir isotherms. The binary Freundlich equation proposed by Fritz and Schlünder was appropriate for fitting the data of both binary systems, while the extended Langmuir equation was used successfully for only the Fe(III)–Cr(VI) system.

The simultaneous biosorption of copper(II) and chromium(VI) to *C. vulgaris* from binary metal mixtures was investigated by Aksu *et al*. (1999) in a single-staged batch reactor as a function of V_o/X_o ratio (volume of wastewater containing heavy metal mixture/quantity of biosorbent) at different orders of second metal ion addition and at pH values of 2.0 and 4.0 chosen as the optimum biosorption pH values for chromium(VI) and copper(II), respectively. The sorption phenomenon was expressed by a competitive, multi-component Freundlich adsorption isotherm, which was then used for calculating each residual or adsorbed metal ion concentration at equilibrium ($C_{eq,i}$ or $C_{ad,eq,i}$) at a constant V_o/X_o ratio for a given combination of heavy metals in a single-staged batch reactor. In the cited study, the non-competitive Freundlich isotherm model (Eq. 14) was used for describing the short-term and mono-component adsorption of heavy metal ions by algal cells. However, for binary mixtures, an empirical extension of the Freundlich model has been proposed where the coefficients relating to isotherms could be determined from mono-component isotherm data, except for the biosorption competition coefficients, which had to be determined experimentally. The Freundlich models for the

first and the second components restricted to binary mixtures are given by Eqs. (30) and (31),

$$q_{eqI} = \frac{K_{FI} C_{eqI}^{nI+xI}}{C_{eqI}^{nI} + y_I C_{eqII}^{zI}} \tag{30}$$

$$q_{eqII} = \frac{K_{FII} C_{eqII}^{nII+xII}}{C_{eqII}^{nII} + y_{II} C_{eqI}^{zII}} \tag{31}$$

where K_{FI}, K_{FII}, n_I, and n_{II} are derived from the corresponding individual Freundlich isotherm equations and the six other parameters (noting that xI, yI, zI, xII, yII, and zII are the competitive Freundlich adsorption constants of the first and second metal ions, respectively, for the binary system) are the competition coefficients for two metal ion species.

The biosorption of heavy metal ion mixtures by the biomass in a batch reactor can be considered as a single-staged equilibrium operation. Consideration of the single-stage equilibrium operation would depend on two basic constraints, that of equilibrium (shown in Eqs. (30) and (31)) and that of a mass balance. The mass balance for the first component in the mixture is given by,

$$V_0 C_{0I} + X_0 q_{0I} = V_0 C_{eqI} + X_0 C_{eqI} \tag{32}$$

$$V_0 (C_{0I} - C_{eqI}) = X_0 q_{0I} + X_0 q_{eqI} \tag{33}$$

$$-\frac{V_0}{X_0}(C_{eqI} - C_{0I} = (q_{eqI} - q_{0I}) \tag{34}$$

where C_{0I} is the initial concentration of the first component (mg L^{-1}); C_{eqI} is the residual concentration of the first component at equilibrium (mg L^{-1}); q_{0I} is the amount of the first component adsorbed per unit weight of algae at the beginning (mg g^{-1}); q_{eqI} is the amount of the first component adsorbed per unit weight of algae at equilibrium (mg g^{-1}); V_0 is the volume of solution containing heavy metal ion mixture in the batch reactor (l); and X_0 is the amount of biosorbent in the batch reactor (g)

Equation (34) belongs to a straight line for the first metal ion, and the line passes through points (C_{0I}; q_{0I}) and (C_{eqI}; q_{eqI}) with ($-V_0$:X_0) slope. This is the operating line for this stage at a known concentration of the second metal ion. As q_{eqI} and C_{eqI} values are known from experimental data for the first metal ion in the mixture, the single-staged batch operation can be shown in a figure on the same coordinates by drawing the operation line and equilibrium curve for the first metal ion at a known combination and pH value. V_0:X_0 for a desired purification or C_{eqI} and q_{eqI} values at a given V_0:X_0 and a second metal ion concentration can be determined. The initial metal ion concentration of the first metal ion must be equal to,

$$C_{0I} = C_{eqI} + C_{ad,eqI} \tag{35}$$

where $C_{ad,eqI}$ is the adsorbed concentration of the first component at equilibrium (mg L^{-1}). The value of $C_{ad,eqI}$ can be calculated easily from Eq. (35). If a calculation is required, then Eq. (34) can be rearranged as:

$$-\frac{V_0}{X_0}(C_{eqI} - C_{0I}) = \frac{K_{FI}C_{eqI}^{nI+xI}}{C_{eqII}^{xI}} - q_{0I} \tag{36}$$

The amount of the first metal adsorbed per unit weight of biomass at the beginning of the biosorption (q_{0I}) is equal to 0.0, so Eq. (36) can be rewritten:

$$-\frac{V_0}{X_0} = \frac{K_{FI}C_{eqI}^{nI+xI}}{(C_{eqI} - C_{0I})(C_{eqI}^{xI} + y_I C_{eqII}^{zI})} \tag{37}$$

As K_{FI}, n_I, K_{FII}, and n_{II} can be found from experimental data, Eq. (37) also provides the $V_0{:}X_0$ ratio for desired purification or C_{eqI} and C_{eqII} (or indirectly $C_{ad,eqI}$ and $C_{ad,eqII}$) at a given $V_0{:}X_0$ ratio for a given heavy metal mixture at a known combination. Equation (37) can also be rewritten for the second metal ion in the same manner.

Thus the copper(II)-chromium(VI) multi-ion system was defined with the multi-component Freundlich adsorption isotherm and used to model the adsorption of a binary system to *C. vulgaris* in a single-staged batch reactor as a function of $V_0{:}X_0$ ratio and second metal ion concentration at pH 2.0 and 4.0. The pH of the biosorption medium, the order of addition of the metal ions, and the amount of biosorbent ($V_0{:}X_0$ ratio) strongly affected the equilibrium uptake of the first metal ion by the algae. The individual Freundlich constants evaluated from the non-competitive isotherms were used to find the competitive Freundlich constants in a competitive Freundlich model describing multicomponent adsorption equilibrium. These constants were used in Eq. (37) to calculate the residual concentration of the first metal ion at a known second metal ion concentration and the $V_0{:}X_0$ ratio in a single-staged equilibrium operation.

The equilibrium isotherms for the first metal ion at the known second metal ion concentrations with the operation line with $V_0{:}X_0$ slope were also developed to predict the residual concentrations of the first metal ion. It was considered that these two methods may be used successfully to estimate the residual concentrations of the first and second metal ions in a mixture at equilibrium. *C. vulgaris* biomass offers a practical approach for removing mixtures of copper(II) and chromium(VI) ions from waste waters containing mainly these two components. Using low $V_0{:}X_0$ ratios, high purification yields can be obtained for the first metal ion at its optimum pH value and at low second metal ion concentrations or for desired purifications of the first metal ion, $V_0{:}X_0$ ratios, pH, and second metal ion concentrations. Parameters can be chosen according to Eq. (37) by using individual and competitive Freundlich constants in a single-staged batch reactor up to 150 mg/L initial metal ion concentration for each metal ion. Multi-staged reactors can

also be designed and operated by estimating a sufficient amount of algae for a known volume of waste water (choosing V_0:X_0) with a known heavy metal ions combination, especially if required purification cannot be provided in a one-staged reactor when studying higher metal ion concentrations.

In the work of Leyva *et al*. (2001), single and simultaneous Cd(II) and Zn(II) adsorption isotherms from aqueous solution onto activated carbon were determined experimentally. Single isotherms for these ions were fitted to Langmuir isotherms, while the simultaneous adsorption isotherms was fitted to the bisolute Langmuir isotherm modified with an interaction factor. Experimental data for single adsorption isotherms for Zn(II) and Cd(II) onto C (carbon) were fitted to the Langmuir isotherm (Eq. 11).

The constants for this isotherm were obtained by a least-squares method based on the optimization algorithm of Rosenbrock-Newton. The average percent deviation was calculated, and a reasonable fit to the experimental data was obtained based on application of the Langmuir isotherm. The Freundlich isotherm (Eq. 15) was also tested, but produced a weaker goodness of fit compared to the Langmuir isotherm. The maximum molar uptake of Zn(II) averaged 1.6 times that of Cd(II). This result was explained by the author as probably being related to the electrostatic attraction between the very heterogeneous surface of the activated carbon and the metal ions in solution. Another possible explanation for the relatively high Zn(II) selectivity was related to the ability of both Cd(II) and Zn(II) to be adsorbed at one class of surface sites, while Zn(II) was exclusively adsorbed on other class of surface sites. Thus the single adsorption isotherm of Zn(II) can be represented by a dual-site Langmuir isotherm, known as the bi-Langmuir isotherm. However, a Scatchard plot (*q/C vs. q*, presented in the paper) of the single solute adsorption data of Zn(II) did not suggest that Zn(II) was adsorbed on two kinds of sites. Thus, it was said that the single-site Langmuir isotherm was appropriate to represent the single adsorption of both metal ions (Leyva *et al*. 2001).

The simultaneous adsorption of Cd(II) and Zn(II) was also studied, as these ions usually occur together in industrial wastewaters. In multicomponent systems, the adsorption isotherm of a certain solute also depends on the concentration and characteristics of the other solutes in the aqueous solution. The solute of interest may be in competition with other solutes for the same active adsorption sites. The experimental data for simultaneous Cd(II) and Zn(II) adsorption were interpreted with the bisolute Langmuir isotherm. The competitive Langmuir isotherms for Cd(II) and Zn(II) are represented as follows:

$$q_{Cd} = \frac{q_{m,Cd} K_{Cd} C_{Cd}}{1 + K_{Cd} C_{Cd} + K_{Zn} C_{Zn}} \tag{38}$$

$$q_{Zn} = \frac{q_{m,Zn} K_{Zn} C_{Zn}}{1 + K_{Cd} C_{Cd} + K_{Zn} C_{Zn}} \tag{39}$$

The constants of these two isotherms are from the single-solute Langmuir isotherms. The experimental molar uptake values of Cd(II) and Zn(II) were compared to the molar uptake values of Cd(II) and Zn(II) predicted with the bisolute Langmuir

isotherm, and it was found that the bisolute Langmuir isotherm overestimated the molar uptake of Zn(II) with an average percent deviation of 94.0%. However, it underestimated the molar uptake of Cd(II), and the average percent deviation was 33.36%. Thus, the binary adsorption data were not properly described with the bisolute Langmuir isotherm. The literature reports that the bisolute Langmuir model provides a reasonable fit to the multicomponent adsorption data when the $q_{m,i}$ values for each metal evaluated from single-solute Langmuir isotherm are similar to each other. As previously noted in this study, $q_{m,Zn}$ is approximately 1.6 times greater than $q_{m,Cd}$. Jain and Snoeyink (1973) assumed that some adsorption occurs without competition, because not all sites were available to all solutes. Consequently, the bisolute Langmuir isotherm was modified for systems in which the $q_{m,i}$ values of components were different, proposing the following isotherm for the solute with the higher $q_{m,i}$, which in the cited study was Zn(II):

$$q_{Zn} = \frac{(q_{m,Zn} - q_{m,Cd})K_{Zn}C_{Zn}}{1 + K_{Zn}C_{Zn}} + \frac{q_{m,Cd}K_{Zn}C_{Zn}}{1 + K_{Cd}C_{Cd} + K_{Zn}C_{Zn}} \tag{40}$$

The isotherm for the solute with the lower $q_{m,i}$ is the same as that represented in Eq. (38), and the constants are from the single-solute Langmuir isotherms. In Eq. (40), the difference between the maximum molar uptakes is the number of sites with noncompetitive adsorption. The modified bisolute Langmuir model was applied to the experimental data for simultaneous Cd(II) and Zn(II) adsorption and it overpredicted the molar uptake of Zn(II), with an average deviation of 112.7%. Thus the modified bisolute Langmuir isotherm failed to predict the molar uptake of Zn(II), and its prediction had a higher average percent deviation than that obtained with the bisolute Langmuir isotherm.

Ho and McKay (1999b) modified the bisolute Langmuir isotherm with an interaction factor, η, and obtained an excellent fit of the adsorption data of Cu(II) and Ni(II) onto peat. The model proposed by these authors can be represented as follows,

$$q_{Cd} = \frac{q_{m,Cd}K_{Cd}\left(\dfrac{C_{Cd}}{\eta_{Cd,Cd}}\right)}{1 + K_{Cd}\left(\dfrac{C_{Cd}}{\eta_{Cd,Cd}}\right) + K_{Zn}\left(\dfrac{C_{Zn}}{\eta_{Zn,Cd}}\right)} \tag{41}$$

$$q_{Zn} = \frac{q_{m,Zn}K_{Zn}\left(\dfrac{C_{Zn}}{\eta_{Zn,Zn}}\right)}{1 + K_{Cd}\left(\dfrac{C_{Cd}}{\eta_{Cd,Zn}}\right) + K_{Zn}\left(\dfrac{C_{Zn}}{\eta_{Zn,Zn}}\right)} \tag{42}$$

where $\eta_{i,j}$ is the interaction factor of metal i for the adsorption of metal j. This interaction factor is specific to each metal ion in a given system and depends upon the other metal ions present. In the cited study, the best interaction factor was obtained by fitting the

isotherm models to the experimental data with a least-squares method that employs an optimization algorithm.

The values of the interaction factors were calculated and found to be as follows: $\eta_{Cd,Cd} = 1.02$; $\eta_{Zn,Cd} = 3.29$; $\eta_{Cd,Zn} = 0.089$; and $\eta_{Zn,Zn} = 1.26$. The experimental molar uptake and the molar uptake predicted with the bisolute Langmuir isotherm that had been modified with the interaction factor were compared, and it was found that the bisolute Langmuir isotherm interpreted the experimental data for both ions reasonably well. The average percent deviation was 18.8% for Cd(II) and 31.0% for Zn(II), which are the lowest values for all the models tested in the cited work. Thus, the experimental data for simultaneous Cd(II) and Zn(II) adsorption onto carbon correlated well with the bisolute Langmuir isotherm modified with an interaction factor. The simultaneous adsorption isotherms for Cd(II) and Zn(II) were always reduced compared to the single adsorption isotherms for these ions. The Zn(II) adsorption isotherm was affected more by the presence of the other ion than Cd(II). The adsorption isotherm for a given ion is always reduced by the presence of the other because the two ions compete for some of the same active sites.

The adsorption behavior of Cu(II) and Mn (II) cations in the presence of other metal ions that display strong or intermediate affinities for adsorption sites was systematically investigated, taking into consideration the following factors: (1) metal ion site competition; (2) charge accumulation near the carbon surface; and (3) speciation of the metal ions. Two multicomponent adsorption models were proposed, and the results were then compared to two models presented in the literature (Dastgheib and Rockstraw 2002b).

For modeling multicomponent systems comprised of species whose single–solute isotherms obey the Freundlich Isotherm, a multicomponent Freundlich equation was used. The first equation of this type was proposed for binary systems by Fritz and Schlünder (1974, 1981), as provided in Eq. (43),

$$q_1 = \frac{K_1 C_1^{n1+\beta11}}{C_1^{\beta11} + \alpha_{12} C_2^{\beta12}} \tag{43}$$

where q_1 and C_1 are the concentrations of solute 1 in the solid and liquid phases, respectively; C_2 is the concentration of the solute 2 in liquid phase; K_1 and n_1 are Freundlich equation constants in the single solute 1 system; and β_{11}, α_{12} and β_{21} are constants that are determined from the least squares analysis of the binary data.

The second multicomponent Freundlich equation, which was proposed by Sheindorf *et al*. (1981), was derived under the assumption that: (1) each component in a single system obeys the Freundlich model and (2) for each component in multicomponent system, the adsorption energies of different sites are distributed exponentially, with the distribution function being identical to that for the single-component system. The proposed binary system equation is shown in Eq. (44),

$$q_1 = K_1 C_1 (C_1 + \eta_{12} C_2)^{n_1 - 1} \tag{44}$$

where η_{12} is the interaction parameter (with other parameters are defined in the same manner as Eq. (43)).

Thus the proposed equation, written for solute 1 in a binary system of solutes 1 and 2, can be shown as,

$$q_1 = \left[\frac{K_1 C_1^{n_1}}{K_1 C_1^{n_1} + a_{12} K_2 C_2^{n_2} + b_{12} C_2^{n_{12}}} \right] K_1 C_1^{n_1} \qquad (45)$$

where q_1 and C_1 are the concentrations of solute 1 in the solid and liquid phases, respectively; C_2 is the concentration of solute 2 in the liquid phase; K_1, n_1, K_2, and n_2 are the single component Freundlich constants, and a_{12}, b_{12}, and n_{12} are interaction constants obtained from a least squares analysis of the binary data. The term inside the bracket on the right hand side of Eq. (45) represents the overall competition and interaction factor, and has a value of less than or equal to unity (when $C_2 \to 0$, this term is equal to 1). The term $a_{12} K_2$ can be condensed to a single term, and was considered as one constant.

It was found in most cases that the value of 0.5 for n_{12} in Eq. (45) gave acceptable results. Using this assumption, Eq. (45) was reduced to a form that has only two interaction constants, as shown by Eq. (46),

$$q_1 = \frac{(K_1 C_1^{n_1})^2}{K_1 C_1^{n_1} + a_{12} K_2 C_2^{n_2} + b_{12} C_2^{0.5}} \qquad (46)$$

The general case of the proposed multicomponent Freundlich model is Eq. (47),

$$q_i = \frac{(K_i C_i^{n_i})^2}{K_i C_i^{n_i} + \sum_{j=1}^{m} a_{ij} K_j C_j^{n_j} + b_{ij} C_j^{ij}} \qquad (47)$$

where q_i and C_i represent concentrations of solute i in the solid and liquid phases, respectively; C_j represents the concentration of other solutes in liquid phase; K_i, n_i, K_j, and n_j are the single-component Freundlich constants; a_{ij}, b_{ij}, and n_{ij} are binary interaction constants obtained from $a_{ii} = b_{ii} = 0$; and m is the number of solutes.

Least squares analysis was used to find the constants of Eqs. (43 through 46). In each case, the objective function, as defined in Eq. (48), was minimized

$$\varphi = \sum_{i=1}^{m} \left(\frac{q_{\exp,i} - q_{cal,i}}{q_{\exp,i}} \right)^2 \qquad (48)$$

In Eq. (48), $q_{exp,i}$ is the experimental value of the metal ion uptake in binary system at data point I, $q_{cal,i}$ is the calculated value of metal ion uptake (from the selected model), and m is the number of data points.

To evaluate and compare the performance of each model, average relative error (ARE%) and root mean squares error (RMSE%) were calculated for each binary system. The large calculated values of RMSE% corresponding to Eq. (44) demonstrated that this model did not predict the metal ion adsorption isotherms in binary systems particularly well. Equation (43) and the proposed model in Eq. (45) were both found to be good models for predicting adsorption isotherms of metal ions in binary systems, as demonstrated by low RMSE% of different binaries.

Samples of dead biomass from the marine brown algae *Fucus ceranoides*, *Fucus vesiculosus*, and *Fucus serratus* were studied for their ability to remove cadmium from aqueous solutions by Herrero *et al.* (2006). A non-ideal competitive adsorption isotherm model (NICCA) (Kinniburgh *et al.* 1999), which described very well the competition between protons and metal ions, in contrast to a simpler discrete competitive Langmuir model, was applied. This model is a semi-empirical, thermodynamically consistent model, which implicitly accounts for a variable degree of heterogeneity of the sorbent. The basic NICCA equation for the overall binding of species i in the competitive situation is,

$$\theta_i = \frac{(K_i c_i)^{n_i}}{\sum_i (K_i c_i)^{n_i}} \frac{\left[\sum_i Kc_i^{n_i}\right]^p}{1 + \left[\sum_i Kc_i^{n_i}\right]^p} \tag{49}$$

where θ_i is the coverage fraction of the species i, K_i is the median value of the affinity distribution for species i, p is the width of the distribution (usually interpreted as a generic or intrinsic heterogeneity seen by all ions), and n_i is an ion-specific non-ideality term. Strictly speaking, c_i should be the local concentration of species i at the binding site, *i.e.*, the bulk concentration (or activity) corrected for the double layer effect (for instance, the concentrations in the Donnan phase). In this work, the bulk concentrations was used instead, and therefore, the metal binding constants calculated were conditional parameters (referred to 0.05 M ionic strength). The following normalization condition was used to calculate the amount of species i bound, q_i,

$$q_i - \theta_i = (n_i / n_H) q_{max,H} \tag{50}$$

where $q_{max,H}$ is the maximum binding capacity for protons, which can be calculated from the equivalence point of the acid-base titrations in absence of heavy metal. The ratio n_i/n_H was interpreted by Kinniburgh *et al.* (1999) in terms of stoichiometry and cooperativity. When this ratio is less than one, then the maximum binding of species i is lower than the total amount of sites (defined as the amount of titratable protons), which would be a consequence of some degree of multi-dentism. On the other hand, a value of n_i/n_H greater than one would reflect some degree of cooperativity. Finally, if $n_i/n_H=1$, it can be demonstrated that the maximum proton/metal exchange ratio is one, and the NICCA

isotherm reduces to the generalized (multicomponent) Langmuir-Freundlich isotherm (GLF):

$$\theta_i = \frac{(K_i c_i)}{\sum_i (K_i c_i)} \frac{\left[\sum_i (K_i c_i)\right]^p}{1+\left[\sum_i (K_i c_i)\right]^p} \tag{51}$$

If only the proton binding is considered (*i.e.*, absence of competing ions) in Eqs. (50) and (51), then the LF isotherm is recovered,

$$q_H = q_{\max,H} \frac{(K_H c_H)^{m_H}}{1+(K_H c_H)^{m_H}} \tag{52}$$

where now the heterogeneity parameter m_H describes the combined effect of n_H and p ($m_H = n_{Hp}$). In the case of a homogeneous system (no chemical heterogeneity), $m_H = 1$, and then the Langmuir isotherm is obtained. For instance, the ideal Langmuir competitive isotherm for the binding of Cd^{2+} (assuming a 1:1 stoichiometry) would be,

$$\theta_{Cd} = \frac{K_{Cd} C_{Cd}}{1 + K_H c_H + K_{Cd} c_{Cd}} \tag{53}$$

with $q_{Cd} = \theta_{Cd} q_{max,H}$.

It was found that the fit of the NICCA model to the cadmium binding data (discarding the data at pH 6 and lower metal concentrations) was satisfactory.

Other Models

In addition to the relatively well known isotherm approaches summarized on previous pages, one of the goals of the present review is to provide some guidance on alternative equations that have been demonstrated in at least one study involving metal removal but not widely used as those discussed earlier. Such approaches may have potential to become more widely used in the future.

Incorporation of Donnan relationships

Schiewer and Volesky (1997a) used biomass of the brown alga *Sargassum* for the biosorption of Cd^{2+} ions. This work provided a mathematical model for predicting the equilibrium of proton and metal ion binding as a function of metal ion concentration, pH, and ionic strength. Since the presence of sodium significantly influenced Cd binding, it is recommended to use models that incorporate ionic strength effects. Although swelling of the biomass particle was observed, a simple Donnan model that assumed a rigid particle already yielded a good prediction of the experimental data. A combined Donnan-Biosorption Isotherm equation was derived that allowed for direct calculation of cation

binding without interactions. Three versions of the Donnan model were considered: one that assumes a rigid particle (DORI), one (DOSWa) that accounts for swelling by a linear correlation (Eq 54), and one (DOSWb) that accounts for swelling by a more complex relation (Eq 55).

Since the swelling of sorbent increased with the number of free sites C, the following simple linear relationship between the specific particle volume and C was assumed,

$$V_m = Y_V C \ \text{(L/g)} \tag{54}$$

where Y_v is a constant that has to be determined from the experimental data. For C approaching zero (*i.e.*, all sites are occupied), electrostatic effects and therefore the volume are irrelevant (*i.e.*, it does not matter that the value calculated for V_m approaches zero). Equation 54 expresses that the charge density per volume is constant, independent of the degree of site occupation.

Since, the swelling not only increased significantly with C but, additionally, it decreased with $^M q$ (the metal ion binding (mequiv/g)), the following swelling correlation was considered:

$$V_m = 1 + 0.5(C^2 - {}^M q) \ \text{L/g} \tag{55}$$

Schiewer and Wong (2000) investigated the binding of protons and metal ions by three brown seaweeds *Sargassum hemiphyllum, Colpomenia sinuosa*, and *Petalonia fascia* as well as the marine green alga *Ulva fascia* as a function of metal concentration, pH, and ionic strength. Differences in overall biosorption behavior were explained as a result of different numbers of binding sites, affinities for metal complexation, and charge density. These relationships were predicted using the Donnan model combined with an ion exchange biosorption isotherm for covalent binding of metals (Cu and Ni) and protons.

The concentration factor $[H]_p/[H]$ was modeled according to the Donnan equilibrium, whereby the concentration of any ion was assumed to be homogeneous throughout the biomass particle, and the negative charge of the biomass was balanced by counter-ions such as protons (H), sodium (Na), or divalent metal ions (M), whose concentration factor was determined by:

$$\lambda = [H]_p / [H] = [Na]_p / [Na] = \left([M^{2+}]_p / [M^{2+}] \right)^{0.5} \tag{56}$$

One main factor determining K is the ionic strength. K decreases with increasing ionic strength, approaching a value 1.0.

A pH-sensitive isotherm equation was derived, which allows for the calculation of the amount of metal and protons bound covalently.

$$CH = C_t \left(K_H [H]_p \right) / \left(1 + K_H [H]_p + \left(K_M [M]_p \right)^{0.5} \right) \ \text{(mequiv/g)} \tag{57}$$

$$CM_{0.5} = C_t \left(K_M [M]_p \right)^{0.5} / \left(1 + K_H [H]_p + \left(K_M [M]_p \right)^{0.5} \right) \text{ (mequiv/g)} \qquad (58)$$

The Donnan model with particle swelling (DOSW) was represented by the following equation:

$$V_m = Y_V C \text{ (L/g)} \qquad (59)$$

where Y_V is a ftting parameter and C is the number of free carboxyl groups (i.e., assumed not covalently bind to any cation). The following equations were derived by combining the Donnan model Eq. (56) with the isotherm equations (60) and (61):

$$q_H = C_t \left(K_H [H] + [H] Y_V (1 - 1/\lambda) \right) / \left((1/\lambda) + K_H [H] + \left(K_M [M] \right)^{0.5} \right) \text{ (mequiv/g)} \qquad (60)$$

$$q_M = C_t \left(\left(K_M [M] \right)^{0.5} + 2[M] Y_v (\lambda - 1/\lambda) \right) / \left((1/\lambda) + K_H [H] + \left(K_M [M] \right)^{0.5} \right) \text{ (mequiv/g)} \qquad (61)$$

The Donnan model was successfully used to account for the ionic strength effects in pH titrations and in metal binding. In metal binding experiments at high ionic strength swelling of the biomass particles was observed. The model fit improved when compared to the Donnan model for rigid particles when particle swelling proportional to the number of free binding sites was assumed.

Sundman *et al*. (2008) characterized the interactions between Ca^{2+}, Cu^{2+}, and two different fibre materials—a fully bleached softwood kraft pulp, and a chemically modified fully bleached softwood kraft fibre material—aiming for a better understanding of the interactions between water suspended cellulose fibres and metal ions. The study was conducted as a function of pH (2 to 7), both in the absence and presence of an excess of Na^+ ions (0 to 100 mM NaCl). For both fibre materials, adsorption data collected in the absence of Na^+ were fully explained by the non-specific Donnan ion-exchange model. However, in the presence of an excess of NaCl, the data clearly indicated that higher amounts of divalent metal ions adsorbed in comparison to the prediction of the Donnan model. Therefore, to model these data, specific metal ion–fibre surface complexes were assumed to form, in addition to the Donnan ion-exchange. It was found that the Donnan ion exchange model satisfactorily described Ca^{2+} and Cu^{2+} ion adsorption by both fibre materials when no excess of Na^+ ions was present in the fibre suspensions. On the other hand, in an excess of ionic medium, the Donnan model underestimated the Ca^{2+}- and Cu^{2+}-ion uptake in all experiments. The deviation was greatest for the native low-charged fibre material and at the highest ionic medium.

Lumped parameter isotherm model

Schiewer and Wong (1999) used a lumped parameter isotherm model, where they emphasized the need to incorporate pH effects into the isotherm model. Since pH is one of the key parameters in biosorption, it is desirable to use isotherm equations that can accommodate pH as one model variable. Their model also incorporates ion exchange

constants, reflecting that the biosorbent is initially saturated with some ions that have to be released when the metal ion is consumed. Ion exchange constants do not, however, take into account that the degree of binding site occupation may change. Therefore, multicomponent isotherm models have to be proposed that can account for ion exchange and pH effects. The model needs to be based on a 1:2 binding stoichiometry, whereby one divalent metal ion M binds to two binding sites B. Two different approaches have been proposed, *i.e.*, to use ion exchange constants that assume the formation of B_2M complexes or a multicomponent isotherm assuming the formation of $BM_{0.5}$ complexes.

These isotherm models can be represented as:

$$q_M / q_H = BM / BH = K_x [M]/[H] \text{ for B+M = BM} \tag{62}$$

$$q_M{}^2 / q_H{}^2 = BM_{0.5}{}^2 / BM^2 = K_x [M]/[H]^2 \text{ for 2B+M = 2BM}_{0.5} \tag{63}$$

$$q_M / q_H{}^2 = 2B_2M / BH^2 = 2K_x [M]/[H]^2 \text{ for 2B+M B}_2\text{M} \tag{64}$$

The main advantage of the $BM_{0.5}$ and B_2M models is that they adequately represent the possible occurrence of divalent metals occupying two binding sites. Therefore, these stoichiometric assumptions are better suited to model the exchange between metals and protons. The $BM_{0.5}$ and B_2M models yield slightly lower deviations from the experimental data in comparison to the BM_b model, but all have similar magnitudes. The cited authors found that for Cu binding, the B_2M model was better than the $BM_{0.5}$ stoichiometry, while the reverse was true for Ni. This improved performance for $BM_{0.5}$ for Ni was due to different isotherm shapes, whereby the $BM_{0.5}$ model showed rather gradual changes of ion binding with metal concentration. In either case, the stoichiometric assumption that yielded the better fit displayed a slope in the exchange plot much closer to 1.0 compared to the other model. It can be concluded that the slope in the log/log plot for metal proton ion exchange is the best indicator of the appropriateness of the stoichiometric assumptions.

The B_2M model can be advantageous at very low metal concentrations, where the $BM_{0.5}$ model sometimes tends to overpredict the metal binding. Since however both stoichiometric assumptions typically fit equally well and since the $BM_{0.5}$ model offers the additional advantage of being much simpler to use (no iterations are required), it is recommended to use the $BM_{0.5}$ model. An exception is when utilizing the assumption that binding sites must be a suitable distance from each other in order to form a stable complex. Thus, the lesser affinity in *Ulva* in the cited work may be caused by a lack of suitably spaced sites (*i.e.*, the individual carboxyl sites may be too far apart to allow bidentate binding).

Other multicomponent fits

Srivastava *et al.* (2006) studied the competitive adsorption of Cd(II) and Zn(II) ions onto bagasse fly ash (BFA) from binary systems and used different isotherm models to study the equilibrium of systems.

Various monocomponent isotherm equations such as those of Freundlich (Eq. 14), Langmuir (Eq. 11), and Redlich–Peterson (R–P) (Eq. 23) were used to describe the equilibrium characteristics of adsorption; the Redlich–Peterson (R–P) and the Freundlich models represented the single ion equilibrium adsorption data better than the Langmuir model. Equilibrium isotherms for the binary adsorption of Cd(II) and Zn(II) ions on BFA had been analyzed by non-modified Langmuir, modified Langmuir, extended-Langmuir, Sheindorf–Rebuhn–Sheintuch (SRS), non-modified R–P, and modified R–P adsorption models. These multicomponent isotherm equations that have been used are presented as follows:

Non-modified competitive Langmuir model

The extension of the basic Langmuir model for component i in a N-component system to competitive adsorption can be formulated as follows:

$$q_{e,i} = \frac{q_{m,i} K_{L,i} C_{e,i}}{1 + \sum_{J=1}^{N} K_{L,j} C_{e,j}} \tag{65}$$

where $q_{m,i}$ and $K_{L,i}$ are derived from the corresponding individual Langmuir isotherm equations.

Modified competitive Langmuir isotherm

Individual adsorption constants may not define exactly the multi-component adsorption behavior of metal ion mixtures. For that reason, better accuracy may be achieved by using modified isotherms related to the individual isotherm parameters and the correction factors. An interaction term, $\eta_{L,i}$, which is a characteristic of each species and depends on the concentrations of the other components, has been added in the competitive Langmuir model. The modified competitive Langmuir isotherm is given as,

$$q_{e,i} = \frac{q_{m,i} K_{L,i} \left(C_{e,i} / \eta_{L,i} \right)}{1 + \sum_{J=1}^{N} K_{L,j} \left(C_{e,i} / \eta_{L,i} \right)} \tag{66}$$

where $q_{m,i}$ and $K_{L,i}$ are derived from the corresponding individual Langmuir isotherm equations, and $\eta_{L,i}$ values are estimated from competitive adsorption data. For binary mixtures, this equation can be rewritten as the first and the second component, respectively, and the two equations can be solved simultaneously to obtain the multicomponent Langmuir adsorption constants for each component.

Extended Langmuir isotherm

Assuming that the surface sites are uniform, and that all the adsorbate molecules (ions) in the solution compete for the same surface sites, the extended Langmuir equation for multicomponent systems can be written as

$$q_{e,i} = \frac{q_{max} K_i C_{e,i}}{1 + \sum_{J=1}^{N} K_j C_{e,j}} \tag{67}$$

Sheindorf–Rebuhn–Sheintuch (SRS) model

    A Freundlich-type multi-component adsorption isotherm known as the Sheindorf–Rebuhn–Sheintuch (SRS) equation was derived by Sheindorf *et al.* (1981), to represent experimental data. A general SRS equation for the adsorption isotherm for component i in a N-component system is given as:

$$q_{e,i} = K_{F,i} C_{e,i} \left(\sum_{J=1}^{N} a_{ij} C_{e,j} \right)^{n_i - 1} \tag{68}$$

    The pre-exponential coefficient $K_{F,i}$ and the exponent n_i are determined from the mono-component systems. The competition coefficients a_{ij} describe the inhibition to the adsorption of component i by component j, and can be determined from the thermodynamic data, or more likely, from the experimental data of multicomponent systems. The SRS equation assumes that (I) each component individually obeys the Freundlich isotherm; (II) that for each component in a multicomponent adsorption system, there exists an exponential distribution of site adsorption energies,

$$N_i(Q) = \alpha_i \exp\left(-\beta_i Q / RT\right) \tag{69}$$

where a_i and b_i are constants; and (III) the coverage by each adsorbate molecule (or ion) at each energy level Q is given by the multicomponent Langmuir isotherm equation:

$$\theta_i(q) = \frac{K_i C_{e,i}}{1 + \sum_{J=1}^{N} K_j C_{e,j}} \tag{70}$$

where,

$$K_j = K_{0j} \exp\left(\frac{q}{RT}\right)$$

Integration of $N_i(Q)\theta_i(Q)$ over energy levels in the range of $-\infty$ to $+\infty$ yields Eq. (71), and the competition coefficients are defined as $a_{ij} = K_{0j}/K_{0i}$ and thus $a_{ji} = 1/a_{ij}$. The SRS equation was successfully applied to a multicomponent equilibrium adsorption of different types of contaminants,

$$\theta_i = \frac{\alpha_i RT b_{0i}}{n_i} C_i \left(\sum_{j=1}^{k} b_{0j} C_j\right)^{n_i - 1} = A_i C_i \left(\sum_{j=1}^{k} a_{ij} C_j\right)^{n_i - 1} \tag{71}$$

where

$$A_i = \frac{\alpha_i RT b_{0i}^{n_i}}{n_i} \qquad \text{and} \qquad a_{ij} = b_{0j} / b_{0i}$$

Non-modified competitive Redlich–Peterson model

The competitive non-modified R–P model related to the individual isotherm parameters only is given as follows,

$$q_{e,i} = \frac{K_{R,i} C_{e,i}}{1 + \sum_{J=1}^{N} a_{R,j} C_{e,j}^{\beta,j}}$$ (72)

where $K_{R,i}$, $a_{R,I}$, and β_i are the R–P parameters derived from the corresponding individual R–P isotherm equations. The competitive non-modified R–P model is rearranged to the following modified competitive R–P Model to take the characteristics of each species into account,

$$q_{e,i} = \frac{K_{R,i} \left(C_{e,i} / \eta_{R,i} \right)}{1 + \sum_{J=1}^{N} a_{R,j} \left(C_{e,j} / \eta_{R,j} \right)^{\beta,j}}$$ (73)

where values of $\eta_{R,i}$ are estimated from competitive adsorption data.

Marquardt's percent standard deviation (MPSD) was used to test the adequacy and accuracy of various isotherm model fits with the experimental data. Based on a linearly regression analysis, Srivastava *et al*. (2006) showed that R^2 was closer to unity for the R–P and the Freundlich models compared to the Langmuir model. Thus it was concluded that equilibrium adsorption data of single component adsorption, *i.e.* Cd(II) and Zn(II) ion, could be represented more appropriately by the R–P and the Freundlich models in the studied concentration range and at lower concentrations, since the Langmuir isotherm did not adequately represent the equilibrium sorption. The single-component Langmuir constants are Q^o (monolayer saturation at equilibrium) and b (corresponding to the concentration where the amount of metal ion bound to adsorbent is equal to $Q^o/2$ and which indicates the affinity of the metal ions to bind with adsorbent). The results of this study showed that the amount of Zn(II) ions per unit weight of BFA for the complete monolayer surface coverage was higher than that of Cd(II), and a large value of b implied strong bonding of Zn(II) ions to BFA. K_F and n, the single-component Freundlich constants (indicating the adsorption capacity and adsorption intensity, respectively) were also calculated, and the BFA displayed greater heterogeneity for Cd(II) than for Zn(II) ions. The value of n was found to be 1, which implied that both the Cd(II) and Zn(II) ions were favorably adsorbed by BFA at pH 6.0. The magnitude of K_F also showed higher uptake of Zn(II) than Cd(II) ions by BFA at pH 6.0. It was noted that the Redlich–Peterson constant b normally lies between 0 and 1, indicating a favorable adsorption. The experimental and predicted equilibrium uptake (q_e) evaluated from the single-component Langmuir, Freundlich, and Redlich–Peterson models for the individual adsorption of Cd(II) and Zn(II) onto BFA at pH 6.0 were also compared, and the MPSD values were calculated. Based on the lower MPSD values, the R–P and Freundlich models displayed better fit to the experimental adsorption data than the Langmuir model.

Studies comparing alternative multi-component models to fit data

The simultaneous adsorption data of Cd(II) and Zn(II) on the BFA was also fitted to multi-component isotherm models (Srivastava *et al.* 2006). The multi-component non-modified Langmuir model displayed a poor fit to the experimental data (MPSD = 101.6). All the modified Langmuir coefficients ($\eta_{L,i}$) estimated were much greater than 1.0, indicating that the non-modified multi-component Langmuir model related to the individual isotherm parameters could not be used to predict the binary-system adsorption. However, the use of the interaction term, $\eta_{L,i}$, in the modified Langmuir model (MPSD = 28.3) improved the fit of the non-modified Langmuir model. The use of the multi-component extended-Langmuir model in the cited study showed its inadequacy to represent the experimental data (MPSD values were large). The K_i values, reflecting the affinity between the adsorbent and the metals in the binary systems by using the BFA were found to be 0.04 L/mg for both Cd(II) and Zn(II). The overall total metal ions uptake (q_{max}) by BFA is 7.24 mg/g. These values were found to be considerably lower than the sum of the maximum total capacities of Cd(II) and Zn(II) ions resulting from the single component adsorption systems. For that reason, it was concluded that the adsorption sites of Cd(II), and Zn(II) in binary systems onto BFA may likely be partially overlapped. These lower metal ion uptake results also implied that there may be a variety of binding sites on the adsorbents showing partial specificity to the individual metal ions. The information obtained from the maximum capacities seems to violate the basic assumptions of the Langmuir model, *i.e.* that the entire adsorbent surface is homogeneous and that there is no lateral interaction between the adsorbate molecules. Consequently, the affinity of each binding site for the adsorbate molecules should be uniform. The use of interaction terms, $\eta_{R,i}$, for the modified R–P model (MPSD = 24.1) improved the fit of the non-modified R–P model (MPSD = 52.0); however, the SRS model (MPSD = 15.4) provided the best-fit to the binary adsorption data of Cd(II) and Zn(II) onto BFA. Thus, the SRS isotherm was found to best represent the binary system adsorption. This improved SRS performance was expected, as BFA has a heterogeneous surface, and the adsorption of the single metal ions had also been well represented by the Freundlich isotherm equation. It was evident that the modification of the Freundlich equation, as given by the SRS model, took into account the interactive effects of individual metal adsorbate ions between and among themselves and the adsorbent reasonably well. Therefore, the binary adsorption of metal ions onto BFA can be represented satisfactorily and adequately by the SRS model. The multicomponent SRS model is applicable to those systems where each component individually obeys the single-component Freundlich isotherm.

The isotherm coefficients can be determined from the mono-component isotherm except for the adsorption competition coefficients, a_{ij}, which have to be determined experimentally. The competition coefficients, a_{ij}, describe the inhibition to the adsorption of component i by component j. The two components for the cited study were found to obey the single-component Freundlich model individually. The competition coefficients a_{ij} and a_{ji} were estimated from the competitive adsorption data for Cd(II), Ni(II), and Zn(II) ions by using the MS EXCEL 2002 program. A comparison of the competition coefficients in the adsorption isotherm equation shows that the uptake of the strongly adsorbed Zn(II) was significantly inhibited by the presence of Cd(II) (a_{21} = 2.70).

Similarly, the uptake of Cd(II) by BFA was suppressed in the presence of Zn(II) ion in the solution ($a_{12} = 2.15$).

Three-dimensional (3-D) adsorption isotherm surfaces were used to evaluate the performance of the binary metal ions adsorption system. It was found that the SRS model predictions for the simultaneous adsorption of Cd(II) and Zn(II) ions by BFA from aqueous solution were very satisfactory.

Srivastava *et al*. (2009a) analyzed the competitive adsorption of Cd(II), Ni(II), and Zn(II) ions onto rice husk ash (RHA) from ternary metal ion mixtures. Various isotherm equations such as those of Freundlich (Eq. 6), Langmuir (Eq. 2), and R-P (Eq. 14) were used to describe the monocomponent equilibrium characteristics of adsorption of individual ions onto RHA. The MPSD error values were the lowest for the Freundlich model, followed by the R-P and Langmuir models. Therefore, the equilibrium adsorption data of Cd(II), Ni(II), and Zn(II) ion adsorption on RHA could be represented appropriately by the Freundlich model within the studied concentration range. RHA has a heterogeneous surface. It is, therefore, expected that the Freundlich and R-P isotherm equations can better represent the equilibrium sorption data than the Langmuir isotherm model. The simultaneous sorption data of Cd(II), Ni(II), and Zn(II) from the ternary mixture onto RHA was fitted to the multicomponent isotherm models, *viz.*, nonmodified, modified, and extended Langmuir models (Eq. 2); nonmodified and modified R-P models (Eq. 14); and the SRS model. On the basis of the MPSD error function, it was found that the simultaneous sorption phenomena of Cd(II), Ni(II), and Zn(II) ions on the RHA could be adequately represented by the SRS model.

The sorption of heavy metals (lead, copper, and cadmium) by a marine algal biomass *Sargassum sp*. was studied in single and multiple metal-ion systems (Sheng *et al*. 2007). The equilibrium data for the single metal ion system was studied with the help of the Langmuir adsorption isotherm model (Eq. 11). The effect of the presence of multiple metal ions on the biosorption performance was investigated, and the results were evaluated using the modified competitive Langmuir model and modified Jain-Snoeyink model.

The extension of the basic Langmuir model to account for competitive adsorption in multiple-metal systems can be formulated as follows,

$$q_{e,i} = \frac{q_{\max,i} b_i C_{e,i}}{1 + \sum_{i=1}^{n} b_i C_{e,i}} \tag{74}$$

where the terms $q_{\max,i}$ (monolayer sorption capacity) and b_i (affinity of sorbent for the sorbed species) are derived from the corresponding individual Langmuir isotherm equations; $q_{e,i}$ and $C_{e,i}$ are, respectively, the uptake and final concentration when adsorption equilibrium is reached, and n is the number of metal ions in solutions. The Langmuir model assumes that each component is adsorbed onto the surface according to ideal solute behaviors, where there is no interaction or competition between molecules involved under homogeneous conditions. To account for nonideal systems using the Langmuir theory, Jain and Snoeyink introduced an additional term into Eq. 74 for binary metal systems,

$$q_{e,1} = \frac{\left(q_{\max,1} - q_{\max,2}\right)b_1 C_{e,1}}{1 + b_1 C_{e,1}} + \frac{q_{\max,2} b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \tag{75}$$

where $q_{\max,1} > q_{\max,2}$. The additional term on the right-hand side of Eq. 75 (proportional to the quantity $q_{\max,1}$ - $q_{\max,2}$) is the Langmuir expression for the amount of solute 1 adsorbed on to the surface without competition. The second term on the right hand side represents the amount of solute 1 adsorbed onto the surface in competition with solute 2. The amount of solute 2 adsorbed onto the sorbent surface can be calculated from Eq 74.

All the model parameters in these competitive isotherms for multiple-metal systems may be derived from single-component isotherms. Indeed, better accuracy may be achieved by extracting additional coefficients from the multiple-metal isotherms. For instance, an interaction term η, which is a characteristic of each species and is dependent on the sorption properties of the sorbents, has been defined in the modified competitive isotherms.

The modified competitive Langmuir model takes the form

$$q_{e,i} = \frac{q_{\max,i} b_i \left(C_{e,i}/\eta_i\right)}{1 + \sum_{i=1}^{n} b_i \left(C_{e,i}/\eta_i\right)} \tag{76}$$

For a binary system, the modified Jain-Snoeyink model becomes

$$q_{e,1} = \frac{\left(q_{\max,1} - q_{\max,2}\right)b_1\left(C_{e,1}/\eta_1\right)}{1 + b_1\left(C_{e,1}/\eta_1\right)} + \frac{q_{\max,2}b_1\left(C_{e,1}/\eta_1\right)}{1 + b_1\left(C_{e,1}/\eta_1\right) + b_2\left(C_{e,2}/\eta_2\right)} \tag{77}$$

The root-mean-square error (RMSE) was used to check the adequacy of the model. The sorption data for single metal system at different pH values were well-modeled by the Langmuir isotherm. However, in case of binary and tertiary metal systems, the original competitive Langmuir model and the Jain-Snoeyink model failed to fit the experimental data adequately, with all the R^2 values being less than 0.70. Experimental data fitted both the modified competitive Langmuir model and the modified Jain-Snoeyink model well. It was evident that the modified models, with the introduction of the interaction coefficient (η), considerably improved the accuracy of the modeling. Furthermore, it was also shown that the interaction coefficient η derived from the binary metal system could be successfully applied to the ternary metal system, thus indicating the possibility of predicting biosorption performance of such complex systems, based on the modeling parameters obtained from simpler experiments.

The lead (II) biosorption potential of *Aspergillus parasiticus* fungal biomass was investigated in a batch system (Akar *et al*. 2007b). Freundlich (Eq. 14), Langmuir (Eq. 11), and Dubinin–Radushkevich (D–R) isotherms (Eq. 16) were used for the biosorption isotherm modelling. Results indicated that the Langmuir, Freundlich, and D–R isotherm models are suitable for describing the lead (II) biosorption equilibrium by *A. parasiticus*

in the studied concentration range with the regression coefficient (R^2) values more than 0.97. The R_L (affinity between sorbent and sorbate using Langmuir constants) value for this study was 1.73×10^{-2}, indicating that the biosorption of lead (II) was favorable. The Freundlich constants K_F and n indicate the biosorption capacity of the biosorbent and a measure of the deviation from linearity of the biosorption, respectively. The adequate description of the experimental results with all of the isotherm models investigated in this study implied that the biosorption of lead (II) ions onto *A. parasiticus* biomass was complex, involving more than one mechanism. The biosorption process could be described by ion exchange as the dominant mechanism, in addition to complexation with groups at the surface of this biosorbent. The ion exchange mechanism was confirmed by the E value obtained from D-R isotherm model as well.

The biosorption of chromium(VI) from saline solutions onto dried *Rhizopus arrhizus* was studied as a function of pH, initial chromium(VI), and salt (NaCl) concentrations in a batch system by Aksu and Balibek (2007). The equilibrium sorption data were analysed by using Freundlich (Eq. 14), Langmuir (Eq. 11), Redlich–Peterson (Eq. 23), and Langmuir–Freundlich (Sips) models. The two- and three-parameter adsorption models, using non-linear regression technique and isotherm constants, were evaluated depending on salt concentration.

The Langmuir–Freundlich (Sips) model used in the cited study is another three-parameter empirical model for the representing equilibrium biosorption data (Eq. 78). This model suggests that the equilibrium data follow Freundlich isotherm at lower solute concentration, and thus, do not obey Henry's law, but that they follow a Langmuir pattern at higher solute concentration,

$$q_{eq} = \frac{AC_{eq}^m}{1 + BC_{eq}^m} \tag{78}$$

where A, B, and m are the Langmuir–Freundlich parameters. Values for $m >> 1$ indicate heterogeneous adsorbents, while values closer to or even equal to 1.0 indicate a material with relatively homogenous binding sites. In this case, the Sips model is reduced to the Langmuir equation.

Thus the equilibrium data were fitted to these isotherm models, and the values of average percentage errors and linear regression coefficients were the criteria for the selection of the most suitable isotherm model. On the basis of lower average percentage errors (in the range 0.8 to 2.4) and higher linear regression coefficients (in the range 0.998 to 1.000), the three-parameter Langmuir–Freundlich (Sips) model best described the chromium(VI) sorption isotherm data compared to other models examined, which suggested the monolayer, homogeneous sorption in single as well as salt-added binary-systems. The relatively lower percentage errors also indicated that both the two-parameter Langmuir and three-parameter Redlich–Peterson models were also very suitable for describing the biosorption equilibrium of chromium(VI) by the fungal cells in all cases. The other two-parameter model of Freundlich exhibited a poor fit to the biosorption data of chromium(VI) with an average percentage error more than 8.3.

The value of n (Freundlich constant), which was significantly higher than unity, indicated that chromium(VI) ions were favorably adsorbed under all the experimental

conditions examined. The values of *n* at different salt concentrations also indicated that decreased chromium(VI) biosorption intensity was affected by salt addition into biosorption medium. The magnitude of the constant K_F (Freundlich constant) showed a relatively easy uptake of chromium(VI) ions from aqueous solution, with high adsorptive capacity of biomass for chromium(VI) in both single and binary systems. The presence of salt at any initial concentration was found to reduce the K_F constant significantly. The salt added at different levels also affected the Langmuir constants (Q^o and *b*). Dried *R. arrhizus* exhibited the maximum biosorption capacity (Q^o) for single chromium(VI) biosorption. The addition of salt decreased the Q^o value of chromium(VI) biosorption to an insignificant extent. A high value of the other Langmuir parameter, *b*, indicated a high affinity of the biosorbent for the sorbate. The highest *b* value obtained for monometal conditions also decreased with the addition of salt, indicating its negative effect on chromium(VI) biosorption. Related biosorption parameters were also calculated according to the three-parameter isotherm of Redlich–Peterson using a non-linear regression method for chromium(VI) biosorption at different salt levels. The Redlich–Peterson constant, K_{RP}, indicated that the adsorption capacity of biosorbent also diminished with increasing salt concentration. It is noted that *β* normally lies between 0 and 1, indicating favorable biosorption. In the case considered, the value of *β* was 1.0 for 50 g/L salt containing medium and tended to unity for other salt concentrations studied, suggesting that the isotherms approached the Langmuir form. The corresponding Langmuir–Freundlich parameters of *A*, *B*, and *m* for different salt concentrations were also calculated. Constant *A*, indicating the biosorption capacity and affinity of biosorbent to chromium(VI) ions, also decreased with salt addition. The value of *m*, an indicator of heterogeneity index, which was calculated to be about 1.0 for all levels of salt, showed that the chromium(VI) sorption data obtained in the cited study tended towards the Langmuir form rather than the Freundlich form, and thus, the fungus had a homogeneous surface. The results showed that three-parameter models represented the biosorption isotherm data much better than two-parameter models for all cases, with low percentage error values.

Again all these parameters changed with respect to the level of salt, and the results could be used to predict the adsorption behavior of chromium(VI) in an aqueous solution at a specific salt concentration. When isotherm constants were plotted against the salt concentration, the functional relationship between isotherm constants and salt concentration were not linear for the entire range of salt concentration. The results showed that the Freundlich and Langmuir parameters decreased following a second-order polynomial function of salt concentration with high linear regression coefficients. An exponential relationship between the Redlich–Peterson parameters (a_{RP} and K_{RP}) of chromium(VI) and salt concentration was obtained (*β* is assumed as 1 for all cases) with the correlation coefficients of 0.935 and 0.981, respectively. The relationship between the Langmuir–Freundlich model constants of *A* and *B* of chromium(VI) and salt concentration also followed an exponential equation with a high linear regression coefficient, while other Langmuir–Freundlich parameter, *m*, varied linearly with salt concentration.

The sorption of hexavalent chromium by marine brown algae *Cystoseira indica*, which was chemically-modified by cross-linking with epichlorohydrin (CB1, CB2),

oxidized by potassium permanganate (CB3), or only washed by distilled water (RB), was studied with variations in the parameters: contact time, pH, initial metal ion concentration, and solid/liquid ratio (Basha *et al*. 2008). Langmuir (Eq. 11), Freundlich (Eq. 14), and Dubinin–Radushkevich models (Eq. 16) were used to describe the equilibrium between the Cr(VI) sorbed on the four pretreated biomasses of *C. indica* (q) and Cr(VI) ions in the solution. It was found that the Dubinin–Radushkevich isotherm model was in good agreement with all the experimental data as compared to the Langmuir and Freundlich isotherm models. The magnitude of *E* (mean free energy, kJ/mol), as obtained in the cited work, was useful for estimating the type of sorption reaction. The *E* values obtained were around 15 kJ/mol, which is in the energy range of an ion-exchange reaction, *i.e.*, 8 to 16 kJ/mol. This *E* value suggests that biosorption of Cr(VI) by *C. indica* may be classed as an ion exchange reaction.

Chakravarty *et al*. (2008) used newspaper pulp as an adsorbent for the removal of copper from aqueous medium. The experimental data were analyzed using Freundlich (Eq. 14), Langmuir (Eq. 11), Dubinin–Radushkevich (D–R) (Eq. 16), and Redlich-Peterson (R–P) (Eq. 23) isotherm models. Their results showed that adsorption data fit reasonably well to the Langmuir, Freundlich, and R–P isotherms, as was reflected by the high correlation coefficients (R^2). The Freundlich constant *n* increased with increasing initial Cu concentration. The D–R isotherm showed a definite trend for the K_{DR} value. However, the R^2 in D–R isotherm decreased with increasing initial concentration of Cu. No definite trend was observed for the Langmuir constants *b* and Q^o. The calculated R_L value (affinity) for adsorption of Cu(II) on the newspaper pulp adsorbent were found to be in the range of 0 to 1 at all initial Cu(II) concentrations, which confirms the favorable uptake of Cu(II) in the sorption process.

El Nemir *et al*. (2008) used a new activated carbon developed from date palm seed wastes, generated in the jam industry, for removing toxic chromium from an aqueous solution. The equilibrium data were tested using several isotherm models, including the Langmuir (Eq. 11), Freundlich (Eq. 14), Redlich–Peterson (Eq. 23), Temkin (Eq. 19), Dubinin–Radushkevich (Eq. 16), Koble–Corrigan (79), and generalized isotherm (80) equations.

The Koble–Corrigan equation used in the cited study is another isotherm model that depends on the combination of the Langmuir and Freundlich equations in one non-linear equation for representing the equilibrium adsorption data. It is represented as follows,

$$q_e = \frac{aC_e^n}{1 + bC_e^n} \tag{79}$$

where *a*, *b*, and *n* are the Koble–Corrigan parameters, which were obtained by solving Eq. (79) using SPSS version 10.0 computer program.

The generalized isotherm equation was also tested for correlation of the equilibrium data. The linear form of the generalized isotherm is given by,

$$\log\left[\frac{Q^o}{q_e} - 1\right] = \log K_G - N_b \log C_e \tag{80}$$

where K_G is the saturation constant (mg L^{-1}); N_b the cooperative binding constant; Q^o the maximum adsorption capacity of the adsorbent (mg g^{-1}) (obtained from the Langmuir isotherm model); and q_e (mg g^{-1}) and C_e (mg L^{-1}) are the equilibrium chromium concentrations in the solid and liquid phases, respectively.

In the cited study, four different linear forms of Langmuir isotherm were used, which are presented as follows (El Nemir *et al*. 2008):

Form	*Linear equation*	
Langmuir-1	$\dfrac{C_e}{q_e} = \dfrac{1}{bQ^o} + \dfrac{1}{Q^o} XC_e$	(81)
Langmuir-2	$\dfrac{1}{q_e} = \left(\dfrac{1}{bQ^o}\right) + \dfrac{1}{C_e}\dfrac{1}{Q^o}$	(82)
Langmuir-3	$q_e = Q^o - \left(\dfrac{1}{b}\right)\dfrac{q_e}{C_e}$	(83)
Langmuir-4	$\dfrac{q_e}{C_e} = bQ^o - bq_e$	(84)

Parameters related to each isotherm were determined by using linear regression analysis, and R^2 was calculated. Their results showed that the linear forms 1 and 2 of the Langmuir isotherm were best fitted for the equilibrium data in comparison to 3 and 4. The experimental data were also found to fit well to the Freundlich model, with $n_F > 1$, indicating that adsorption of Cr^{6+} onto DSC is a favorable physical process. The Koble-Corrigan equation also displayed high R^2 values, which indicates that the Koble-Corrigan equation had a strong goodness of fit to the experimental data. The values of b were 0.01 and 0.02, indicating the combination between heterogeneous and homogeneous adsorption of Cr^{6+} on DSC. The three isotherm constants (A, B, and g) of the Redlich-Peterson isotherm model were also calculated using non-linear regression analysis. The correlation coefficients obtained were comparable to the Langmuir and Freundlich equations, indicating that the Redlich–Peterson isotherm can be representative of the data obtained from the adsorption of Cr^{6+} on DSC. According to the R^2 values, the Temkin isotherm can also characterize the equilibrium adsorption data. However, this isotherm appeared to be less suitable than both the Koble-Corrigan and Redlich-Peterson isotherm models. The results using the D-R isotherm indicated that the D-R model had a poorer fit to the experimental data compared to the Langmuir, Freundlich, Koble-Corrigan, and Temkin isotherm models. The values of E (mean free energy) were also calculated and were found to be in the range of ion-exchange mechanisms, indicating that the adsorption process of Cr^{6+} ion onto DSC was physisorption. The results also showed that the generalized adsorption isotherm represented the equilibrium data reasonably well. The results showed that most of the tested isotherm models fitted well to the experimental

data obtained for the adsorption of Cr^{6+} on DSC. Only the Dubinin-Radushkevich isotherm showed less agreement with the experimental data obtained.

The removal of poisonous Pb (II) from wastewater by different low-cost abundant adsorbents, *e.g.* rice husks, maize cobs, and sawdust was investigated, and the equilibrium adsorption capacity of adsorbents used for lead were measured and extrapolated using linear Freundlich, Langmuir, and Temkin isotherms (Abdel-Ghani *et al*. 2007). The experimental data were found to best fit the Temkin isotherm model.

Biosorption of chromium using suspended and immobilized cells of *Rhizopus arrhizus* was studied by evaluating the physicochemical parameters of the solution such as initial chromium ion concentration in both batch and packed bed reactor. The Langmuir, Freundlich, and Redlich-Peterson adsorption isotherm models were used in the equilibrium modeling. The Freundlich and Redlich-Peterson adsorption isotherm models were found to fit accurately with the experimental data (Preetha and Viruthagiri 2007b).

A need for further comparative evaluation of different isotherm models

Based on the discussion in the foregoing section, it is clear that data from metal sorption studies can be well fitted to a large number of different isotherm models. These models consider various aspects of the problem, including surface characterisitcs of the sorbent, affinity between sorbate and sorbent, potentiality of the sorbent, and the nature of the sorption process. However, two of the earliest models, those of Langmuir and Freundlich, continue to dominate the attention of the majority of researchers. This situation suggests that there may be important opportunities for researchers to compare the goodness of fit of existing or newly generated data to a wider variety of the available isotherm models, as outlined in this article. A goal of such efforts can be to determine which of the more recently developed models offers sufficient benefits in terms of fitting accuracy and mechanistic insights to justify their more frequent usage, with some emphasis placed on making the methods available to engineers in a user-friendly format.

CHEMICAL FACTORS AFFECTING SORPTION

Chemical Complexation

The concept of chemical complexation presupposes that there will be a site-specific interaction between particular kinds of metal ions and functional groups at the sorbate surface (Fourest and Volesky 1996; Kim *et al*. 1998; Merdy *et al*. 2002; Vijayaraghavan and Yun 2008; Lawrance 2010). Based on such concepts, some authors (Paagnanelli *et al*. 2005b; Zhang *et al*. 2005; Lodiero *et al*. 2006; Valex *et al*. 2006) have advocated an approach in which chemical complexation, rather than ion exchange, is used to account for adsorbed amounts as a function of solution concentrations.

Metal specificity

Some of the most cogent evidence in support of a chemical complexation concept of metal ion sorption consists of a dependency of molar adsorption capacities on the identity of the tested metal ion. Such differences have been widely reported, and the following citations are representative (Qadeer *et al*. 1996; Puranik and Paknikar 1999;

Schiewer and Wong 1999; Kogej and Pavko 2001; Iqbal *et al*. 2002; Pardo *et al*. 2003; Chauhan *et al*. 2005b; Kobya *et al*. 2005; Saito and Isogai 2005; Romera *et al*. 2006; Zhang and Banks 2006; Afkhami *et al*. 2007; Arslan and Pehlivan 2008; Chen and Wang 2008b; Krishnani *et al*. 2008b). According to theories of chemical complexation (Lawrance 2010), differences in the ability of a surface site to bind different metals are often attributed to matching the radius of the metal ion, as well as the symmetry (octahedral, *etc*.) of its valence electron orbitals, to the positions of the surface-bound atoms (*e.g.* carboxylate groups) at the site of adsorption.

Hard and soft ions

The concept of hard and soft ions (Pearson 1963) has been used effectively to explain why certain metal ions tend to have greater affinity for certain types of sorbent surfaces (Avery and Tobin 1993; Brady and Tobin 1995; Chen and Wang 2007b,c, 2010; Gadd 2009). To summarize, ions that are called "soft" are those that have relatively loosely held, polarizable outer electrons, so that greater contributions of covalent character can be expected in their interaction with surface sites. Examples include lead and mercury. By contrast, "hard" ions have more closely held, less polarizable outer electrons, so that their interactions are more simply dominated by electrostatic factors. Nickel is a prime example. In some cases the molar amounts of adsorbed ions have been shown to be related to the ionic radius of the metal (Chen and Wang 2007b,c). Avery and Tobin (1993) observed that soft ions can be expected to favor sites containing S and N atoms, whereas hard ions can be expected to favor sites with oxygen atoms.

Demonstration of Metal Ion Interaction with Functional Groups

A large number of studies have provided evidence in support of metal ions interaction with specific functional groups at the substrate surface. Many authors have used shifts in the maxima of infrared light adsorption as evidence for specific interactions (Ashkenazy *et al*. 1997; Guibaud *et al*. 2003; Ahluwalia and Goyal 2005a; Deng and Ting 2005a; Ahalya *et al*. 2006, 2007; Chen and Yang 2006; Murphy *et al*. 2007; Arief *et al*. 2008; Li *et al*. 2008; Bakir *et al*. 2009; Garcia-Reyes *et al*. 2009; Iqbal *et al*. 2009a; O'Connell *et al*. 2010). NMR spectra also have been used to substantiate the involvement of specific chemical sites in the binding of metal ions (Araujo *et al*. 2007). One question that has not been completely resolved by these investigations is whether the observed shifts in IR absorbance maxima might be an effect, rather than indicating a cause of metal ion binding. This lack of certainty regarding cause/effect is because anything that changes the electron density significantly near a functional group can be expected to have an impact on the energy content of the associated covalent bonds. It follows that the presence of a metal ion in a fixed position on a substrate surface will change the IR spectra associated with adjacent functional groups, whether or not they each have a positive effect on the bonding mechanism.

In particular, IR evidence has supported the participation of carboxylate groups in metal ion binding (Ahluwalia and Goyal 2005a; Gardea-Torresdey *et al*. 2002). Several studies have supported such a conclusion by selectively converting the existing carboxylic acid groups to another form and displaying a substantial decrease in metal uptake (Beveridge and Murray 1980; Fourest and Volesky 1996; Ashkenazy *et al*. 1997;

Kapoor and Viraraghavan 1997; Tiemann *et al.* 1999; Romero-Gonzalez *et al.* 2001; Bai and Abraham 2002; Tiemann *et al.* 2002; Chubar *et al.* 2003; Meunier *et al.* 2003b; Sheng *et al.* 2004b; Southichak *et al.* 2006b; Suksabye *et al.* 2007; Iqbal *et al.* 2009b; Murphy *et al.* 2009a). Chen and Wang (2008a) and Park *et al.* (2008d) used X-ray methods to display evidence of oxygen atom participation in the binding of zinc to yeast cell biomass. Other authors have used the pH-dependency of adsorption as contributing evidence to support the importance of carboxylic acid groups in metal ion binding (Tiemann *et al.* 2000; Malik *et al.* 2002; Guo *et al.* 2008). A related approach, involving immersion calorimetry and shifts in pH, has been pioneered by Lopez-Ramon *et al.* (1999).

Effects of pH on Metal Ion Sorption

Although a great deal of attention has been paid to dissociation constants associated with different kinds of acidic groups at sorbent surfaces, inadequate attention has been paid to the simultaneous effects of pH on the ionic species of metal ions that are present in the bulk solution.

Close inspection of the next to last column in Table A indicates a common theme for the effects of pH on adsorption of metal cations. Authors of several studies have indicated that adsorption is favored by "increasing pH," but only up to a certain limit. The trend with increasing pH (i.e., 3 to 6) is generally explained by increasing dissociation of carboxylic acid groups on the cellulosic substrate, which results in an increasing ion exchange capacity of the material. The climactic upper end of a typical curve of adsorptive capacity *vs.* pH is generally understood to entail an equilibrium between the soluble hydrated metal ion and a corresponding insoluble neutral hydroxide species (Chang *et al.* 1997; Leyva-Ramos *et al.* 1997; Schneider *et al.* 2001; Dastgheib and Rockstraw 2002a; Mohan and Pittman 2006; Sciban *et al.* 2006b; Sheng *et al.* 2007; Demirbas 2008). In addition, certain ions tend to form polynuclear species as they progressively interact with OH$^-$ ions in solution (O'Connell *et al.* 2010).

Essentially the opposite pH dependency is often observed when evaluating the adsorption of Cr(VI) species onto biosorbent surfaces. As shown by many entries in Table A, the highest sorption of Cr from Cr(VI)-containing solutions is generally found within a pH range of about zero to 2 (see, for instance Gupta *et al.* 1999). Under such conditions the cellulosic carboxyl groups are expected to be fully protonated, thus minimizing any electrostatic barrier to sorption of negative chromate ions.

Redox Effects

Changes in the valence state of the metal

During the past decade significant progress has been achieved in understanding the adsorption of metal ions that are prone to changes in their oxidation state. Though chromium has received the greatest attention, valence changes also can play a role in the removal of platinum (Chen *et al.* 2007), mercury (Lloyd-Jones *et al.* 2004; El-Shafey 2010); copper (Chandran *et al.* 2002), gold, silver, and palladium (Cox *et al.* 2005) from aqueous solution. The following researchers have reported evidence for Cr(VI) reduction to Cr(III) accompanying its adsorption (Raji and Anirudhan 1997; Selomulya *et al.* 1999; Han *et al.* 2000; El-Shavey and Canepa 2003; Deng and Ting 2005c; Deng *et al.* 2006;

El-Shafey 2005; Gao *et al*. 2005; Park *et al*. 2004b, 2005b,c, 2006a, 2007a,b, 2008d; Murphy *et al*. 2009b; Suksabye *et al*. 2007, 2009). In certain cases, reduction from Cr(VI) to Cr(V) was observed (Suksabye *et al*. 2009). The reduction of Cr(VI) to Cr(III) has been found to proceed under highly acidic conditions (*i.e.*, pH between 1 and 3) (Candela *et al*. 1995). The reduction of metal ions by microbes has also been demonstrated as a mechanism of metal removal from water (Chandran *et al*. 2002).

Changes in the valence state of the substrate

Research has confirmed an expected balance between reduction and oxidation whenever there is a valence change of a metal during the course of its adsorption. In other words, if the metal is reduced, something else in the system must be oxidized. Several researchers have observed oxidation of surface groups of a cellulose-based sorbent material when reductively adsorbing various precious metals or hexavalent chromium (Cox *et al*. 2005; Park *et al*. 2005a,b, 2006c, 2007b, 2008b; Elangovan *et al*. 2008a; Murphy *et al*. 2009b). Oxidation of the substrate as part of the adsorption mechanism is consistent also with the form of the rate expression that governs the uptake of chromium (Park *et al*. 2005c). Further support for this type of mechanism was provided by Praghakran *et al*. (2009), who showed that the rate of reductive sorption of Cr(VI) was highly dependent on the nature of the substrate, with superior results being achieved using coffee dust. Studies involving the blocking of specific sites showed that both carboxyl goups and amino groups can participate in the reductive adsorption process of Cr(VI) (Park *et al*. 2005d). In the case of chromium (VI) adsorption, it can be considered highly fortuitous that oxidation of the surface often increases the number of carboxylate groups, which are well suited to the bonding of the positively charged Cr(III) ions that result from the process.

Figure 4 provides a schematic of some of the concepts just described. The question mark at the left of the figure represents an intial challenge in accounting for the adsorption of a negative ion onto a predominantly negative cellulose-based material. The rightward arrow represents a combined process in which (a) groups at the substrate surface (or in the bulk phase) are oxidized, (b) the chromium(VI) is reduced to Cr(III), and (c) the positively charged Cr(III) ion is simultaneously or sequentially bound to negative sites at the substrate surface.

A worthy question for future research is to explore whether intentional changes to the state of oxidation of a substrate can be used in order to induce subsequent changes in valence of metal ions, thus facilitating their collection. Such a proposal is consistent with work reported by Berenquer *et al*. (2009) who applied galvanic reduction and oxidation to activated carbon. Changes in the surface groups were observed, similar to what can be achieved by treatment with reducing agents or oxidizing agents. However, it is not yet known whether related approaches could facilitate the conversion of, say, Cr(VI) to the less toxic and more adsorbable Cr(III) form. Such observations raise questions as to whether surface sites also could be manipulated by selecting anaerobic *vs.* aerobic conditions of digestion (Joseph *et al*. 2009).

Fig. 4. Pictorial concept of combined reduction and adsorption of Cr(VI) with simultaneous oxidation of groups at the surface of a cellulosic substrate

Fig. 5. Illustration of one strategy for regeneration of a biosorbant that has become partially or wholey saturated with heavy metal
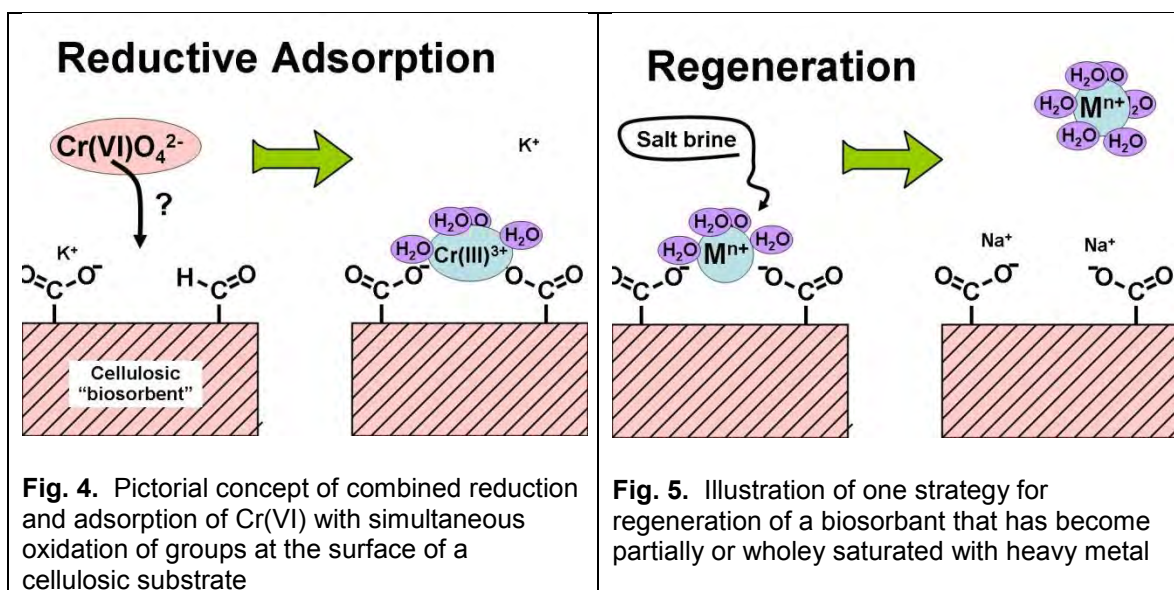
Reversibility of Metal Binding

In order to optimize conditions of regeneration or disposal, it is important to understand what circumstances can lead to the reversal of metal sorption onto cellulose-dried surfaces The most straightforward way to encourage metal ions to go back into solution is to replace those ions with a large excess of something else. Hydrochloric acid is the most commonly specified reagent, as indicated by the many entries in the next to last column of Table A. Regeneration, however, also has been achieved by strong base, or less commonly by a concentrated salt solution. Many studies have demonstrated restoration of a majority of the original sorption capacity after the restorative treatment. Increases in adsorption capacity, relative to the original capacity, have been observed in some cases (Chang *et al*. 1997).

Figure 5 illustrates one way that an ion-exchange material can be regenerated. The left-hand part of the figure depicts a metal ion bound in bi-dentate fashion to a pair of carboxylate groups at a surface. Addition of salt brine (or acid, NaOH, *etc*.) causes the target metal(s) to be released into the brine, while sodium ions are left weakly associated with the carboxylate groups on the sorbate.

CLOSING COMMENTS

Any review of such an active and multifaceted field as biosorption of metals is bound to leave out information or to oversimplify critical details. Fortunately, as noted in the Introduction, subtopics of the field have already been reviewed, often with a particular focus that may be of interest to readers (see Table 1).

The explosive growth in publications in this area, with expected faster pace of technological developments to come, may still be difficult to grasp. Combinations of biomass types, chemical or thermal modificationis, and target metals are often being studied in relative isolation and often without a strong theoretical justification for the combinations of factors that are compared. Some studies appear to just apply well-

known methods to different species of biomass or different metal ions. The scene sometimes can be compared to a wild frontier, in which the first researcher to generate, say, a Langmuir isotherm, can lay claim to having found something new.

The field of study will hopefully continue to mature during the coming decades, and in our opinion two kinds of studies would be very valuable to lead the way into the future. On the one hand, there is a need for mechanistic studies that deal more cogently with the molecular mechanisms, including such issues as binding sites, valence states, coordination chemistry, and the speciation of metals in solution. On the other hand, there need to be a life cycle analysis, considering the wasteproducts of metal remediation operations.

A Need for Studies Related to Proteinacious Binding Sites

One apparent gap in research that can be expected to attract increasing attention during the coming decade concerns the use of engineered proteins for advanced adsorption technologies. A study by Kostal *et al*. (2005) points the way in this direction, showing how biotechnological and nanotechnological principles can be applied. A study by Vinopal *et al*. (2007) showed that certain peptide sequences have highly specific affinity for certain metal ions. In principle, the sorptive properties of enzymatic materials could be optimized by genetic manipulation. Once the optimized biomaterial has been created, the genes could be inserted into a suitable organism to produce suitable quantities for the needed application. It is possible that such proteinaceous biosorbent products could be supported on cellulosic scaffolds, facilitating their use in either batch-type or column-type treatment schemes.

A Need for Application of Nanotechnology Concepts

Given the major attention to nanotechnology during the past decade, there has been a notable lack of consideration of related concepts in the case of biosorption. In particular, the concept of self-assembly (Ninham and Lo Nostro 2010) should be considered relative to the manner in which adjacent hydrated metal cations arrange themselves in various instantaneous configurations at a substrate surface. Attention also should be focused on the nucleation of colloidal precipitates of metal hydroxides as the pH is raised in the neighborhood of a solubility limit (Chang *et al*. 1997; Leyva-Ramos *et al*. 1997; Schneider *et al*. 2001; Sciban *et al*. 2006b; Demirbas 2008). Presumably such precipitated metal hydroxides could either remain as a colloidal suspension or it may be adsorbed onto the biosorbent material. In the latter case, the mechanisms of adsorption may be entirely different from those governing adsorption of the cationic forms of the same metals.

Another aspect of nanotechnology involves accessibility. Metal-binding sites at the surfaces of biomass samples can be effective only if the metal ions are able to reach them. Mesopores in the biomass may have closed up irreversibily at some point due to an uncertain history of the drying of the material (Stone and Scallan 1966). Such effects have the potential to explain the huge ranges (typically three orders of magnitude or more) that have been reported by different researchers for the metal-uptake capacities of nominally similar biomass samples. Future studies need to address these issues science at the nanoscale level.

A Need for Life Cycle Analysis Research

An article by Chojnacka (2010) has helped to define the scope of some needed research related to the life cycle of bioremediation. For a healthy ecosystem it is necessary to account not only for biosorption (which mainly involves dead biomass), but also for bioaccumulation, which involves ingestion and retention within living organisms. The two phenomena can be expected to interact in complex ways, keeping in mind that some metals are prone to building up over time to toxic levels in living tissues.

As was noted in the introduction, there has been inadequate research towards the merits of landfilling or land application as an alternative strategy for dealing with spent cellulose-based sorbent material. Though it is reasonable to be concerned with leachate that contains metals, research is needed to determine whether the metal-binding capacity of the cellulosic material is sufficient such that the resulting concentrations of soluble species remain in a generally safe or beneficial range, especially in the case of metals that can be considered as essential minerals when they are present at low levels. By contrast, the most widely used regeneration schemes require major shifts in pH, leading to the requirement that the pH be adjusted prior to discharge of the water, which will then have a higher level of salinity. Another potentially beneficial strategy that deserves exploration is the incineration of spent biosorbent, making it possible to concentrate the collected metals in the resulting ash. Though there is potential to make use of biosorption as a fuel source, there is need to be concerned about the energy requirement for evaporation of water, as well as measures to reduce airborne particulates.

While there is clear evidence that bio-sorption could be a viable alternative for the remediation of contaminated aquifers, there are several decision factors that companies must consider when selecting an appropriate treatment technology. These factors include but are not limited to treatment cost, volume of contaminated material to be treated, treatment time, site location, the complexity of the target pollutant, and the surrounding water quality. Technologies that merely change the form of toxic wastes, such as in adsorption processes without proper removal, may lead to future problems and costs. Therefore, effective remediation treatment technologies must consider the entire fate of wastes over a longer period. It would be easy to say that these factors are independent. However, it's more likely that the decision complexity is increased due to the interdependency of these factors. Further, companies that would like to select in-situ soil remediation options must weigh that approach against dig-and-haul operators, who remove contaminated soil to landfill sites at a possibly cheaper cost. Consequently, the decision to utilize bio-sorption processes, regardless of whether it is a proven technology, is a complex decision.

A Need for Non-Selective Sorption

The mining industry has provided early stimulus for research into metal removal technology. Perhaps as a consequence, many of the studies cited in this review dealing with simultaneous adsorption of more than one type of metal contain the implicit assumption that highly specific adsorption of certain classes of metal may be advantageous. However, it would appear that the multi-component nature of typical biomass samples renders them more suitable, in principle, for a significantly different application, the removal of a wide range of pollutants simultaneously. Biosorbents have

the potential for use during polishing treatments of both freshwater and wastewater. One can expect that the public will become increasingly aware, of the importance of metal ion control in both tap water and in water discharged to the environment. By contrast, in cases where highly selective sorption of certain metal ions is required, perhaps as a preliminary step in the isolation of pure metals or compounds, it would make sense to employ relatively pure chelating agents. As one option, chelating functional groups can optionally be bound to cellulosic supports, depending on the needs of the process.

Another area that requires research attention is the use of cellulosic materials to remove not only heavy metals, but also organic toxins. It is reasonable to expect that various industrial outfalls and municipal wastewater streams may contain both heavy metals and organic contaminants. The subject of biosorption of organic materials such as dyes will be addressed in Part 2 of this series.

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APPENDIX

Table A. Tabulation of Research Publications for Removal of Metal Ions from Dilute Aqueous Solution by Use of Raw or Modified Lignocellulosic Materials

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
TREE MATERIALS						
WOOD						
Hardwood						
Fagus (_b_eech)	Sawdust	Cr(VI)	16	.031	80 min. optimum at pH 1.0; Langmuir fit	Acar and Malkoc 2004
Mangifera indica	Sawdust	Cu(II)	10	.016	Langmuir fit ; regen. with acid	Ajmal et al. 1998
Quercus (oak sawdust)	HCl	Cu(II), Ni(II), Cr	3.2,3.3, 1.7	.05,.06, 0.033	Pseudo 2nd order rate; Langmuir fit	Argun et al. 2007
Neem biomass		Zn(II)	140	2.1	Best pH 4-5; 2nd order rate; Langmuir fit	Arshad et al. 2008
Beech, linden, Poplar sawdust		Cu(II)	__	__	Best pH 3.5-5; ion exchange; Langmuir fit	Bozic et al. 2009
Walnut sawdust		Cd(II), Ni(II)	__	__	Pb(II) and Cd(II) adsorbed in preference to Ni(II); ion exchange ; Langmuir fit	Bulut & Tez 2007b
Rosewood	CH_2O	Cr(VI)	15-23	.29-.44	Best pH 3; Treatment increased uptake; first-order rate	Garg et al. 2004
Betula sp.		Cu(II)	5	0.079	Sawdust less effective than algal biomass	Grimm et al. 2008
Casia f biomass		Ni(II)	20-173	.34-2.9	Best pH 6; bark more effective than pods, stem, leaves; smaller particles more effective; 2nd order rate; Langmuir fit	Hanif et al. 2007
Aspen	Bleach, hydrolys.	Cu(II)	0.9-2.2	.01-.04	Higher pH favored to 5.5; Langmuir fits; Bleached>untreated>hydrolyzed>>lignin; carboxyl groups key; competition (Ca, Na, Al); ion exchange & complexation	Huang et al. 2009
Papaya	Hybrid w fungal	Cd(II)	18, 142	.16,1.3	The hybrid adsorbed much more than the sum of the components; 2nd order rate; Langmuir fit.	Iqbal et al. 2007

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Beech sawdust	Aromatic CH_2O res	Cd(II), Zn(II), Co(II), Ni(II)	__	__	Mutual sorption binary mixtures; 2.4 meq/g; regenerated with HCl	Miyauchi et al. 2007
Papaya		Cu(II), Cd(II), Zn(II)	__	__	Best pH 5; 2nd order rate; Langmuir fit; regen. with HCl	Saeed et al. 2005a
Oak, locust	CH_2O, NaOH	Cu(II), Zn(II)	4-6, 4-7	.06-.09, .06-.11	NaOH boosted adsorption; CH_2O did not	Sciban et al. 2006a
Poplar		Cu(II), Zn(II), Cd(II)	4-6, 6, 0.7	.06-.09, .09,.01	Multilayer adsorption fit; hindrance from other ions	Sciban et al. 2007
Carpenter's dust		Cr(VI)	40	0.77	Best pH 2; Langmuir fit	Sharma & Forster 1994a
Maple sawdust		Ni(II)	__	__	Higher pH favored to 5; chelation ion exchange; regen. with acid	Shukla et al. 2005
Maple sawdust		Cu(II)	61	0.96	Ion exchange	Yu et al. 2000
Sawdust		Pb(II), Cu(II)	1-3,1-2	.01,.03		Yu et al. 2001
Maple sawdust		Cr(VI)	5	0.10	Tested at pH 6; Langmuir fit; ion exchange	Yu et al. 2003
Softwood						
Cryptomeria jap		Cr(VI)	72-91	1.4-1.6	Tests at pH 3; Langmuir fit	Aoyama et al. 2004
Spruce sawdust	Phosph-orylated	Pb(II), Cd(II), Ni(II	224, 56, 26	1.08, .50,.44	Pb > Cd > Ni	Holan & Volesky 1995
Spruce sawdust		Cd(II), Cu(II), Ni(II), Pb(II), Zn(II)	__	__	2.1 to 4.3x10(-2) meq g(-1) ; ion exchange; calcium solution can be used for regeneration	Marin & Ayele 2002
Spruce sawdust		Cd(II), Cu(II), Ni(II), Pb(II), Zn(II)	__	__	Column experiments; competition	Marin & Ayele 2003
Juniper fibers	NaOH	Cd(II)	9-30	.08-.27	Pseudo 2nd order rate; Langmuir fit	Min et al. 2004
Juniper wood		Cd(II)	3	0.027	The bark performed much better	Shin et al. 2007
Pinus sylvestr.		Cd(II), Pb(II)	9, 10	.08, .05	Best pH 5.5; pseudo 2nd order rate; Langmuir fit; pore diffusion control; ion exchange;	Taty-Costodes et al. 2003

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Unspecified						
Sawdust, unsp.		Cr(VI)	9.6	0.18	Best pH 4.5-6.5; 2nd order rate; Langmuir fit; exothermic	Baral et al. 2006
Sawdust		Cr(VI)	16	0.31	Best pH 2; Langmuir fit	Dakiki et al. 2002
Sawdust, mill		Cu(II)	__	__	Langmuir fit; ion exchange	Larous et al. 2005
Wood		Cu(II), Pb(II)	3, 8	.05,.04	Citric acid treatment increased adsorption by about 10X; 2nd order rate	Low et al. 2004
Cellulose beads		W, Mo, V, Ge, Sb oxoanions	—	—	Tungstate, molybdate adsorption successful; higher pH favored to 5.5	Mistova et al. 2007
Wood pulp		Na(I), Mg(II), Ca(II), Mn(II), Ba(II)	—	—	Ion exchange selectivity can be calculated	Rudie et al. 2006
Three sawdusts		Cu(II)	—	—	Softwoods effective at low conc; hardwoods effective at high conc.	Sciban & Kalasnja 2004a
Poplar, various sawdusts		Cu(II)	2-3	.03-.05	Tests at pH 4; Langmuir fit; higher pH favored for Cu(II), Zn(II), Ni(II), Cd(II)	Sciban & Kalasnja 2004b
Oak sawdust, Black locust SD	NaOH	Cu(II), Zn(II)	4-6, 4-7	.06-.09, .06-.11	NaOH treatment boosted Cu uptake 2.5-5X; Ni 15X; also reduces further leaching	Sciban et al. 2006b
Sawdust, Rice husk, Coir pith		Cr(VI)	1.5, 0.6, 0.2	0.029, 0.012, 0.004	Freudlich fits	Sumathi et al. 2005
Mechan. fibers						
Newsprint		Cu(II)	30	0.47	HIgher pH best ; 2nd order rate; Langmuir fit ; endothermic	Chakravarty et al. 2008
Kraft fibers						
Kraft pulp fibers		Fe(III), Cr(III), Pb(II), Cd(II)	—	—	Metal adsorption ↑ with ↑ pH	Abdel-Aal et al. 2006
Unbleached kraft		Ca(II)	1-2	.02-.05	Donnan theory with carboxyl and phenol groups; higher pH favored; bleaching reduces Ca uptake, especially at high pH	Duong et al. 2004

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
BARK						
Pine bark, (also cones, needles)		Cd(II), Cu(II), Ni(II), Pb(II)	9-38, 6-16, 3-13, 10-29	.08-.34, .09-.25, .05-.22, .05-.14	Higher pH favored to 7; smaller particles higher uptake; binary competition; adsorption mainly in cell wall ; ion exchange; free radicals play role, Langmuir fit; partial regen. with HCl	Al-Asheh & Duvnjak 1998
Larch bark		Cr(VI)	31	0.60	Tests at pH 3; Langmuir fit	Aoyama & Tsuda 2001
Pine bark	$Fe^{2=}$, H_2O_2	Cd(II)	10-13	.09-.12	Results depended on the ratio of Fe^{2+} to H_2O_2. 1st order rate; Langmuir fit; exothermic	Argun & Dursun 2008a
Pine bark	HCl	Cu(II)	__		Best at pH 5	Argun et al. 2005a
Pine bark		Ni(II)	21	0.36		Argun et al. 2005b
Pine bark	Various	Cd(II), Pb(II), Cu(II), Ni(II)	12-20	.11-.18	NaOH > Fenton reag. > polymerization	Argun et al. 2009
Cork		Cu(II), Zn(II), Ni(II)	40, 50, 20	.63,.76, .34	Higher pH better; ion exchange less important for Zn(II); role of carboxylate groups	Chubar et al. 2003
Pinus radiata	CH_2O + H_2SO_4 or NNO_3	U	37	0.16	Treatments enhanced uptake, with nitric acid preferred; formaldehyde prevented color bleed	Freer et al. 1989
Tree barks		Cu(II), Cd(II), Cr(III), Fe(II), Fe(III), Pb(II), Hg(II), Ni(II), Zn(II)	22-44, 47, 0.4, 35, 19, 90, 50, 33-43, 44	.35-.69, .42,.01, .63,.34, .43,.25, .56-.83, 0.67	Uniform metal distribution; binding to acidic sites; higher pH favored; regen. with acid; inverse correlation of molar uptake with atomic radius; metal recovery by pyrolysis	Gaballah & Kilbertus 1998
Eucalyptus		Cd(II)	15	0.13	Pseudo 2nd order rate; Langmuir fit	Ghodbane & Hamdaoui 2007
Eucalyptus		Hg(II)	33	0.16	Pseudo 2nd order rate; Langmuir fit	Ghodbane & Hamdaoui 2008
Picea, pinus, larix, pseudotsuga, tectona, afzelia	CH_2O	Pb(II), Zn(II), Cr(III), Fe(II), Cu(II)	__	__	Pectins and tannins important; grain size; regeneration with HCl	Gloaguen & Morvan 1997

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Azadirachta indica		Zn(II)	33.5	0.51	Particle size important; best pH 6; pseudo 2nd order rate; Langmuir fit;	King et al. 2008a
Guava		Hg(II)	3.4	0.016	Best pH 9; 2nd order rate; Freundlich fit	Lohani et al. 2008
Cork powder		Cr(III)	6.3	0.21	Tested at pH 4; Langmuir fit	Machado et al. 2002
Mango & neem		Cs(I)	__	__	First order rate; Freundlich fit; endothermic; irreversible	Michra et al. 2007
Pine bark	Pelletize, citric acid	Cu(II), Zn(II), Cd(II), Ni(II)	75, 53, 50, 27	2.1,.81, .44,.46	Langmuir fit	Oh & Tshabalala 2007
Pine bark, tannins		V(V), Re(VII), Mo(VI),Ge(6), As(V), Cd(II), Hg(II), Al(III), Pb(II), Fe(II), Fe(III), Cu(II)	346	0.78	Eval at pH 2; bark was more effective than the tannins from the bark	Palma et al. 2003
Eucalyptus	CH$_2$O	Cu(II), Cr(III), Cd(II), Ni(II)	166,37, 252, 44	2.6,.71, 1.2,.75		Saliba et al. 2002b
Eucalyptus bark & other materials		Cr(VI), Cr(III), Mg(II), Ca(II)	45	0.87	Eucalyptus bark best for Cr(VI) removal; best pH for Cr(VI) was 2; Freundlich fit;	Sarin & Pant 2006
Coniferous (15)		Cd(II)	10-14	.19-.27	Barks varied considerably for different ions; Freundlich fit	Seki et al. 1997
Juniper bark		Cd(II)	10	0.19	Higher pH favored to 6; bark uptake 3-4 X higher than then wood; approximate stoichiometry with Ca release	Shin et al. 2007
Mango & neem		Hg(II), Cr(III),	172, 35	0.86, 0.67	Hg(II) sorbed, but not Cd(II); first order rate; Freudlich fit; competition by anions & cations	Tiwari et al. 1999
Cork, yohimber		Cu(II), Ni(II)	3-8, 4-8	.05-.13, .07-.14	Best pHs 6-7; salt competition; Langmuir fits; regen. with HCl	Villaescusa et al. 2000
Bark	CH$_2$O	Cd(II), Cu(II), Pb(II), Zn(II), Ni(II), Co(II), Mn(II	28, 18, 68, 2, 2, 2, 2	.25,.29, .33,.03, .03,03, .04	Formaldehyde treatment reduced color leaching; ion exchange mechanism	Randall et al. 1974

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
FOLIAGE						
Eucalyptus leaves		Cu(II), Zn(II), Cd(II), Pb(II)	__	__	Ratio, pH, contact time, concentration; 2 hr to max. adsorp.; effective for mixed systems	Abdel-Ghani et al. 2008
Conifer needles		U(VI), Cu(II), Cd(II)	40-90, 4-12, 8-18	.17-.38, .06-.19, .07-.16	$UO_2^{2+}>>Cu^{2+}>>Cd^{2+}=Zn^{2+}>Co^{2+}=Ni^{2+}>Mn^{2+}$	Aoyama et al. 1991
Conifer needles		Cr(VI)	6.3	0.12	Tests at pH 3; Freundlich fit	Aoyama et al. 1999
London plane tree		Cr(VI)	68-76	1.3-1.5	Tests at pH 3; Langmuir fit	Aoyama 2003
Yerba mate leaf stems		Cd(II)	4.8	0.042	The pure lignin sample showed higher uptake; Langmuir fit	Basso et al. 2004
Pine needles		Cr(VI)	22	0.42	Best pH 2; Langmuir fit	Dakiki et al. 2002
Palm flower	Acid	Cr(VI), Cr(III)	7, 6	.13,.12	2nd order rate; acid treatment helped Cr(VI) uptake, hurt Cr(III)	Elangovan et al. 2008b
Rubber leaf		Cu(II)	8.4	0.13	Langmuir fit; ion exchange/complexation	Hanafiah & Ngah 2009
Petiolar sheath		Pb(II), Ni(II), Cd(II), Cu(II), Cr(III), Zn(II)	11, 7, 11, 8, 5, 6	.05,.12, .10,.13, .10,.09	$Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cr^{3+}$; best pH 4; regenerable	Iqbal et al. 2002
Petiolar sheath		Cd(II), Cu(II), Zn(II)	See above	See above	Cd > Cu > Zn; Langmuir fit; regenerable	Iqbal & Saeed 2002
Teak leaves		Cu(II)	95	1.5	Best pH 5.5; pseudo 2nd order rate; Langmuir fit	King et al. 2006
Syzygium cumini		Pb(II)	32	0.15	Langmuir fit	King et al. 2007
Syzygium cumini		Zn(II)	36	0.55	Langmuir fit	King et al. 2008b
Tectona grandis		Cu(II)	15	0.24	2nd order rate; Langmuir fit; exothermic	Kumar et al. 2006a
Tectona grandis		Zn(II)	16	0.24	2nd order rate; Langmuir fit; exothermic	Kumar et al. 2006b
Rosa c. petals	NaOH	Pb(II), Zn(II)	88, 74	.42,1.1	Best pH 5 ; pseudo 2nd order rate; Langmuir fit	Nasir et al. 2007
Hevea b. leaf pdr		Cu(II)	9	0.14	Best pH 4-5 ; pseudo 2nd order rate ; Langmuir fit; exothermic	Ngah & Hanafiah 2008a
Hevea b. leaf pdr		Cu(II)	15	0.24	Pseudo 2nd order rate; diffusion control; Langmuir fit best	Ngah & Hanafiah 2008b

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Hevea b. leaf pdr	CH_2O	Cu(II)	8-9	.12-.14	Pseudo 2nd order rate; Langmuir fit; ion exchange/complexation; regenerate with HCl or EDTA	Ngah & Hanafiah 2009
Ficus religiosa		Pb(II), Cr(VI)	17, 6	.08,.12	Ion exchange; pseudo 2nd order rate; Langmuir fit	Qaiser et al. 2007
Ficus religiosa		Pb(II)	37	0.18	Pseudo 2nd order rate; Langmuir fit; ion exchange; regen. with HNO_3	Qaiser et al. 2009
Tobacco dust		Pb(II), Cu(II), Cd(II), Zn(II), Ni(II)	40, 36, 30, 25, 24	.19,.57, .27,.38, .41	Surface acidity; ion exchange and surface complexation; regen. with HCl	Qi & Aldrich 2008
Teak leaves		Cd(II)	30	0.27	Best pH 5.5; pseudo 2nd order rate; Langmuir fit	Rao et al. 2010
Palm frond (also bark, EFB)	NaOH	Cu(II), Zn(II)	8-14, 6-130	.13-.22, .09-2.0	Freundlich uptake ; Regeneration with NaOH, EDTA, HCl, HNO_3 ; binding sites damanged	Salamantinia et al. 2007
Beech leaves		Cd(II)	__	__	Freundlich fit	Salim et al. 1992
Saltbush, *Atriplex*		Cu(II), Pb(II), Zn(II)	68,300, 33	1.1,1.4, 0.50	Freundlich fit	Sawalha et al. 2007
4 organic wastes		Cr(VI)	3-30	.06-.58	Best pH 1.5-3; anaerobically digested biomass was more effective	Sharma & Forster 1994a
Leaf mold	Fungal decay	Cr(VI)	20-40	.38-.76	Best pH 2, 2nd order rate	Sharma & Forster 1994b
Leaf mold	Fungal decay	Cr(VI)	26	0.50	Very little reduction took place when using leaf mold; activated carbon caused reduction	Sharma & Forster 1996a
CONES						
Nordmann fir		Ni(II)	__	__	Best pH 6.5; Langmuir fit.	Aksakal et al. 2008
Pine cone	HCl	Cu(II)	__	__	Best at pH 3	Argun et al. 2005a,b
Pine cone	Fenton	Cd(II), Pb(II)	2-11, 2-10	.02-.10, .01-.05	Fenton oxidation greatly increased uptake; 1st order rate; exothermic; Langmuir fit	Argun et al. 2008
Thuja		Ni(II)	12.4	0.21	Pseudo 2nd order rate; Langmuir fit	Malkoc 2006

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Cupressus cones		Cr(VI)	119	2.3	Best pH 0.2-0.5; higher temperature favored; Langmuir fit; irreversible by NaOH, etc.	Murugan & Subramanian 2003
Thuja orientalis		Cu(II)	19	0.30		Nuhoglu & Oguz 2003
Thuja orientalis		Cr(VI)	49	0.94	Best pH 1.5	Oguz 2005
Pinus sylvest		Cu(II), Zn(II)	25, 16	.39,.24	2nd order rate; Langmuir fit	Ucun et al. 2009
NUT SHELLS						
Coconut, almond, ground nut, walnut	-	Cr(VI),	90+, 2.4-22, 6, 2.3-18	1.7+, .05-.42, .12, .04-.35	Tamarindus seed outperformed nut shells; lower pH favored; Langmuir fits	Agarwal et al. 2006
Walnut, hazelnut, almond shells	-	Cu(II)	4-7	.06-.11	Best pH 6; chelation & ion exchange	Altun & Pehlivan 2007
Coconut coir	Amino, PAM graft, Fe(III)	Cr(VI)	143	2.8	The grafted, Fe^{3+}-treated coir adsorbed Cr(VI); Pseudo 2nd order rate; Langmuir fit; NaOH regeneration	Anirudhan et al. 2010
Brazil nut shells		Cd(II), Ni(II)	19	0.17	Sorbents favored different metals; Langmuir fit	Basso et al. 2002a
Hazelnut, almond		Ni(II), Cd(II), Pb(II)	1.6,0.9, 3.5,1.5, 4.4,2.5	.03,.02, .03,.01, .02,.01	Selectivity: Pb(II) > Cd(II) > Ni(II); pseudo 2nd order rate ; ion exchange ; Langmuir fit ; exothermic	Bulut & Tez 2007a
Hazelnut shells		Cd(II), Zn(II), Cr(III), Cr(VI)	5, 3, 2, 18	.04,.05, .04,.35	Best pH 2.5-3.5 for Cr(VI); Langmuir fits; HSAB model; anionic removal mechanism	Cimino et al. 2000
Almond shell		Cr(VI)	11	.21	Best pH 2; Langmuir fit	Dakiki et al. 2002
Coconut coir		Cr(VI)	6-27	.12-.52	Phenolic sites; organic matter oxidation; recovered by calcination	Gonzalez et al. 2008
Coconut copra		Cd(II)	1.8-4.5	.02-.04	Higher pH favored to 5; Langmuir fit; exothermic	Ho & Ofomaja 2006a
Coconut copra		Pb(II)	36-47	.17-.23	Langmuir fit	Ho & Ofomaja 2006b
Coconut fiber	Unmod, thiolated	Hg(II), As(III), Pb(II)	__	__	Pb (II) > Hg (II) > As (III); seudo 2nd order rate; particle diffusion model	Igwe et al. 2008

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Pecan shells	Oxygen level	Cu(II)	83	1.30	Oxygen addition increased affinity but decreased yield of carbon	Klasson et al. 2009
Acorn		Cr(VI)	31.5	0.60	Best pH 2; pseudo 2nd order rate; Langmuir fit	Malkoc & Nuhoglu 2007a
Acorn		Cr(VI)	12-63	.23-1.2	Best pH 2; smaller particles increased uptake;	Malkoc et al. 2006a
Coir pith	CTAB	Cr(VI)	76	1.5	Best pH 2; 2nd order rate; slight proportion of reduction; Langmuir fit	Namasivayam & Sureshkumar 2008
Coir pith	CTAB	Mo(VI)	58	0.60	Best pH 3; 2nd order rate; Langmuir fit	Namasivayam & Sureshkumar 2009
Coconut copra		Cd(II)	1.7	0.015	Higher pH favored to 5.5; pseudo 2nd order; ion exchange equilibria	Ofomaja & Ho 2007
Coconut copra		Cd(II)	3	0.03	Langmuir fit	Ofomaja & Ho 2008
Coir pith		U	90-220	.38-.92	Best pH 4-6.6; Langmuir fit	Parab et al. 2005
Coir pith		Co(II), Cr(III), Ni(II)	13, 12, 16	.22,.23, .27	Pest pHs 4.3, 3.3, 5.3; pseudo 2nd order rates; Langmuir fits	Parab et al. 2006
Coir pith		Co(II)	__	__	Best pH 4-7; 2nd order rate; Langmuir fit; regen. with HCl	Parab et al. 2010
Hazelnut, almond		Pb(II)	28, 8	.14, .04	Best pH 6-7; Langmuir fit; ion exchange/complexation	Pehlivan et al. 2009a
Green coconut		Cd(II), Cr(III), Cr(VI)	236,62, 42	2.1,1.2, .81	Langmuir fit best for Cd(II); Freundlich best for Cr(III)	Pino et al. 2006
Delonix regia		Cr(VI)	12	0.23	Best pH <3; reduction & sorption; pseudo 2nd order rate; Langmuir fit;	Prasad & Abdullah 2010
Coir	Oxidation	Cu(II)	3-7	.05-.11	Oxidation increased uptake; Langmuir fit; regen. with HCl; ion exchange	Shukla et al. 2009
Coir, jute, sawdust, nut s.	Dye	Pb(II)	26	0.13	Monochlorozine dye enhanced Pb uptake; 2nd order rate ; Langmuir fit	Shukla & Pai 2005b
Groundnut shells		Cu(II), Ni(II), Zn(II)	8, 10, 18	.12,.17, .28	Reactive orange dye moderately enhanced uptake; Langmuir fits	Shukla & Pai 2005c
Coir fibers	H_2O_2	Ni(II), Zn(II), Fe(II)	4, 8, 7	.07,.12, .12	Oxidation more than doubled uptake; higher pH favored; Langmuir fits; regen. with NaOH	Shukla et al. 2006

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Coir pith		Cr(VI)	138-318	2.7-6.1	Best pH 2; Langmuir fit; endothermic; adsorbed mainly in reduced form	Suksabye et al. 2007
Coir pith		Cr(VI)	43	0.83	ESR study at pH 2; pseudo 2nd order rate; lignin sites reduced Cr(VI) to Cr(III); but cellulose reduced it to Cr(V)	Suksabye et al. 2009
Coir	Oxidized	Ga(III)	19 (14)	0.27	Oxidation increased uptake;higher pH favored to 3; pseudo 2nd order rate; Langmuir fit; regen. with HCl	Suryavanshi & Shukla 2009
Coconut husk & palm press fibers		Cr(VI)	29, 14	.56,.27	Best pHs 1.5 to 5 or 3;	Tan et al. 1993
CROP RESIDUALS						
Husk						
Rice husk		Pb(II)	__		Metal adsorption ↑ with ↑ pH; Fit the Temkin isotherm model	Abdel-Ghani et al. 2007
Rice husk	PO_4^{3-}	Cd(II)	90	0.80	Column operation effective; Langmuir fits	Ajmal et al. 2003
Rice husk		As(III), As(V)	__	__	Tests below saturation; KOH regeneration worked.	Amin et al. 2006
Bengal gr. husk		Cr(VI)	92	1.8	Best at pH 2; Agitation helped; Langmuir fit	Ahalya et al. 2005
Cajus cajan husk		Fe(III), Cr(VI)	__	__	Best pH 2 & 2.5; Involvement of carboxyl, OH, amide; Langmuir fit	Ahalya et al. 2007
Rice husk	Boiling, CH_2O	Cr(VI)	6-10	.11-.19	Best pH 2; minor enhancement due to CH_2O; functional groups; not Langmuir fit	Bansal et al. 2009
Groundnut husk	Ag	Cr(VI)	7	0.13	Uptake favored by oxidation of substrate by Ag; Freundlich fit	Dubey & Krishna 2007
Rice husk		Cr(VI)	55-210	1.1-4.0	Best pH 1.8-2.8; Reductive adsorption at pH 2; rate laws;	El-Shafey 2005
Rice husk	H_2SO_4	Cd(II), Se(IV)	24-27, 17-20	.21-.24, .22-.25	Pseudo 2nd order rates; Low pH preferred for Se(IV); above 4 for Cd(II); ion exchange (Cd); Langmuir fits	El-Shafey 2007b
Rice husk		Pb(II)	__	__	Effective adsorption; Freundlich fit	Khalid et al. 1998a
Rice husk		Cd(II)	__	__	Effective adsorption; Freundlich fit	Khalid et al. 1998b

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Rice husk		Hg(II)	1.3	0.0065	Effective adsorption; Freundlich fit; endothermic	Khalid et al. 1999
Rice husk	Ca, Mg	Pb(II), Hg(II), Cu(II), Co(II), Mn(II), Cd(II), Zn(II), Ni(II),	58, 58, 11, 10, 8, 8, 8, 6	.28,.29, .17,.17, .15,.07, .12,.10	Calcium and magnesium originally present were displaced	Krishnani et al. 2008b
Rice husk	Epichlor, NaOH, NaHCO$_3$	Cd(II)	8-20	.07-.18	Pseudo 2nd order rate; Langmuir fit	Kumar & Bandyopadhyay 2006a
Rice husk	Na$_2$CO$_3$	Cd(II)	12	0.11	Column; breaktrough; regeneration with HCl	Kumar & Bandyopadhyay 2006b
Cocoa shell		Pb(II)	74	0.36	Cocoa shells more effective than cedar bark	Meuneir et al. 2002
Rice husk	Phos-phate	Pb(II), Cu(II), Zn(II), Mn(II)	No eval	No eval	Column tests; benefits of phosphate treatment	Mohan & Sreelakshmi 2008
Lathyrus s. husk		Cd(II)	35	0.31	95% uptake; pseudo 2nd order rate; Langmuir fit; ion exhcnage; Cd present as micro-precipitate; regen. with acid	Panda et al. 2006
Black gram husk		Cd(II)	39	0.35	Regen. with HCl	Saeed & Iqbal 2003
Black gram husk		Pb(II), Cd(II), Zn(II), Cu(II), Ni(II)	50, 40, 34, 26, 20	.24,.36, .52,.41, .34	Pb > Cd > Zn > Cu > Ni; Langmuir fits; best pH 5 ; little competition ; regen. with HCl	Saeed et al. 2005b
Mung bean husk		Cd(II)	36	0.32	Pseudo 2nd order rate; Langmuir fit; ion exchange release of alkaline earth metals	Saeed et al. 2009
Rice husk		Cd(II), Pb(II), Al(III), Cu(II), Zn(II)	1.5, 5, - , - , -	.01,.02	To meet EPA limits; smaller particles had much higher capacity	Tarley & Arruda 2004
Rice husk	Epichlor-ohydrin; base	Cd(II)	9-20	.08-.18	Pseudo 2nd order rate; Langmuir fit	Upendra and Manas 2006
Oriza sativa		Pb(II)	7	0.034	Best pH 5	Zulkali et al. 2006
Maize tassel		Pb(II)			Best pH 7; diffusioin control	Zvinowanda et al. 2008a

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Maize tassel		Pb(II), Se, Sr, U, V	2.6, - , -, -	0.01	Pseudo 2nd order rate; Langmuir fit; competition	Zvinowanda et al. 2009a
Maize tassel		Cr(VI), Cd(II)	4.5-9, 135	.09-.17, 1.2	Best pHs 2, 5-6, resp.	Zvinowanda et al. 2009b
Stalks, etc.						
Cassava waste	Thioglyco llic acid	Cu(II), Cd(II), Zn(II)	95	1.5	Thioglycollic acid treatment enhanced binding.; 20-30 minutes mixing sufficient.	Abia et al. 2003
Cicer arientinum		Fe(III)	72	1.3	Langmuir fit; regeneraton possible	Ahalya et al. 2006
Olive stone		Cd(II)	5-10	.04-.09	Higher temperature favored; Langmuir fit best	Calero de Hoces et al. 2006
Grape waste	Sulfuric	Cr(VI); also Cr(II), Fe(III), Zn(II), Cd(II), Pb(II)	99	1.9	Cross-linked grape waste was effective for all of the ions; Langmuir fit	Chand et al. 2009
Grape stalk, coffee waste	EDTA	Cu(II), Ni(II)	2, 1.5; 2.5, 3	.03,.03; .04,.05	Best pH 5.5; severe competition by EDTA; pseudo 2nd order rate; Langmuir fit;	Escudero et al. 2008
Pomegranate		Cr(VI)	11	0.21	Best pH 1, pseudo 2nd order rate, Langmuir fit	El Nemr 2007
Grape bagasse		Cd(II), Pb(II)	54, 42	.48,.20	Best pHs 7 & 3; Langmuir fits	Farinella et al. 2007
Grape bagasse		Cd(II), Pb(II)	87, 89	.77,.43	Best pHs 7 & 3; Langmuir fits; Pb tended to win competition; column removal	Farinella et al. 2008
Grape stalk, bark, olive stone		Cr(VI)	60, 35, 15, 8	1.2,.67, .29, .15	Best pH 2-3, salt-tolerant; Langmuir fit	Fiol et al. 2003
Grape stalk	Alginate	Cr(VI)	__	__	Second order rate; diffusion control; Langmuir fit	Fiol et al. 2004
Casava waste	Raw; Acid-treat	Cd(II), Zn(II)	87, 56; 647, 559	.77,.86; 5.8,8.5	Best pH 4.5-5.5; diffusion control; sulfhydrul-metal bonds preclude regeneration	Horsfall & Abia 2003
Caladium bicolor		Pb(II), Cd(II)	88, 66	.42,.59	Best pH 7; Langmuir fit	Horsfall & Spiff 2004
Casava tuber waste		Pb(II)	86	0.41	Ion exchange	Horsfall et al. 2005
Caladium bicolor		Pb(II), Cd(II)	49, 52	.24,.46	Sticking probability model	Horsfall & Spiff 2005a

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Fluted pumpkin	Mercapto ethanoic	Ni(II)	13, 42	.22,.72	The treatment enhanced uptake; Langmuir fit; exothermic	Horsfall & Spiff 2005b
Fluted pumpkin	Sulfanyl acetic	Pb(II), Cd(II), Zn(II)	__	__	Pseudo 2nd order rate; exothermic	Horsfall & Spiff 2005c
Casava tuber bark waste		Cd(II), Cu(II), Zn(II)	6-26, 33-91, 22-83	.05-.23, .05-1.4, .34-1.3	Pseudo-2nd order rate; Langmuir fit; exothermic	Horsfall et al. 2006
Olive waste		Cr(VI)			Best pH 2; endothermic	Malkoc et al. 2006b
Grape stalk		Pb(II), Cd(II)	50, 28	.24,.25	Best pH 5.5; pseudo 2nd order rate; Langmuir fit; interference by NaCl, NaClO$_4$; regeneration by HCl or EDTA	Martínez et al. 2006a
Olive waste		Pb(II), Cd(II)	14-19	.07-.09	Higher pH favored to 7; sorbent judged to be only moderately good; regeneration possible	Martínez et al. 2006b
Olive pomace	H$_3$PO$_4$, H$_2$O$_2$	Cu(II), Cd(II)	30, 11	.47,.10	Phosphoric acid treatment best ; carboxylic acids important; Langmuir fit	Martin-Lara et al. 2008
Olive waste		Pb(II)	6-23	.03-.11	Carboxylic acids important; Langmuir fit	Martin-Lara et al. 2009
Rice straw, cotton stalks, bagasse	Phospho-rylation; NaOH	Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ni(II), Pb(II), Zn(II)	__	__	NaOH treatment increased uptake	Nada et al. 2002a
Rice straw, cotton stalks, bagasse	Phospho-rylation; NaOH	Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ni(II), Pb(II), Zn(II)	__	__	Optimum phorphorylation reaction	Nada et al. 2002b
Cotton stalks	Chloro-sulfonic, phos oxy chloride	Sr(II), As(III), Cu(II), Ni(II)	16, 4, 4, 9	.18,.05, .06,.15	Best pH 3; having both phosphate & sulfonate groups promoted metal uptake.	Nada et al. 2006
Cotton stalks	Phosph orylated	Pb(II), Cu(II), Ni(II), Co(II), Cr(III), Cd(II)	52, 20, 18, 27, 39, 27	.25,.31, .31,.46, .75,.24	Not as high sorption as phosphorylated lignin	Nada & Hasan 2003

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Grape waste	HCl media	Au(III)	1900	9.6	First order rate; reduction; Au particles formed on substrate; endothermic	Parajuli et al. 2008
Wheat, soybean straws, corn	1% NaOH	Cu(II), Ni(II), Cd(II), Pb(II)	__	__	Certain combinations of biomass and metal worked better; 1% NaOH treatment much better than CH_2O, acid, or 4% NaOH	Sciban et al. 2008
Sunflower stalks		Cu(II), Zn(II), Cd(II), Cr(III)	29, 31, 42, 27	.46,.47, .37,.52	Uptake fell with temperature, except for Cr(III)	Sun & Shi 1998
Grape stalk		Cu(II), Ni(II)	10-16, 11-18	.16-.25, .19-.31	Best pH 5.5-6; Langmuir fit	Villaescusa et al. 2004
Olive husk		Pb(II), Cd(II), Cu(II), Zn(II)	33, 17, 3.4, 3.3	.16,.15, .05,.05	Freundlich fits; severe competition with Cu(II) as the clear winner	Volpe et al. 2003
Corn stalk		Cd(II)	3.4	0.030	Best pH 7; pseudo 2nd order rate; Freundlich fit	Zheng et al. 2010
FOOD RESIDUALS						
Bagasse						
Sugar cane	Triethyle ne-tetramine	Cu(II), Cd(II), Pb(II)	60-222	.94-3.5	Succinylation after 2X mercerization, then derivatized with triethylenetetramine; Langmuir fits	Alves Gurgel & Gil 2009
Sugar cane, oil cake		Cr(VI)	6, 12	0.12, 0.23	Best pH 2; Langmuir fit	Garg et al. 2007
Sugar cane		Ni(II)	No eval	No eval	Best pH 7.5	Garg et al. 2008a
Sugar cane, corn cob, oil cake		Cd(II)	69-106	0.61	Best pH 6; Langmuir fit	Garg et al. 2008b
Sugar cane		Cr(VI)	__	__	Best pH 2	Garg et al. 2009
Sugar cane	Anearo-bic dig.	Zn(II), Cd(II)	__	__	Increased adsorption capacities; biogas as biproduct	Joseph et al. 2009
Sugar bagasse	5N NaOH, EDTA	Cu(II), Cd(II), Pb(II)	39-93, 88-149, 192-333	.61-1.5, .07-1.3, .93-1.6	Mercerization greatly increased adsorption capacities.	Karnitz et al. 2009

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Sugar bagasse	NaOH, EDTA dianhydr	Ca(II), Mg(II)	16-54, 14-43	0.4-1.4, .58-1.8	Modified sugarcane bagasse showed higher adsorption than modified pure cellulose.	Karnitz et al. 2010
Sugar bagasse	H_2SO_4, drying	Cr(VI)	___	___	Saline waters, brackish conditions; best results with H_2SO_4 charring	Krishnani et al. 2004
Sugar bagasse, soy bean hull	Epichloro hydrin	Ca(II)	36, 52	0.9,1.3	Idea of single use	Laxzlo & Dintzis 1994
Bagasse	Phospho-sulfonat.	Cr, Fe, Cu(II), Zn(II), Cd(II), Pb(II), Ni(II), Co(II)	3, 4, 0.9, 0.7 1.1,3.3, 0.4, 0.5	.06-.07, .01,.01, .01,.02, .01,.01	On a molar basis Cu(II) and Pb(II) were favored over other divalent cations	Nada et al. 2003
Bagasse	Various COO Rx	Cu(II), Ni(II), Cr(III), Fe(III)	99-381, 80-470, 440, 84-469	1.6-6.0, 1.4-8.0, 8.46, 1.5-8.4	Carboxymethylated bagasse > periodote oxidized > succinylated .	Nada & Hassan 2006
Sugar bagasse	Micro-wave rad	Cu(II), Hg(II)	76, 481	1.2,2.4	Best pH 6	Orlando et al. 2002
Sugar bagasse		Cr(VI)	13	0.25	Best pH 2; Langmuir fit	Sharma & Forster 1994a
Soy bean hull, etc.	Citric ac	Cu(II)	91	1.43	Best results with low lignin, low density materials, high anionic charge	Wartelle & Marshall 2000
Agricultural waste		Cr(VI)	58-103	1.1-2.0	Langmuir fits	Wartelle & Marshall 2005
Areca food waste		Cd(II), Cu(II)	1, 3	.01,.05	Best pH 5.6; Langmuir fit; regen with HNO_3	Zheng et al. 2008
Sugar beet pulp						
Sugar beet		Cu(II)	16-29	.25-.46	Best pH 4; Langmuir fit; activation energy.	Aksu & Isoglu 2005
Sugar beet	$FeCl_3$ loaded	Cr(VI)	5	0.10	Evaluated at pH 4.4; Langmuir fit	Altundogan 2005
Sugar beet	NaOH, citric acid	Cu(II)	55-204	.87-3.2	Pretreatment increased adsorption greatly; ion exchange pseudo 2nd order rate; exothermic, Langmuir fit	Altundogan et al. 2007
Sugar beet		Cd(II), Cu(II), Ni(II), Pb(II), Zn(II)	53, 39, 21,120, 32	.47,.61, .36,.58, .49	Cu≈Pb>>Cd≈Zn>Ni>Ca; Langmuir fits except Ca; ion exchange/chelation	Dronnet et al. 1997

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Sugar beet		Cu(II), Ni(II), Pb(II)	30, 12, 60	.47,.20, .29	HIgher pH favored ; diffusion control	Gerente et al. 2000
Sugar beet		Cu(II), Zn(II)	31, 36	.49,.55	60-97% uptake; best pH 5.5; Freundlich fit	Pehlivan et al. 2006
Sugar beet		Cd(II), Pb(II)	46, 44	.41,.21	Best pH 5; ion exchange/complexation; limited regeneration by acid	Pehlivan et al. 2008
Sugar beet pulp		Cu(II), Zn(II), Cd(II), Ni(II)	21	0.33	Three different pKa sites; surface complexation; competition: Cu2+ > Zn2+ > Cd2+ > Ni2+	Reddad et al. 2002a
Sugar beet pulp		Pb(II), Cu(II), Zn(II), Cd(II), Ni(II)	49, 12, 10, 17, 8	.24,.19, .15,.19, .14	Langmuir fit; molar affinities: Cu2+ > Zn2+ > Cd2+ > Ni2+	Reddad et al. 2002b
Sugar beet pulp	Hot HCl, NaOH	Ni(II), Cu(II)	12-21; 21-29	.20-.36, .33-.46	Saponification and base extraction increased uptake; 2nd order rate; Langmuir fit	Reddad et al. 2002d
Sugar beet pulp		Cr(III), Cr(VI)	__	__	Strong pH effects; reduction of Cr(VI)	Reddad et al. 2003
Sugar beet pulp		Cr(VI)	17	0.33	Best pH 2; Langmuir fit	Sharma & Forster 1994a
Other						
Soya cake		Cr(VI)	32	0.62	The biomass reduced Cr(VI) at pH 1, high adsorption	Daneshvar et al. 2002
Wheat bran extract		Cr(VI)	35	0.67	Best pH 2.1; Langmuir fit; adsorption consumes protons, consistent with reduction to Cr(III)	Dupont & Guillon 2003
Avena m (oat)		Cr(VI)	2.5-3.4	.05-.07	Tests at pH 2; binding increased with temperature; Langmuir fit; regen. with HCl; reduction to Cr(II) occurred	Gardea-Torresdey et al. 2000a
Hop byproducts	Dried, ground	Pb(II)	74	0.36	HIgher pH favored to 5; regen. with citrate	Gardea-Torresdey et al. 2002
Carrot residues		Mn(II), Ni(II), Co(II), Cu(II)	5, 6.5, 6.3, 12	.09,.11, .11,.19	First-order rates; Langmuir fits	Guzel et al. 2008
Rice polish		As(III), As(V)	0.07-0.08	0.0009-0.0011	Regen. with NaOH	Hasan et al. 2009a
Coffee beans	degrease	Cd(II)	6.7	0.06	Best pH 3-5; Langmuir fit; ion exchange; regen. by HCl or HNO_3	Kaikake et al. 2007

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Corn cobs		Cu(II)	26	0.41	Pseudo 1st order rate; Langmuir fit; anionic complexes not removed at all; regenerable with acidic H_2O_2	Khan and Wahab 2007
Apple residue		Cu(II)	9-34	.14-.54	Chemical mod increased uptake 5X; best pH 5.5-7; competition (Pb); Langmuir fit	Lee & Yang 1997
Apple residue	Phosph oxychlor	Cu(II), Pb(II), Cd(II)	No eval	No eval	Regenerable	Lee et al. 1998
Apple residue		Cu(II), Pb(II), Cd(II)	No eval	No eval	Esterificaiton of carboxyl groups decreased adsorption	Lee et al. 1999
Corn cobs	Citric ac., nitric ac. oxidized	Cd(II)	—	—	Oxidation by citric, nitric acids increased uptake by 11X, 3.8X, resp.; higher pH favored to 6; ion exchange; carboxylic sites; regen. by lowering pH	Leyva-Ramos et al. 2005
Wine waste		Cr(III)	10-16	.19-.31	Higher temperature favored; Langmuir fits	Li et al. 2004
Banana pith		Cu(II); Cu(II), Ni(II), Cr(III), Zn(II)	9-14	.14-.22	Pb(II) > Cu(II) > Ni(II) > Cr(III) > Zn(II); best pH 5; Langmuir fit	Low et al. 1995a
Rice hull	EDTA	Cu(II), Cr(III), Ni(II), Pb(II)	9,10, 9,29	.14,.19, .15,.14	Higher pH favored	Low et al. 2000
Apple residue	P(V) oxy-chloride	Cu(II), Zn(II), Ni(II)	25-102, 20-72, 18-65	.39-1.6, .31-1.1, .02-1.1	Greatest affinity for copper; enhaced uptake by P oxychloride; regenerated with HCl	Maranon & Sastre 1991a
Apple residue	Xanthat., phosph.	Cu(II), Zn(II), Ni(II)	—	—	Langmuir fits	Maranon & Sastre 1991b
Apple residue	Xanthat., phosph.	Cu(II), Zn(II), Ni(II)	—	—	Langmuir fits	Maranon & Sastre 1991b
Apple residue	Oxidation Crosslink Carbxym Xanthat Phospha		—	—	The treatments increased structural stability and decreased swelling	Maranon et al. 1991

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Apple residue	Acidic groups	Cu(II), Zn(II), Ni(II)	25-102, 20-72, 18-65	.39-1.6, .31-1.1, .31-1.1	Flow-through; regeneration with HCl	Maranon & Sastre 1992a
Apple residue	P(V) oxy-chloride	Cu(II), Zn(II), Ni(II)	__	__	Preconcentration; regeneration with HCl	Maranon & Sastre 1992b
Rice bran, cotton hulls, soy hulls		Zn(II); Cu(II), Ni(II).	7-41 (Zn)	.11-.63	Extrusion stabilized materials had higher performance than expander-stabilized; great loss of capability on HCl regeneration	Marshall & Johns 1996
Soybean hulls	NaOH, citric ac,	Cu(II)	25, 43-155	.39,.68-2.4	Citric acid treatment increased uptake by 6X	Marshall et al. 1999
Soybean hulls	NaOH, citric ac,	Cu(II), Cr(VI)	25-155, 14-46	.39-2.4, .27-.88	Citric acid treatment increased uptake by 6X	Marshall & Wartelle 2006
Cococa shells		Pb(II), Cu(II)	18	0.09	Lead and copper removed from acid leachate from soil; affinity decreased in following order: ion exchange; Pb>>Cu>Fe>Al>Cr>>Co>Zn>Mn>Cd>Ni	Meunier et al. 2003a
Cococa shells		Pb(II)	33	0.16	Competition with hardness ions; ion exchange; carboxyl & amine groups involved	Meunier et al. 2003b
Rice hulls		Hg(II), Cr(III)	__	__	First order rate; Freundlich fit; endothermic	Mishra et al. 1998
Rice hulls		Cs(I)	24	0.18	Higher pH favored; Freundlich fit; ion exchange/complexation	Mishra et al. 2007
Cotton	LiCl, NaOH, acid	Mg(II), Mn(II), Sr(II)	1, 1, 1	.04,.02, .01	Alkali and activating agents decreased crystallization and increased uptake	Nada et al. 2009a
Cotton linters	Phosphorylation	Cu(II), Fe, Mn(II), Ni(II), Pb(II), Zn(II)	__	__	Phosphorous shown by spectrophotometry	Nada et al. 2005
Carrot residues		Cr(III), Cu(II), Zn(II)	45, -, -	0.87	Langmuir fit	Nasernehad et al. 2005
Rice bran		Cr(VI), Cr(III), Ni(II)	0.07, 0.1, -	0.0013, 0.0019	Pseudo 2nd order rate; Freundlich fits	Oliveira et al. 2005

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Coffee husks		Cu(II), Cd(II), Zn(II), Cr(VI)	4-7, 3-6, 3.5-4.5, 3-6	.06-.11, .03-.05, .05-.07, .06-.05	Tests at pH 4; 48-98% uptake; pH optima; pseudo 2nd order rates; Langmuir fits	Oliveira et al. 2008
Bean wastes		Pb(II)	427	2.06	Langmuir fit; endothermic	Ozcan et al. 2009
Wheat bran	H_2SO_4	Pb(II)	83	0.40	Best pH 6; Langmuir fit; exothermic	Ozer 2007
Wide assortment		Cr(VI)	__	__	Reductive adsorption mechanism shown	Park et al. 2007
Hops: *Humulus l*		Cu(II), Zn(II), Cr(III), Cr(VI)	No eval	No eval	Cr(VI) was reduced to Cr(III) for adsroption; surface complexes	Parsons et al. 2002
Rice polish		As(III), As(V)	0.14, 0.15	0.0018, 0.0020	Pseudo 2nd order rates; Langmuir fits; exothermic	Ranjan et al. 2009a
Rice polish		As(III), As(V)	0.067, 0.079	0.0009, 0.0010	Flow column tests; regen. with 10% NaOH	Ranjan et al. 2009b
Tomato root; Tobacco root		Sr(II)	24; 13	0.27; 0.15		Scott et al. 1998
Corn cobs		Cu(II), Cd(II)	7-12, 3-6	.11-.19, .03-.05	Langmuir fits; Competitive sorption; Cu had stronger binding; interaction factors	Shen & Duvnjak 2004
Corn cobs		Cu(II), Cd(II)	1-7, 3-7	.02-.11, .03-.06	Modified Langmuir fit; thermodynamics	Shen & Duvnjak 2005a
Corn cobs		Cu(II)	__	__	Surface reaction model; mass transfer control	Shen & Duvnjak 2005b
Corn cobs		Cu(II), Cd(II)	6, 9	.09,.08	Kinetic modeling; diffusion control	Shen & Duvnjak 2005c
Jute	Dye, H_2O_2	Cu(II), Ni(II), Zn(II)	8, 5, 6	.13,.09, .09	Both treatments increased uptake moerately; higher pH favored; Langmuir fit	Shukla & Pai 2005a
Jute, sawdust, groundnut shells	Dye	Pb(II)	19	0.09	Monochlorozine dye enhanced Pb uptake; 2nd order rate ; Langmuir fit	Shukla & Pai 2005b
Rice bran		Cr(VI)	286	5.5	Best pH 2; Langmuir fit; desorption at high pH	Singh et al. 2005a
Rice polish		Cd(II)	10	0.09	Langmuir fit	Singh et al. 2005b
Wheat bran		Cd(II)	48-63	.43-.96	Langmuir fit; exothermic	Singh et al. 2006
Corn cob		Hg(II), Pb(II)	__	__	Langmuir fits; ion exchange	Stefan et al. 2010
Rice hulls	Dye	Pb(II), Hg(II), Cd(II)	22, 30, -	.11,.15, -	Regen. with acid	Suemitsu et al. 1986

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Corn cob	Citric ac, H_3PO_4	Cd(II), Cu(II), Pb(II), Ni(II), Zn(II)	47-66, 35-45, 85-149, 28-38, 29-35	.42-.58, .55-.71, .41-.72, .48-.65, .44-.54	Adsorption capacities favorable to ion exchange resins	Vaughan et al. 2001
SEEDS						
Tamerindus	-	Cr(VI)	55-98	1.1-1.9	Decreasing pH favored; Langmuir fit	Agarwal et al. 2006
Mustard oil cake		Ni(II)	85-92	1.4-1.6	Cu(II)> Zn(II), Cr(VI), Mn(II), Cd(II), Ni(II) and Pb(II); 2nd order rate; higher temperature favored; endothermic	Ajmal et al. 2005
Wheat shells		Cu(II)	__	__	Best pH 5-6	Basci et al. 2003
Mirabilis jalapa		Cd(II)	22	0.20	The pure lignin sample showed higher uptake; Langmuir fit	Basso et al. 2004
Peanut shell	Pelletiz.	Cu(II), Cd(II), Zn(II), Pb(II)	8	0.13	Pelletization did not hurt uptake	Brown et al. 2000
Peanut shell	NaoH wash, heat acid	CD(II), Cu(II), Ni(II), Pb(II), Zn(II)	__	__	Outperformed commercial resins	Chamarthy et al. 2001
Peanut shell	Wet, dry	Se(IV)	12-17	.15-.22	Wet sorbent worked better; first-order rate; higher pH favored to 7; Langmuir fit; elemental metal found on substrate; substrate becomes oxidized	El-Shafey 2007a
Taramind	H_2SO_4	Cr(VI)	30	0.58	Best pH 1-3; 2nd order rate; Langmuir fit; regeneration by acid or base	Gupta & Babu 2009
Peanut shell	Citric ac	Co(II), Ni(II)	29-270	.49-4.6	140 $^{\circ}$C, minor moisture esterification; major enhancement; best pH 7 for adsorption; Langmuir fit	Hashem et al. 2005a
Palm kernel fiber		Pb(II)	50	0.24	Pseudo 2nd order rate; Langmuir fit; endothermic	Ho & Ofomaja 2005
Palm kernel fiber		Cu(II)	4-13	.06-.20	Pseudo 2nd order rate	Ho & Ofomaja 2006c
Peanut husk, sawdust		Pb(II), Cr(III), Cu(II)	4-5, 2.5-3.5, 2.5-3.5	.02-.03, .05-.07, .04-.06	2nd order rate; Langmuir fit	Li et al. 2007

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Ocimum basilica.		Cr(VI)	205	3.9	Best pH 1.5; Langmuir fit	Melo & D"Souza 2004
		Cu(II)	__	__	Best pH 6; Freundlich fit	Mohammad et al. 1997
Wheat bran		Cd(II)	10-25	.09-.22	Pseudo 2nd order rate; Langmuir fit	Nouri et al. 2007
Goundnut husk	EDTA Rx	Cd(II), Pb(II)	40, 39	.36,.19	Particle diffusion control	Okiemen et al. 1991
Sago waste		Cu(II), Pb(II)	12, 47	.19,.23	Best pHs 4-5.5; 2nd order rate; Langmuir fits	Quek et al. 1998
Peanut shell	Wash, citric ac., H₃PO₄		__	__	Acid treatments increased uptake;	Waywoyo et al. 1999
Peanut hull		Cu(II)	21	0.33	Best pH 5.5; pseudo 2nd order rate; Langmuir fit; ion exchange; exothermic	Zhu et al. 2009
FRUIT STONE						
Olive stone	H₂SO₄	Cd(II)	128	1.14	Time required 15 min ; ion exchange	Aziz et al. 2009
Olive stone		Cd(II)	__	__	Neutral pH best, smaller size, more effective; pseudo 2nd order rate	Blazquez et al. 2005
Olive stone		Cr(III), Cr(VI)	__	__	Best pH 4-6 and 2, resp. ; reductive adsorp.	Blazquez et al. 2009
Olive stone		Cd(II), Cr(III), Pb (II)	3, 7, 10	.03,.13, .05	Pseudo 2nd order rate; Cr>Cd>Pb takeup;	Calero et al. 2009
Olive waste		Cr(III), Cu(II), Zn(II)	__	__	Humic-like fraction polymerin; uptake Cr(III) > Cu > Zn; ion exchange; some specificity	Capasso et al. 2004
Olive cake		Cr(VI)	33	0.63	Compared vs. sawdust, pine needles, almond shell, cactus leaves, charcoal at pH 2; wool best, most selective first-order; Langmuir fits	Dakiky et al. 2002
Olive cake		Pb(II), Cd(II)	18-28, 11	.09-.14, .10	Regeneration with acids	Doyurum & Celik 2006
Olive stone		Pb(II), Ni(II), Cu(II), Cd(II)	9, 2, 2 , 8	.04,.03, .03,.07	Best pH 5.5-6; pseudo 2nd order rate; Langmuir fit; adsorption-complexation	Fiol et al. 2006
Olive stone		Cd(II), Cr(III), Pb(II)	__	__	Pseudo 2nd order rate; Sips fit; endothermic	Hernainz et al. 2008
Olive stone, wastes, prunings	Cr(III) presence	Pb(II), Cr(III)	4-8, 3-4	.02-.04, .03-.04	Affinity for Pb(II) > Cr(III); site competition; multicomponent isotherms; Sips fit	Hernainz et al. 2009

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Olive stone		Cd(II)	0.2	0.002	Higher pH favored to 6; pseudo 2nd order rate; Langmuir fit	Kula et al. 2008
Olive pomace		Pb(II), Cu(II), Cd(II)	2-15, 1-5, 1-7	.01-.07, .02-.08, .01-.06	Best pH for Cd(II) is 6.5; Langmuir fits; carboxylic an phenolic groups involved	Pagnanelli et al. 2003
Olive pomace		Cu(II), Cd(II)	No eval	No eval	Competition; Langmuir fit; specific sites	Pagnanelli et al. 2005a
FRUIT PEEL						
Orange peel		Ni(II)	86-96	.47-1.6	Ni(II) > Cu(II) > Pb(II) > Zn(II) > Cr(II); First-order kinetics; enothermic, higher temperature favored; regeneration possible	Ajmal et al. 2000
Bael fruit	H_3PO_4	Cr(VI)	17	0.33	Phosphoric acid developed pores; best pH 2; pseudo 2nd order; Langmuir fit	Anandkumar & Mandal 2009
Banana, orange		Cu(II), Co(II), Ni(II), Zn(II), Pb(II)	8	0.12	Best with increasing pH to 7; effective for trace removal	Annadurai et al. 2003
Pea, bean, fig, Medlar peels		Cd(II)	98-148	.87-1.3	Pseudo 2nd order rate; Langmuir fit	Benaissa 2006
Pomegranate peel	Act. Carb	Pb(II), Cu(II)	__	__	2nd order rates; Langmuir fits	El-Ashtoukhy et al. 2008
Orange waste	Phospho	Pb(II), In(III), Ga(III),Zr(IV), Cu(II), Fe(III)	238,80, 49,105, 62,171	1.1,.70, .70,1.2, 1.0,3.1	Effective to concentrate metals.	Ghimire et al. 2008
Mango peel		Cu(II), Ni(II), Zn(II)	46, 40, 28	.72,.68, .43	$Cu^{2+}>Ni^{2+}>Zn^{2+}$; best pH 5-6 ;	Iqbal et al. 2009a
Mango peel		Cd(II), Pb(II)	69, 99	.61,.48	Pseudo 2nd order rate ; 75% due to carboxyl and 25% due to OH groups ; ion exchange ; regenerable	Iqbal et al. 2009b
Orange peel	Alkalis, crosslink	Cd(II)	47	3.8	Citric acid treatment had biggest benefit; best pH 6; regen. with HCl	Li et al. 2007
Orange peel	Alkalis, acids	Cd(II), Zn(II), Co(II), Ni(II)	59, 79, 72, 72	.52,1.2. 1.3,1.2	Pretreatments increased uptake moderately; Langmuir fit	Li et al. 2008
Banana skin, etc.		Cr(VI), Cr(III)	No eval	No eval	Best pH 1.5-4; Complete reduction by biomass (more effective than $FeSO_4$	Park et al. 2008a

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Fruit gum powder		Cr(VI)	218	4.2	Tested at pH 1.0; Freundlich fit	Samantanoi et al. 1997
Orange peel	Saponif., citric ac.	Pb(II)	253	1.22	Best pHs 4.5-6, pseudo 1st order rates;	Xuan et al. 2006
Cobs						
Maize			__		Increasing pH; Fit the Temkin isotherm fit	Abdel-Ghani et al. 2007
Maize	Phosphat Sulfonate Carboxyl	Zn(II), Pb(II), Ni(II), Fe, Cr	14, 19, 21	0.21, 0.09, 0.36	Sodium binding capacities increased with negative groups and crosslinking	Nada et al. 2009b
Maize		Cr(VI)	14	0.27	Best pH 2; Langmuif fit	Sharma & Forster 1994a
Tea leaves						
Waste tea leaves	Dried	Pb > Fe > Zn > Ni	73 (Pb)	0.35	Carboxyls bind Pb, Fe; -OH binds Ni, Zn; Langmuir fit	Ahluwalia and Goyal 2005a
Tea wastes		Cu(II), Cd(II)	9, 11	.14,.10	Competition; not Langmuir fit	Cay et al. 2004
Tea wastes		Ni(II)	15	0.26	Langmuir fit; sl. endothermic; irreversible	Malkoc & Nuhoglu 2005
Tea wastes	Bed, flow	Cr(VI)	34-56	.65-1.1	Best pH lowest; smaller particles increased capacity	Malkoc & Nuhoglu 2006a
Tea wastes	Bed, flow	Ni(II)	7-11	1.1-.19	Smaller particles increased capacity	Malkoc & Nuhoglu 2006b
Tea wastes		Cr(VI)	55	1.1	Best pH 2; Langmuir fit; endothermic	Malkoc & Nuhoglu 2007b
Tea, coffee, nut shells		Cr(VI), Cd(II), Al(III)	1.5, 1.3	.03,.01	Al uptake noted; first order rate; Freundlich fit	Orhan & Buyukgungor 1993
Tea wastes, coffee wastes		Cr(VI)	45, 39	.87,.75	Reduction to Cr(III) by phenolics in the tea, then adsorption; Toth fit better than Langmuir	Prabhakaran et al. 2009
STRAW, GRASSES						
Wheat straw, grass		Cr(III)	20	0.38	Low cost; pseudo 2nd order rate; Langmuir fit; regeneration vs. ashing	Chojnacka 2006
Wheat straw		Cd(II), Cu(II)	15, 11	.13,.17	Higher pH favored; 2nd order rate; Langmuir fits; chemisorption proposed	Dang et al. 2009
Wheat straw		Zn(II), Ni(II)	__	__	High pH favored; no effect of particle size; little competition	Doan et al. 2008

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Wheat bran		Cr(III), Hg(II), Pb(II), Cd(II), Cu(II), Ni(II)	93, 70, 62, 21, 15, 12	1.8,.35, .30,.19, .24,.20	Ion exchange, complexation, size exclusion	Farajzadeh & Monji 2004a
Wheat bran	NaCl	Cr(III), Hg(II),	__	__	The salt treatment helped adsorption	Farajzadeh & Monji 2004b
Rice straw	tartaric	Cr(VI)	3.2	0.06	Best pH 2; smaller particle size better; reduction promoted by sulfate, inhibited by nitrate; Langmuir fit	Gao et al. 2008
Sorghum straw		Cr(III)	7-13	.13-.25	Carboxyl and OH groups; Regenerated with nitric acid; desorbed by EDTA	Garcia-Reyes et al. 2009
Straw xanthate; Alkali-treated straw		Cr(III)	1.9; 3.9	0.037, 0.075	Best pH 3.6-3.9; Langmuir fit	Kumar et al. 2000
Steam expl. wheat	Fe-mod.	Cr(VI)	9	0.17	Langmuir fit	Li et al. 2004a
Spent grain		Cd(II), Pb(II)	17, 36	.15,.17	Pseudo 2nd order rates; Langmuir fits; EDTA prevented sorption	Low et al. 2000
Spent grain		Cu(II)	10.5	0.17	Pseudo 2nd order rate; Langmuir fit	Lu & Gibb 2008
Wheat bran	H_2SO_4	Cr(VI)	91-133	1.8-2.6	Best pH 1.5; first order rate; Langmuir fit; exothermic	Ozer & Ozer 2004
Wheat bran	Dehyd-rated	Cu(II)	52-65	.82-1.0	Best pH 5; exothermic	Ozer et al. 2004b
Wheat bran	H_2SO_4	Cd(II)	43-101	.38-.90	Best pH 5.4; first order rate; Langmuir fit	Ozer & Pirincci 2006
Rice bran		Cd(II), Cu(II), Pb(II), Zn(II)	1, 0.4, 4, 0.1	.01,.01, .02,.00	Freundlich fit	Montanher et al. 2005
Alfalfa		U	No eval	No eval	Higher pH favored to 4.5; carboxyl groups dominant	Parsons et al. 2006
Barley straw		Cu(II), Pb(II)	4, 23	.06,.11	Higher pH favored to 6; Langmuir fit	Pehlivan et al. 2009b
Rice bran	H_3PO_4	Ni(II)	102	1.7	Higher pH favored to 6; pseudo 2nd order rate; Langmuir fit; ion exchange	Zafar et al. 2007
WEEDS, PLANTS						
Parthenium hyst.		Cd(II)	__	__	Best at pH 3-4; 2nd order rate; Langmuir fit; endothermic; 82% recovery by HCl	Ajmal et al. 2006

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Paspalum notatum	Acid	Ni(II), Cu(II), Al(III), Fe(III)	3-6, 2-4, 3-14, 3-8	.05-.10, .03-.06, .11-.52, .05-.14	Acid pretreatment increased sorption on the root material	Araujo et al. 2007
Salvinia cucullata		Cr(VI)	232	4.5	Lower pH best; 2nd order rate; diffusion control; Langmuir fit	Baral et al. 2007
Arundo donax		Cd(II), Ni(II)	__	__		Basso et al. 2002a
Cactus		Cr(VI)	7	0.13	Best pH 2; Langmuir fit	Dakiki et al. 2002
Cactus		Cu(II), Cd(II), Fe(III), Ni(II), Zn(II), Pb(II)	10, 0.4, 0.2, 8, 1.5, 3	.16,.03, .00,.14, .02,.01	Oxalate formation was involved, not just ion exchange	Davila-Jimenez et al. 2003
Alfalfa biomass		Ni(II)	4	0.07	Best pH 5-6; regen. with HCl	Gardea-Torresdey et al. 1996b
Alfalfa biomass		Cd(II), Cr(III), Cr(VI), Pb(II), Zn(II)	7, 8, 0, 43, 5	.06,.15, 0, .21, .08	Best pHs ca. 5; recoverable by HCl	Gardea-Torresdey et al. 1998
Alfalfa biomass		Au(III)	No eval	No eval	Accumulation involves reduction to elemental;l favored by low pH; bioreduction	Gardea-Torresdey et al. 2000b
Alfalfa biomass		Cr(III)	No eval	No eval	Carboxyl ligands involved; bidentate complex	Gardea-Torresdey et al. 2002
Convolvulus arv.		Cd(II), Cr(VI), Cu(II)	4, 1.5, 0.6	.04,.03, .01		Gardea-Torresdey et al. 2004b
Moss		Cu(II)	23	0.36	Pseudo 2nd order rate; Langmuir fit	Grimm et al. 2008
Tree fern		Zn(II), Cu(II), Pb(II)	8, 11, 40	.12,.17, .19	Decreased size beneficial; Langmuir fit	Ho et al. 2002
Tree fern		Cu(II)	12	0.19	Pseudo 2nd order rate; Langmuir fit; endothermic	Ho 2003
Tree fern		Cd(II)	12	0.11	Pseudo 2nd order rate; non-linear kinetic model	Ho 2004
Tree fern		Pb(II)	35	0.17	Best pH 4-7; Pseudo 2nd order rate; ion exchange	Ho 2005

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Coriandrum sativ.		Hg(II), CH_3Hg^+	2, 2	0.01 0.01	Carboxylic acid groups involved	Karunasagar et al. 2005
Sunflower stem		Cr(III)	83	1.6	Exothermic; selective; suppressed by anions, cations, Fe(II), Fe(III), Y(III); Dubinin-Radushkevich fit	Malik et al. 2005
Sunflower stem		Hg(II)	58	0.29	Dubinin-Radushkevich fit; enhancements and suppressions by anions, cations	Malik et al. 2006
Saltbush, *Atriplex*		Cr(VI), Cr(III)	0-4, 6-27	0-0.08, .12-.52	Tests at pH 5, which is unfavorable for Cr(VI); Langmuir fits	Sawalha et al. 2005
Saltbush, *Atriplex*		Cd(II), Cr(III), Cr(VI)	36, 30, 30	.32,.58, .58	Freundlich fits; ion exchange	Sawalha et al. 2006
Alfalfa biomass		Cu(II), Pb(II)	20, 43	.31,.21		Tiemann et al. 1999
Alfalfa biomass		Fe(II), Fe(III)	3	.05	Best pH 5	Tiemann et al. 2000
Solanum elaeag.		Cu(II), Pb(II), Cr(III), Zn(II), Ni(II)	46, 32, 43, 12, 13	.72,.15, .83,.18, .22	Esterification used to confirm binding by carboxylic acid groups	Tiemann et al. 2002
AQUATIC PLANT						
Fresh water						
Eichhornia c	Live	Cd(II), Zn(II)	1-10, 1-12	.02-.19, .01-.18	Metals at high levels inhibited growth; competition; slow uptake with time	Hasan et al. 2007
Eichhornia c	Dried powder	Cr(VI)	92	1.8	Best pH 2; Langmuir fit	Hasan et al. 2010
Eichhornia c roots		Eu(III)	13	0.086	Binding to carboxylate groups of root hairs	Kelley et al. 1999
Ceratophyllum d.		Cu(II), Pb(II), Zn(II)	6, 45, 14	.09,.22, .21		Keskinkan et al. 2004
Eichhornia c roots		Cu(II)	21	0.33	Batch tests, agitated; best pH ca. 5; Langmuir fit; EDTA prevents uptake by biomass	Low et al. 1994
Eichhornia c		Cr(VI)	__	__	Pseudo 2nd order rate; hydroxyl group; Freundlich fit	Mohanty et al. 2006
Agave lechuguilla		Cr(III)	26-36	.50-.69	Langmuir fit	Romero-Gonzalez et al. 2005

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Agave lechuguilla		Cr(III)	14	0.27	Langmuir fit; interactions with carboxyl groups	Romero-Gonzalez et al. 2006
Azolla filiculoides		Pb	93	0.45	Best pH 3.5-4.5	Sanyahumbi et al. 1998
Eichhornia c	Dried		__	__	Biomass can be placed in bags for use	Schneider et al. 1995
Phragmites reed		Cu(II), Cd(II), Ni(II), Pb(II), Zn(II)	0.5,0.4, 0.5,0.7, 0.6	.01,.00, .01,.00, .01	Best pH neutral, except acidic for Pb(II); Langmuir fits; regen. with acid	Southichak et al. 2006a
Phragmites reed	pH	Pb(II)	17	0.08	Langmuir fit; carboxyl groups involved	Southichak et al. 2006a
V. sprilas, *Eichhornia c.*, etc.	Dried	Cd(II), Ni(II), Zn(II), Cu(II), Cr(III), Pb(II)	2.6,2.1, 4.1,3.0, 2.8,1.0	.02,.04, .06,.05, .05,.00	Langmuir & Freundlich fits; non-competition; ion exchange	Verma et al. 2008
Alligator weed		Cr(VI)	20-24	.38-.46	Best pH 1; pseudo 2nd order rate	Wang et al. 2008
Alligator weed		Cr(VI)	__	__	Best pH 1; pseudo 2nd order rate; Langmuir fit; endothermic	Wang et al. 2009
Azolla filiculoides	Cross-linked	Cr(VI)	71-120	1.4-2.3	Best pH 2; Langmuir fit	Zhao & Duncan 1997a
Azolla filiculoides	Dried	Ni(II)	43	0.73	Best pH 6.5; regen. with acid	Zhao & Duncan 1998a
Azolla filiculoides		Zn(II)	45	0.69	Best pH 6; regen. with acid	Zhao & Duncan 1999
Water hyacinth roots		Cu(II)	23	0.36	Best pH 5.5; mesoporous; ion exchange	Zheng et al. 2009
Seaweed						
Various sp.	Species	Cu(II), Ni(II), Pb(II), Zn(II), Cd(II)	No eval	No eval		Aderhold et al. 1996
Turbinaria ornate		Cr(III)	31	0.60	Tests at pH 3.5; Langmuir fit	Aravindhan et al. 2004a
Sargassum wight.		Cr(VI)	35	0.67	Tests at pH 3.5-3.8; Langmuir fit	Aravindhan et al. 2004b
Ascophyllum nod.		Ni(II), Zn(II), Al(III), Sb(III)	__	__	Competition shown; participation of weak and strong acid groups	Bakir et al. 2009
Cystoseira indica	Epichlor	Cr(VI)	18-24	0.35	Best pH 3; cross-linking with epichlorohydrin; ion exchange; not Langmuir fit	Basha et al. 2008
Cystoseira indica	Epichlor	Cu(II), Ni(II)	__	__	Best pH 6; 2nd order rate; Ion exchange; Langmuir fit; HCl regeneration successful	Basha et al. 2009

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Sargassum sp.	Acid, base, Ca, CH_2O, glutaral.	Cu(II), Pb(II), Zn(II), Cd(II), Ni(II)	57-114, 210,43, 71, 26	.90-1.8, 1.0,.66, .63,.44	Pb>Cu>Zn>Cd>Ni; Higher pH better; ion Exchange; regen. with HCl (90%); functional groups	Chen & Yang 2005
Sargassum sp.	CH_2O	Cu(II), Pb(II)	57-76, 144	.90-1.2, 0.69	CH_2O increased uptake 20%; functional groups; coordination model; ion exchange	Chen & Yang 2006
Sargassum sp.		Cr(III)	136	2.6	Emphasis on rates; Langmuir fit	Cossich et al. 2004
Sargassum sp.		Cd(II), Zn(II)	120	1.1	Pseudo 2nd order rate; Langmuir fit	De Britto et al. 2007
Sargassum sp.		La(III), Eu(III), Yb(III)	118, 129, 138	0.85, 0.85, 0.80	Favored by higher pH; Eu > La > Yb; confirmed by Ca release	Diniz & Volesky 2005
Reed, water lily	Acid	Cr(VI), Cr(III)	9, 7	.17,.13	2nd order rate; Cr(VI) was reduced by tannins, phenolics, etc.; acid treatment enhanced uptake; alkali treatment hurt Cr(VI) uptake	Elangovan et al. 2008a
Sargassum fl.		Cd(II), Pb(II)	103, 219	0.92, 1.06	Strong, weak acid groups, sulfonate vs. carboxylate; bidentate complex of Cd(II)	Fourest & Volesky 1996
Posidonia oc.	EDTA	Cu(II)	__	__	Not as effective as activated carbon	Gabaldón et al. 2007
Porphyra & Ulva		Pb(II)	139	0.67	Can be separated from zinc by this sorbent	Ghimire et al. 2007
Laminaria japon.	Epichlor	Pb(II), Fe(III), Cd(II), La(III), Ce(III)	279,85, 124, 121, 122	1.4,1.5, 1.1,.87	Concentration factor 74 for Pb(II) with Zn(II)	Ghimire et al. 2008
Posidonia ocean.		Cu(II)	57-86	.90-1.4	Seagrass; Langmuir fit; regen. with HCl	Izquierdo et al. 2010
Laminaria japon.	Ca load	Pb(II), Cu(II)	__	__	Kelp had higher affinity for Pb; ion exchange	Lee & Suh 2000
5 brown seaweed			64-95	__	Pseudo 2nd order rate; Langmuir fit	Lodeiro et al. 2005
Sargassum sp., orange peel, bracken fern		Cr(III)	__	__	Carboxyl group content correlated with uptake; Langmuir fit; regeneration with sulfuric acid and sodium citrate	Lodeiro et al. 2008
Ascophyllum n.		W, Mo, V, Ge, Sb metal oxo-anions	__	__	Tungstate, molybdate, and vanadate adsorbed effectively	Mistova et al. 2007

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Various species	Acetone	Cu(II), Cr(III), Cr(VI)	27-65, -, -	.42-1.0	Blocking carboxyl, amino groups hurt uptake; some reactions suppressed reduction to Cr(III)	Murphy et al. 2009a
Various species		Cr(VI)	__	__	Reduction was an important part of mechanism; ion exchange	Murphy et al. 2009b
Sargassum glau.	Protonat	Pb(II), Cd(II)	244, 27	1.2,.24	Bed; ion exchange; partial regeneration by HCl (60%)	Naddafi et al. 2007
Ecklonia sp.	Thermal	Cr(VI), Cr(III)	15-38	.29-.73	Thermal treatment made biomass a better reductant but with less affinity for the Cr(III)	Park et al. 2004a
Ecklonia sp.	Proton-ated	Cr(VI)	234	4.5	Tests at pH 2.5; complete reduction to Cr(III) by biomass, with some of the latter appearing in solution	Park et al. 2004b
Ecklonia sp.	Acid treatment	Cr(VI)	No eval	No eval	Amination helped adsorption, whereas esterification of carboxyls had a smaller effect	Park et al. 2005d
Ecklonia sp.	Cr(III), other metals	Cr(VI)	No eval	No eval	Most metals did not affect Cr(VI) reduction by the biomass	Park et al. 2006a
Ecklonia sp.	Two-stage pH	Cr(VI), Cr(III), Zn(II)	No eval	No eval	Reductive adsorption of Cr(VI); ion exchange of the others; start at pH 1.5-2.5, then raise the pH to 4-5	Park et al. 2006b
Ecklonia sp.		Cr(VI)	No eval	No eval	Flow column; neural network modeling	Park et al. 2006c
Ecklonia sp.		Cr(VI)	No eval	No eval	Complete surface reduction; was Cr(III) in bound state	Park et al. 2008d
Sargassum sp.	Drying	Cr(VI)	__	__	Drying reduced porosity	Rocha et al. 2006
Seaweed waste		Cd(II)	60-140	.53-1.3	Best pH 6-8; two pKa sites correspond to carboxyls and thiols or amines. Esterification reduced uptake markedly; ion exchange	Romero-Gonzalez et al. 2001
Sargassum fluit.	Dead	Cd(II), Cu(II), Zn(II)	34-302, 171, 174	.30-2.7, 2.7, 2.7	Multicomponent Langmuir fit; ion and proton exchange; 2-site model; competition for sites	Scheiwer & Volesky 1995

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Sargassum sp.		Cu(II)	133	2.1	Ion exchange; carboxyl and sulfate sites; Donnan alanysis	Scheiwer 1999
Four species		Cu(II), Ni(II)	64-197, 65-170	1.0-3.1, 1.1-2.9	Cu binding 10X stronger than Ni; brown algaes had much higher uptake; stoichiometric binding	Scheiwer & Wong 1999
Marine algae		Cu(II), Ni(II)	171, 135	2.7, 2.3	Site characterization	Scheiwer & Wong 2000
Sargassum f		U	8	0.03	In presence of other ions; spent biomass was calcined for storage	Silva et al. 2009
Sargassum		Ag(I), Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II), Zn(II), Cr(III)	43-65, 56-79, 35, 57-67, 22-33, 18-37, 248, 26-39, 68	0.4-0.6, 0.5-0.7, 0.6-0.6, 0.9-1.1, 0.4-0.6, 0.4-0.6, 1.1-1.2, 0.4-0.6, 1.3	Langmuir fits; Cr(III) > Pb ≈ Cu > Ag ≈ Zn ≈ Cd > Ni ≈ Co >> Cr(VI) > As(V) low salt; salt inhibited sorption; ion exchange	Tsui et al. 2006
Ecklonia m		Cu(II), Ni(II), Cd(II)	No eval	-	Copper wins the competitions	Williams et al. 1998
Ecklonia		Cr(III)	35	0.7	Higher pH preferred; carboxyl binding sites; hydrolysis reactions at higher pH	Yun et al. 2001
Sargassum p		Cd(II)	146	1.3	Carboxyl groups binding; complexation	Yun & Volesky 2003
Brown seaweed, other biomass		**Multi-metal:** Cu(II), Pb(II), Zn(II), Ni(II) **Alone:** Cu(II), Pb(II), Zn(II), Ni(II)	2-117 23, 41, 13, 12	0.2 0.4, 0.2, 0.2, 0.2	Chromatographic effect due to differing affinities of metals	Zhang & Banks 2006

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Loofa						
Loofa alone		Ni(II)	6	0.10	Not as effective as when coated by bacterium	Akhtar et al. 2004
Chlorella sorokin.	Immob.	Ni(II)	48-60	0.8-1.0	Immobilized *Chlorella sorokin.* on Loofa worked best at pH 4+; HCl regeneration	Akhtar et al. 2004
Sargassum fluit.	Proton	Cu(II)	62, 54	1.0, 0.8	Elution of the exchanged ions	Kratochvil et al. 1995
Sargassum fluit.	Acid or Ca^{2+}	Cu(II)	75	1.2	Ion exchange; how to regenerate not critical	Kratochvil et al. 1997
Sargassum fluit.	Proton	Cr(III), Cr(VI)	38, 60	0.73, 1.2	Best pH 2 for Cr(VI); simultaneous anion exchange & reduction;	Kratochvil et al. 1998
Sargassum fluit.		U(VI)	560		Higher pH favored to 4; Langmuir fit; hydrolyzed U species; regen. w. HCl	Yang & Volesky 1999a
Sargassum fluit.		Cd(II)	75	1.45	Langmuir fit; ion exchange; diffusion control	Yang & Volesky 1999b
Sargassum fluit.	Proton-ated	U(VI)	430	1.8	HIgher pH favored ; ion exchange ; model	Yang & Volesky 1999c
Sargassum sp.	HCl, NaOH, CaCl$_2$, CH$_2$O, glutarald	Cr(VI)	31-58	0.6-1.1	Treatments reduced leaching, did not hurt metal uptake; best pH 2; redox control	Yang & Chen 2008
Microbiota						
Algae						
Fucus serratus		Cu(II)	102	1.61	Effective pH 5; ion exchange; Langmuir fit; alginate mucilage may be key	Ahmady-Asbchin et al. 2008
Oscillatoria angu.		Zn	641	10		Ahuja et al. 1999
Chlorella sorokin.	Immob. on loofa	Ni(II)	48-60	0.82-1.02	Immobilized *Chlorella sorokin.* on loofa worked best at pH 4+; HCl regeneration	Akhtar et al. 2004
Chlorella vulgaris		Cr(VI)	6-28	0.1-0.5	Simultaneous removal of Cr(VI) and Cu(II)	Aksu & Açikel 1999
Chlorella vulgaris		Cr(VI)	27	0.52	Simultaneous removal of Cr(VI) and Fe	Aksu & Açikel 2000
Chlorella vulgaris		Cu(II)	43	0.68	Best pH 4-4.5	Aksu et al. 1992
Chlorella vulgaris		Fe(III), Cr(VI)	21, 25	0.4, 0.5	Best pH 2; metals compete; Langmuir fit.	Aksu et al. 1997
Chlorella vulgaris		Cu(II), Cr(VI)	17-28, 27	0.3-0.5, 0.52	Competitive adsorption of the two metals.	Aksu et al. 1999

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Chlorella vulgaris		Cd(II)	111	1.00		Aksu (2001)
Chlorella vulgaris	Dried	Cd(II), Ni(II)	87, 58	0.78, 0.89	Competition shown; Langmuir fit	Aksu & Donmez 2006
		Cd(II)	28	0.53	Desorption by HCl and pH 1 worked by ion exchange for concentration & regeneration	Aldor et al. 1995
Caulerpa lentillif.		Cu(II), Cd(II), Pb(II)	4.4, 6.7, 11	0.07, 0.06, 0.055	Binary sorption; some mutual sites exist; better at higher pH	Apiratikul & Pavasant 2006
Chlamydomonas	Heat, acid	Cr(VI)	18-26	0.34-0.5	Best pH 2; 2nd order rate; Langmuir fit; NaOH regeneration (96%)	Arica et al. 2005
F .vesiculosus, A. nodosum		Zn(II), Cu(II), Ni(II)	2-25, 4-9, 0.7-3	.02-.39, .06-.14, .01-.05	Bacteria, yeast, fungi, activated sludge, and marine algae were effective; biomass types were suited for different metals.	Bakkaloglu et al. 1998
Spirogyra spp.	NaOH, $CaCl_2$, CH_2O	Cr(III)	30	0.6	Best pH 5; Langmuir fit OK	Bishnoi et al. 2007
Sargassum siliq.		Cr(VI)	60	1.2	Best pH 2; reduction in parallel with adsorption; reduction is a first step in regeneration	Cabtingan et al. 2001
Fucus		Cu(II)	115	1.8	Pseudo 2nd order rate; Langmuir fit	Cochrane et al. 2006
Fucus spiralis		Cd	64	0.57		Cordero et al. 2004
Sargassum sp.		Cd(II)	120	1.1		Cruz et al. 2004
Various algae		Cr(VI)	79-154	1.5-3.0	Tested at pH 2; Langmuif fits	Dönmez et al. 1999
Dunaliella strains		Cr(VI)	46-102	0.9-2.0	Best pH 2; strong competition by salt; pseudo 2nd order rate; Langmuir fit	Dönmez & Aksu 2002
Ulva lactuca		Cr	11	0.2	Best pH 1; not sensitive to salt; pseudo 2nd order rate; Langmuir fit	El-Sikaly et al. 2007
Fucus vesiculosus		Cu(II)	75	1.2		Fourest & Volesky 1997
Spirulina platensis Chlorella vulgaris	Fresh & spent	Cr(VI)	68-76	1.3-1.5	Best pH 1.5; also OK pH 4-5; fresh or spent worked equally; Langmuir fit	Gokhale et al. 2008
Fucus vesiculosus		Cu(II)	23	0.4	Pseudo 2nd order rate; Langmuir fit; regenerated with HCl	Grimm et al. 2008
Spirogyra sp.		Cr(VI)	15	0.3	Best pH 2; Langmuir fit	Gupta et al. 2001

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Oedogonium sp., *Nostoc* sp	Dried	Pb(II)	93-145	0.4-0.7	Best pH 5; 2nd order rate; Langmuir fit; carboxyl and amino groups; endothermic; regenerated with HCl (90%)	Gupta & Rastogi 2008a
Oedogonium sp.,	Dried, NaOH	Cd(II)	80-89	0.7-0.8	NaOH enhancement; 2nd order rate; Langmuir fit; functional groups; regenerable	Gupta & Rastogi 2008b
Oedogonium h.,	Raw, acid treat	Cr(VI)	31-35	0.6-0.7	Acid treatment helped; best pH 2; first order rate; Langmuir fit; groups; regenerated with NaOH (75%)	Gupta & Rastogi 2009
Fucus spp.	Dead	Cd(II)	90	0.8	Higher pH favored to 5; Pseudo 2nd order rate; multi-site model	Herrero et al. 2006
Three algal sp.; *Ascophyllum n.* *Fucs spiralis* *Sargassum nat.*	CH$_2$O	Cd(II)	100, 215, 73, 135	0.9, 1.9, 0.6, 1.2	Best pH 3.5; regen. with HCl	Holan et al. 1993
Ascophyllum n. *Fucus vesiculos.* *Sargassum nat.*		Ni(II), Pb(II) Ni(II), Pb(II) Ni(II), Pb(II)	30, 270-360; 17,220-371; 24-44, 70-220	0.5, 1.3-1.7; 0.3, 1.1-1.8; 0.4-0.9, 0.3-1.1		Holan & Volesky 1995
Chlorella vulgaris	Lyophiil-ized	Au(0)	No eval	No eval	Gold powder and ionic; at least three adsorption sites ionvolved	Hosea et al. 1986
Aphanothece h		Zn(II)	133	2.0		Incharoensakdi & Kitjaharn 2002
Algal biomass	Varieties	Pb(II)	40-270	0.2-1.3	Higher pH favored; regen. at pH<1 (95%) or CaCl$_2$	Jalali et al. 2002
Algal biomass	Ferro-cyanide	Cs(I)	10-100	0.08-0.8	Best pH 4; ferrocyanide enhanced uptake; Langmuir fit; regen. w base	Jalali-Rad et al. 2004
Undaria pinnat.		Cu(II)	200	3.2	Uptake of Cu(II) increased 4.5X by oxime; highly selective vs. Ca(II), Cd(II), Pb(II)	Kim et al. 1996
Undaria pinnat.		Pb(II)	340	1.6	Surface complexation model demonstrated	Kim et al. 1998

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Undaria pinnat.		Pb(II), Cu(II), Cd(II)	340	1.6	Xanthation increased adsorption capacity 3X; selective adsorption possible (compared to Ni(II), Zn(II), and Co(II)	Kim et al. 1999
30 strains		Cd(II), Pb(II), Ni(II), Zn(II)	34, 93-270, 22-26, 20-29	0.3, .45-1.3, .37-.45, .32-.45	Langmuir fits; different selectivities, different optimum pHs; phosphorylation beneficial in some cases	Klimmek et al. 2001
Ulva fasciata		Cu(II), Zn(II)	27, 14	0.4, 0.2	Higher pH favored to 5; Langmuir fit	Kumar et al. 2006c
Ascophyllum n		Co(II)	156, 100	2.65, 1.7		Kuyucak & Volesky 1989
Pachymeniopis		Cr(VI)	225	4.3		Lee et al. 2000
3 brown algae	Dead	Cu(II), Pb(II), Zn(II)	164, 538, 136	2.6, 2.6, 2.1	Best pHs 3-6; severe competition	Lee et al. 2002
2 marine agae	CH_2O, glutarald	Pb(II), Cd(II), Cu(II), Ni(II), Zn(II)	378, 130, 85, 89, 60	1.8, 1.2, 1.3, 1.4, 0.9	Modificatio effectiveness : GA > FA > PEI ; Langmuir fits	Leusch et al. 1995
Cystoseira bacc.		Cd(II); Pb(II)	101, 186	0.9, 0.9	Higher pH favored to 4; pseudo 2nd order rate; Langmuir fit; carboxyl group involvement	Lodeiro et al. 2006
Laminaria japon.	Epichlor; $KMnO_4$	Pb(II)	250-346	1.2-1.7	Best pH 5.3; Langmuir combination fit	Luo et al. 2006
Marine algae		Pb(II), Cu(II)	250, 78	1.2, 1.2	Electrostatic and coordination binding	Malik et al. 2002
Ulothrix zonata		Cr(VI)	__	__	Freundlich fit	Malkoc & Nuhoglu 2003
Fucus vesicul.		Cd(II), Pb(II), Cu(II)	108, 211, 106	0.96, 1.00, 1.67	Pseudo 2nd order rate; ion exchange/complexation; Langmuir fit	Matta et al. 2008
Marine algae		Pb(II), Cu(II)	331,83	1.6, 1.3	Modification was effective; best pH 4.5	Matheickal & Yu 1999
Marine algae	$CaCl_2$, heat	Cd(II)	124	1.1	Modification was effective; best pH 5	Matheickal et al. 1999

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Various	Dried	Cu(II)	6-22	0.10-0.35	Carboxyl & amino groups prominent; acidic sites most important	Murphy et al. 2007
Various	Dried	Cr(III), Cr(VI)	63, 46	1.2,0.8	Langmuir fits	Murphy et al. 2008
Chlorella vulgaris, Cladophora crisp. Rhizopus arrhizus		Cr(VI)	2.5-3.5, 2-3, 2.5-4.5	0.07, 0.06, 0.08	Best pHs 1-2; Freundlich fits	Nourbakhsh et al. 1994
Ulothrix zonata		Cu(II)	160	2.5	Langmuir fit	Nuhoglu et al. 2002
Two species		Cr(III)	12-14	0.23-0.27	Best pH 5; competition; carboxyl groups important; Langmuir fit; regen. with H_2SO_4	Onyancha et al. 2008
Cladophora crisp.		Cu(II)	60	1.0	Best pH 4.5; pseudo 2nd order rate; Langmuir fit	Ozer et al. 2004a
Microcystis		Fe(III), Ni(II), Cr(VI)	260, 95, 65	4.6, 1.6, 1.2	Iron adsorbed preferentially with Langmuir fit; Ni and Cr Freundlich fits; carboxyl & amino groups important	Pradhan et al. 2007
Fucus vesiculosus	HCl, Ca, CH_2O, Na_2CO_3, NaOH	Cu(II), Cd(II), Pb(II), Ni(II)	223, 337, 248, 141	0.9-3.8, 0.5-3.0 0.9-1.2, 0.4-2.4	Treatments with Na_2CO_3 and NaOH increased uptake greatly; calcium was the only metal that improved sorption capacities; Langmuir fits	Rincón et al. 2005
Chlorella vulgaris		U	4	0.017		Sakaguchi & Nakajima 1991
Ceramium virgat.		Cr(VI)	26	0.50	Best pH 1.5; pseudo 2nd order rate; Langmuir fit best	Sari & Tuzen 2008
Padina pavonica		Al(III)	77	2.8	Pseudo 2nd order rate; Langmuir fit; ion exchange; edothermic; regen. with HCl	Sari & Tuzen 2009b
Sargassum sp. , Padina sp.		Cd(II), Cr(III), Cr(VI)	64, 15, 10	0.57, 0.28, 0.2	Best pH Cr(VI) at 2; for Cr(III) 3.8; for Cd(II) 5.5; Langmuir fits; simultaneous reduction and adsorption	Sheng et al. 2004a
Several species		Pb(II), Cu(II), Cd(II), Zn(II), Ni(II)	259 Pb 37-72 Cu	1.25Pb 0.6-1.1 Cu	Best pHs 5.5-6'; chelating by carboxyls with participation by ether, ROH, amino groups	Sheng et al. 2004b
Sargassum sp.		Pb(II), Cu(II), Cd(II)	180, 65, 31	0.85, 1.0, 0.6	Higher pH favored; Langmuir fits (competitive); correlations with electronegativities & stability of hydroxides; competition & hogging	Sheng et al. 2007

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Sargassum sp.	PVA gel	Cu(II)	57	0.9	The beads showed slower uptake than free *Sargassum*	Sheng et al. 2008
Sargassum sp.		Cd(II), Zn(II), Cu(II)	157, 118, 77	3.0, 1.8, 1.2	Langmuir fits	Valdman & Leite 2000
Sargassum sp.		Cr(VI)	19	0.36	Column dynamics	Vieira et al. 2008
Ascophyllum n.		Cd(II)	30	0.28	Column studies	Vlosky & Prasetyo 1994
Sargassum sp.		Cu(II)	38	0.60	Column long-term use	Volesky et al. 2003
Micro-algae, etc.		Cu(II)	4-10	.06-.16	Pseudo 2nd order rate; Langmuir fits	Wang et al. 2009
Chlorella fusca		Pb(II)	293	1.4		Wehreim & Wattern 1994
Common marine		Cd(II), Cu(II), Pb(II)	90-123, 51-76, 207-330	0.8-1.1, 0.8-1.2, 1.0-1.6	0.8 to 1.6 mmol/g (dry)	Yu et al. 1999
Alginic acid with cellulose		Cd(II), Cu(II)	79, 32	0.70, 0.50	Best pHs 2-3; competition; regen. with HCl	Zhang et al. 2004
Algae & micro-algae sp.		Cu(II), Cd(II)	21-23, 22-24	0.35, 0.20	Best pHs 4-5 & 6.7, resp.; competition; Freundlich fit; regen by HCl or EDTA	Zhou et al. 1998
BACTERIAL						
Streptomyces	NaOH	Zn(II)	2.9	0.04	NaOH pretreatment increased binding; continuous flow system demonstrated; HCl regeneration successful	Addour et al. 1999
Various		Pb, Zn, Cd, Cr, Cu, Ni	5 to 641	Mass listed	Review article: Fermentation byproducts were effective.	Ahluwalia et al. 2005b
Zoogloea ramig.		Cu	29	0.46		Aksu et al. 1992
Thiobacillus fero.		Cr(III)	509	9.8	Tolerant of Cr(III); best pH 1.4;	Baillet et al. 1998
Streptomyces rim.	NaOH	Ag(I)	63	0.58	Mass transfer control; poor Langmuir fit	Bakhti et al. 2008
Bacillus subtilis		Mn(II), Fe(III), Ni(II), Cu(II), Au(III)	0.8, 3.6, 0.1, 3.0, 0.36	0.01, 0.06, 0.002, 0.05, 1.8	Removal of carboxyl groups precluded metals uptake; removing amines had no effect.	Beveridge & Murray 1980

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Phormidium lam.	In resin	Cu(II), Fe(II), Ni(II), Zn(II)	20-21, 17-18, 13-16, 18-19	.31-.33, .30-.33, .22-.27, .28-.29	Smaller bead size increased rate; regeneration with HCl	Blanco et al. 1999
Rhodococcus		Pb(II)	94	0.45	Competition; 2nd order rate; Langmuir fit	Bueno et al. 2009
Pseudomonas a.	Inactivat.	Hg(II)	180	0.90	Effects of pH, salt, phosphate; Langmuir fit	Chang & Hong 1994
Pseudomonas a.	Live vs. inactivat.	Pb(II), Cu(II), Cd(II)	70-110, 20-24, 30-60	0.3-0.5, 0.3-0.4, 0.2-0.5	Both live & inactivated cells were effective; Higher pH better, eventually has hydroxides; regeneration effective	Chang et al. 1997
Bacterial cellulose	CMC	Cu(II), Pb(II)	13, 60	0.2, 0.3	Good pH 4.5; carboxylation greatly increased uptake	Chen et al. 2009
Pseudomonas p.	Living, non	Cu(II), Zn(II)	13-24, 12-27	0.2-0.4, 0.2-0.4	Living cells adsorbed more; Best pH 4.5-5; Langmuir fits; Regen. By HCl (84%)	Chen et al. 2005
Streptomyces r.	NaOH	Cu(II), Zn(II), Cr(VI)	30, 27, 27	0.5,0.4, 0.5	Poor Langmuir fit	Chergui et al. 2007
Corynebacterium	Protonat.	Pb(II)	568	2.7	Ion exchange with H	Choi & Yun 2004
Streptococcus l.		Pb(II), U	100, 440	0.48, 1.8		Friis & Myers-Keith 1986
Streptococcus e., _Saccharomyces_, _Aspergillus niger_	Nutrients (living)	Cr(VI), Fe(III)	58, 22; 35, 22; 13, 20	1.1,0.4; 0.7,0.4, 0.2,0.4	Higher temperature favored moderately, regeneration with NaOH	Goyal et al. 2003
Aeromonas hydro.	Dead, p-suflone	Cr(VI)	45-42	0.9-0.8	Regenerable with moderate loss of effectiveness	Hasan et al. 2009b
Ten bacterial,	Living	U	22-53	0.1-0.2	actinomycetes > bacteria, yeasts > fungi; Freunlich isotherm; bio activity not needed	Horikoshi et al. 1981
Cyanobacteria	Live, salts	Cr(VI)	17-18	0.35	Best pH 3; moderate repression by salt; pseudo 2nd order rate; Langmuir fit	Kiran et al. 2007
Cyanobacteria	Live	Cr(VI)	111	2.1	Immobilization greatly decreased uptake; regenerable with HCl	Kiran & Kaushik 2008
Pseudomonas a.	Matrices, epichlor, chitosan	Pb(II)	28-34	0.1-0.2	Regeneration with HCl (capacity values multiplied by 1000 factor)	Lin & Lai 2006

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Aeromonas cavi.		Cd(II)	124-155	1.1-1.4	Langmuir fit	Loukidou et al. 2004a
Aeromonas cavi.		Cr(VI)	169-284	3.2-5.5	Pseudo 2nd order rate; higher uptake at lower temperature; Langmuir fit	Loukidou et al. 2004b
Streptomyces r.	NaOH	Zn(II)	30, 80	.45-1.2	NaOH treatment greatly increased capacity	Mameri et al. 1999
Streptomyces n.		Cd(II), Cu(II), Ni(II), Pb(II), Zn(II), Ag(I), Co(II), Cr	3.4, 9, 0.8, 55, 1.6, 38, 1.2, 2.0	.003, 0.14, 0.013, 0.26, 0.024, 0.35, 0.020, 0.038		Mattuschka & Straube 1993
Micrococcus lut.	Hot H_2O, NaOH, CH_2O & mixture	Cu(II)	33+	0.5+	KOH treatment most effective; N and O sites important	Nakajima et al. 2001
Micrococcus lut.		Th, U	18-74, 2-71	.08-.32, .01-.30	Langmuir binary fits	Nakajima & Tsuruta 2004
Zoogloea ramig.		Cr(VI)	2	0.04		Nourbakhsh et al. 1994
Pseudomonas a. on activated C		Cr(VI), Ni(II), Cu(II), Zn(II), Cd(II)	No report	No report	42-84% uptake; Langmuir fits	Orhan et al. 2006
Pantoea sp.		Cr(VI), Cd(II), Cu(II)	54-204, 54, 30	1-4, 0.5,0.5	Best pHs: 3, 6, 5 for Cr(VI), Cd(II), Cu(II); Langmuir fits	Ozdemir et al. 2004
Arthrobacter sp.		Cu(II), Cd(II), Fe	45, 13, 56	0.71, 0.12, 1.0	Ion exchange/complexation; two kinds of acidic sites	Pagnanelli et al. 2000
Pseudomonas p.	Freeze dried	Cd(II), Cu(II), Pb(II), Zn(II)	8.0,6.6, 56, 6.9	.15,.10, .27,.10	Best pHs 7-7.5; 80% removal; Langmuir fit; $M(OH)^+$ complexes	Pardo et al. 2003
Corynebacterium		Cr(VI)	5.7	0.11	Reductive adsroption	Park et al. 2008b
Streptomyce pim.	Ethanol	Cd(II)	5-30	0.04-0.26	Higher pH favored to 5; Langmuir fit; resorbed with EDTA	Puranik et al. 1995

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Streptoverticillium	Boiling water	Pb(II), Zn(II)	58, 21	0.28, 0.32	Boiling water increased uptake by 41-52%; best pHs 3.5-4.5 and 5-6; Langmuir fit; more than one bonding site; regen. HCl, NaHCO$_3$	Puranik & Paknikar 1997
Streptoverticillium		Pb(II), Zn(II), Cd(II), Cu(II), Ni(II), Co(II)	62, 9, 18, 6, 4, 4	0.3+, 0.14, 0.16, 0.10, 0.07, 0.07	Preferential Pb(II) uptake; Langmuir fits predict multi-metal adsorption; Pb2+ > Zn2+ = Cu2+ > Cd2+ > Ni2+ > Co2+	Puranik & Paknikar 1999
Bacillus thuring.		Cr(VI)	29-34	.55-.65	Langmuir fit	Şahin & Öztürk 2005
Bacillus firmus		Pb(II), Cu(II), Zn(II)	467, 381, 418	2.2, 1.8, 2.0		Salehizadeh & Shojaosadati 2003
Microbial bomass		Sr(II)	13-24	.15-.27	On roots; Langmuir fit; regen. by acid	Scott 1992
Streptomyces r	NaOH	Cd(II)	63	0.56	Mass transfer control; Langmuir fit	Selatnia et al. 2004a
Streptomyces r	NaOH	Fe(III)	122	2.18	Langmuir fit	Selatnia et al. 2004b
Streptomyces r	NaOH	Pb(II))	135	0.65	Langmuir fit	Selatnia et al. 2004c
Streptomyces r	NaOH	Ni(II))	33	0.56	Langmuir fit	Selatnia et al. 2004c
Bacillus coagul.; Bacillus megater.		Cr(VI)	40, 31	.77, .60	Dead cells were more effective	Srinath et al. 2002
Sphingomonas p	Living	Cd(II)	No eval	No eval	Living cells adsorbed more	Tangaromsuk et al. 2002
Mucor hiemalis		Cr(VI)	47-54	.90-1.0	Langmuir fit	Tewari et al. 2005
Pseudomonas a.	Drying	La(III),Eu(III), Yb(III)	129,61, 56	.93,.40, .32	Batch; BET fit; drying did not affect uptake; Al(III) antagonism	Texier et al. 1999
Pseudomonas a.	Drying	La(III),Eu(III), Yb(III)	74, 35, 33	.53,.23, .19	Column; Competition: Eu3+ > Yb3+ > La3+	Texier et al. 2000
Pseudomonas f.		Th, U	15, 6	.06,.02		Tsezos & Volesky 1981
Mucor meihei		Cr	60	1.15	Best pH zero	Tobin & Roux 1998
Saccharomyces c, Aspergillus oryzae Bacillus lentus	Fermen-tation byprods.	Cu(II), Zn(II), Cd(II)	10-30, 5-13, 4-80	.16-.47, .08-.20, .04-.71	Nonprotonated biomass had higher uptake; Langmuir fits	Vianna et al. 2000
Corynebacterium	Biomass origin	Ni(II)	102-111	1.7-1.9	Best pH 6	Vijayaraghavan et al. 2008

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
From mine extract	Poly-sulfone	Cd(II)	10-60	.09-.53	3-fold higher uptake than many other candidates; uptake increased greatly by carboxylation, CS_2, thiosulfate; various regeneration solutions	Xie et al. 1996
Bacillus licheni.	Dead	Cr(VI)	60	0.12	Pseudo 2nd order rate; Langmuir fit	Zhou et al. 2007
Staphylococcus, Pseudomonas		Cd(II), Cr(VI)	164, 95-143	1.46, 1.8-2.8	Langmuir fit; Cd wins competition	Ziagova et al. 2007
Actinomycetes, fungi	Living or dead	Cd(II)	—	—	Non-liviing biomass showed greater uptake	Zoubloulis et al. 1997
YEAST						
Yeast biomass	Acetone	Pb(II)	49	0.24	Blocking carboxyl groups hurt adsorption; complexation	Ashkenazy et al. 1997
Saccharomyces c.		Sr(II), Mn(II), Zn(II), Cu(II), Cd(II), Ti(I)	1.3, 0.82, 0.92, 1.3, 2.8, 0.33	0.015, 0.015, 0.014, 0.028+, 0.025+, 0.007	Covalent & electrostatic contributions; explained by hard/soft ion theory; metal complexes can interfere with adsorption	Avery & Tobin 1993
S.rimosus, yeast		Zn(II), Cu(II), Ni(II)	2-26, 4-9, 1-3	.03-.39, .06,.14, .01-.05	Bacteria, yeast, fungi, activated sludge, and marine algae were effective; biomass types were suited for different metals.	Bakkaloglu et al. 1998
Yeast	Hot NaOH	Fe(III), Cu(II), Cr(III), Hg(II), Pb(II), Cd(II), Co(II), Ag(I), Ni(II), Fe(II)	—	—	Selective adsorption: Cu2+ > Cr3+ > Cd2+ and Cu2+ > Pb2+ > Ni2+ >> Cr(VI)	Brady et al. 1994
Distillary		Cu(II), Zn(II), Fe(II), Pb(II), Ag(I)	5, 12, 14,180, 55	.08,.18, .25,.87, 0.51	Pb > U > Ag > Zn greater than or equal to Fe > Cu	Bustard & McHale 1998
Saccharomyces c.		Pb(II)	30	0.14	Immobilized bacterium biomass on pine cone; best pH 5; Langmuir fit	Cabuk et al. 2007
Saccharomyces c.		Cu(II)	No eval	No eval	Biocatalytic reduction by immobilized microbe	Chandran et al. 2002

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Brewer's waste		Pb(II), Ag(I), Cs(I), Sr(II)	86, 43, 1, 8	.42,.40, .01..09	Langmuir fit; uptake correlated with covalent index and electroneativity, opposite to dissociation constant	Chen & Wang 2008b
Saccharomyces c.		Zn(II)	5-43	.08-.66	Ion exchange	Chen & Wang 2007a
Saccharomyces c.		Pb(II), Ag(I), Cr(II), Cu(II), Zn(II), Cd(II), Co(II), Sr(II), Ni(II), Cs(II)	85,41, 12,10, 10,16, 8,11, 6,12	.41, .38 .24,.16, .15,.14, .13,.12, .11,.09	SQAR model; selectivity vs. hard or soft ions shown; Pb(II) and Ag(I) were high outliers	Chen & Wang 2007b
Saccharomyces c.		Pb(II), Ag(I), Cr(III), Cu(II), Zn(II), Cd(II), Co(II), Sr(II), Ni(II), Cs(I)	85, 42, 13, 10, 10, 15, 8, 10, 6, 12	.41,.39, .25,.16, .15,.13, .14,.11, .10,.09	Langmuir fits; uptake increased with increasing covalent character of binding	Chen & Wang 2007c
Saccharomyces c		Zn(II)	20	0.3	Ion exchange demonstrated; binding with oxygen	Chen & Wang 2008a
Saccharomyces c.		Pb(II), Ag(I), Cu(II), Zn(II), Co(II), Sr(II), Cs(I)	87,30, 11, 7, 5, 5, 8	.42,.28, .17,.11, .08,.06, .06	Pb>Ag>Cu>Zn>Co>Sr>Cs; 2nd order rate; Langmuir fit; soft ions preferred; covalent content	Chen & Wang 2010
Ten yeasts	Living	U	16-40	0.1-0.2	actinomycetes > bacteria, yeasts > fungi; Freunlich isotherm; bio activity not needed	Ten bacterial,
Saccharomyces c.		U(VI)	2082	8.7	UO_2^{2+} ions; the cells were destroyed & broken open by the uranyl nitrate	Popa et al. 2003
Rhodotorula rubra		Cd(II), Pb(II)	13, 6.0	0.12, 0.03	Dead biomass preferred; best pHs 4-6; Langmuir fit; desorp. with EDTA or HCl	Salinas et al. 2000
Saccharomyces c	Genetic fusions	Cd(II), Zn(II)	2-3, 1.3-2.0	.02-.03, .02-.03	30% increased uptake due to genetic engineering	Vinopal et al. 2007
Saccharomyces c	Living vs. dead	Cd(II)	70	0.62	Living cells were more effective	Volesky et al. 1993
Candida fused	Live	Cr(VI), Ni(II)	No eval	No eval	Reduction of Cr(VI) involves metabolism; Ni uptake is passive	Yin et al. 2008

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Saccharomyces c	CH$_2$O	Cu(II), Zn(II), Cd(II)	8, 7, 7	.12,.11, .06	Best pHs 5.3, 6, 6.7; regen. with HCl	Zhao & Duncan 1997b
Saccharomyces c	CH$_2$O	Cr(VI)	63	1.2	Low pH best; regen. with HCl	Zhao & Duncan 1998b
FUNGAL						
Aspergillus flavus	Deterg., NaOH, DMSO	Pb(II), Cu(II)	13, 11	.06,.17	Deterg., NaOH, DMSO enhanced sorption.	Akar & Tunali 2006
Aspergillus parasi.		Pb(II)	10-38 (55 at 70 min)	.05-.18	HIgher pH favored to 6; lower temp. better; ion exchange/complexation; Langmuir fit; regeneration possible	Akar et al. 2007
Rhizopus arrhizus	NaCl	Cr(VI)	65-80	1.2-1.5	Best pH 2; salt repressed adsorption; Langmuir fit	Aksu & Balibek 2007
Aspergillus niger	Alkali	Ag(I)	10,000	92	Ion exchange; can be regenerated.	Akthar et al. 1995
Lactarius scrobic.		Pb(II), Cd(II)	56, 53	.27,.47	Best pH 5.5; ion exchange; 2nd order rate; exothermic; regen. 95% with acid treatment.	Anayurt et al. 2009
Lentinus sajor-c; CMC alone; *L. sajor-c on CMC*		Cr(VI)	19, 5, 32	0.37, 0.10, 0.62	Tested at pH 2; Langmuir fits	Arica & Byramoğlu 2005
Rhizopus oligo.		Pb(II)	126	0.61	Best pH 5; Langmuir fit; ion exchange	Ariff et al. 1999
Rhizopus oligo.		Cd(II)	17	0.15		Aloysius et al. 1999
Rhizopus arrhizus		Cr	11	.21	Best pHs 2-7	Bai & Abraham 1998
Rhizopus nigric.		Cr, Pb(II)	47	0.90	Best pH 2; smaller particles better	Bai & Abraham 2001
Four strains	Acetic anhydr., cationics	Cr(VI)	46-200	0.9-3.8	Best pH 2; acetic anhydride rx. with amino groups hurt adsorption; cationic compounds enhanced adsorption; Langmuir fit	Bai & Abraham 2002
Rhizopus nigric.	Support	Cr(VI)	21-119	.40-2.3	Effect of matrix to hold the biomass; regeneration by carbonate or NaOH	Bai & Abraham 2003
S.cerevisiae		Zn(II), Cu(II), Ni(II)	3.4, 3.9, 1.5	0.052, 0.061, 0.025	Bacteria, yeast, fungi, activated sludge, and marine algae were effective; biomass types were suited for different metals.	Bakkaloglu et al. 1998

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Trametes versic.	Live, inactiv.	Cu(II), Pb(II), Zn(II)	117, 230, 109	1.8, 1.1, 1.7	Best pH 4-6; slightly higher uptake on inactivated biomass; Langmuir fit; HCl regeneration 97%	Bayramoglu et al. 2003
Lentinus sajor-c.		Cr(VI)	20-33	.38-.63	Heat treatment enhanced uptake; HCl and NaOH less effective; Langmuir fits	Bayramoglu et al. 2005
Aspergillus fumi		U(VI)	423	1.8	Best pH 5; Inhibited by Al(III), but not other ions; Langmuir fit;	Bhainsa & D'Souza 1999
Rhizopus arrhizus		Sr)II), Cd(II), Cu(II), Mn(II), Zn(II), Pb(II)		.12,.18, .20,.12, .14,.25	$Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Mn^{2+} > Sr^{2+}$; Competition; binding correlated with covalent index; hard ions such as Sr(z+) exhibited onto ionic binding to the metal	Brady & Tobin 1995
Rhodotorula glut.		Pb(II)	74	0.36	Best pH 4.5-5; Langmuir fit; ion exchange and precipitation	Cho & Kim 2003
Aspergillus flavus		Cr(VI)	0.1-0.3	.006	Autoclaving enhanded uptake; Langmuir fits	Deepa et al. 2006
Penicillium c	Graft PAA	Cu(II), Cd(II)	108, 210	1.7, 0.18	Pseudo 2nd order rate; Langmuir fit; endothermic; surface groups; HCl regen.	Deng & Ting 2005a
Penicillium c	PEI, glutaral.	Cu(II), Pb(II) Ni(II)	92,204, 55	1.5,1.0, 0.94	Enhanced sorption; amine association; Langmuir fit	Deng & Ting 2005b
Penicillium c	PEI, glutaral.	Cr(VI)	279	5.4	Positive zeta potl.; effective at pH 4.3-5.5; Langmuir fit; Cr(III) detected on surface	Deng & Ting 2005c
Penicillium c; modified…	PEI, glutaral.	Cr(VI)	26, 224	0.5, 4.3	Pseudo 2nd order rate; partial reduction; some aggregation on surface	Deng & Ting 2006
Aspergillus niger	NaOH	Cr(II), Pb(II)	29,33	.56,.16	Langmuir fit; endothermic	Dursun 2006
Aspergillus niger		Cu(II), Zn(II), Ni(II), Cr(VI)	5, 4, 6, 3	.08,.06, .10,.06	Best pH 4-5 for cations; Langmuir fit; copper and zinc could be co-adsorbed	Filipovic-Kovacevic et al. 2000
Mycelial biomass	NaOH	Ni(II), Zn(II), Cd(II), Pb(II)	5, -, 19, 166	.08, -, .17,.80	Best pHs 5-7; proton exchange; Langmuir fit; controlled by acidity of substrates	Fourest & Roux 1992
Rhizopus arrhizus		Ni(II), Cd(II), Zn(II), Pb(II), Cu(II)	18, 27, 14, 56, 10	.31,.24, .21,.27, .16		Fourest & Roux 1992
Mycelial biomass		Ni(II), Zn(II), Cd(II), Ag(I), Pb(II)	56, 39	0.95, 0.35	Best pH 7 for Pb; cationic activation important	Fourest et al. 1994

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Phanerochaete c., Saccharomyces c. Fomitopsis pinic.		Cd(II)	84, 109, 130	0.75, 0.97, 1.16	Wood-rotting fungal pellets	Gabriel et al. 1996
Aspergillus niger Cladosporium p.; Rhizopus arrhizus Saccharomyces c		Th, Cu, Cu, Th	162, 18, 10, 119	0.70, 0.28 0.16, 0.51		Gadd 1988
Rhizopus arrhizus		Th	97	0.42		Gadd et al. 1988
Aureobasidium p.		Cu	6	0.09		Gadd & Mowll 1995
Aspergillus spp.	Dried, CN^{-}	Au(III), Ag(I), Cu(II)	__	__	Metabolically active fungi worked better	Gomes & Linardi 1996
Phanerochaete c.	Heat , NaOH	Cd(II), Hg(II)	148, 69-79	1.32, .34-.39	NaOH-treated > heat-in activated > active; Best pH 6; Regen. HCl (98%)	Gurisik et al. 2004
White rot fungus		Pb(II), Cr(III), Cr(VI), Cu(II), Zn(II)	__	__	Uptake accompanied by proton release;	Hanif et al. 2010
Various		Pb(II), Cd(II), Ni(II	5-56, 30	.02-.27, .27	Pb > Cd > Ni	Holan & Volesky 1995
18 fungal biomass	Living	U	27-81	0.1-0.34	actinomycetes > bacteria, yeasts > fungi; Freunlich isotherm; bio-activity not needed	Ten bacterial,
White rot (*Phanerochaete chrysosporium*)		Cd(II)	71	.63	Immobilized on loofa sponge	Iqbal et al. 2005
Phanerochaete c	Hybrid w papaya	Cd(II)	71, 142	0.63, 1.3	The hybrid adsorbed much more than the sum of the components; 2nd order rate; Langmuir fit	Iqbal et al. 2007
Phanerochaete c	Live, heat inac	Hg(II), Cd(II)	52-115, 50-80	.29-.57, .44-.71	Heat inactivation favored adsorption; Ca alginate beads; best pH 5-6; Langmuir fit; regen. with HCl (97%)	Kacar et al. 2002
Aspergillus niger		Pb(II), Cd(II), Cu(II)	6.3, 3.2, 2.0	0.030, 0.028, 0.031	Modification of carboxyl and amine groups adversely affected metal uptake; phosphate groups of lipids did not seem to be involved. The ions Ca^{2+}, Mg^{2+} & K^+ were displaced.	Kapoor & Viraraghavan 1997

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Aspergillus niger	NaOH, CH_2O, DMSO, detergent	Pb(II), Cd(II), Cu(II), Ni(II)	2-7.4, 1.3-3.4, 0.7-3.1, 1.8max	.01-.04, .01-.03, .01-.05, .03	Pretreatment significantly increased uptake of Pb, Cd, and Cu, but decreased Ni uptake.	Kapoor & Viraraghavan 1998a
Fungal biomass	Contin-uous	Pb(II), Cd(II), Cu(II), Ni(II)	10, 4, 3, 1	.05,.04, .05,.02	Immobilization in sulfone matrix beads filled with fungal biomass powder	Kapoor & Viraraghavan 1998b
Aspergillus niger	NaOH (boiling)	Pb(II), Cd(II), Cu(II),	8-10, 3-4, 0.3-3.6	.04,.05, .03,.04, 0-.06	Pretreatment increased uptake, except for Ni; live fungi more effective; higher pH favored; Langmuir fit; competition; regen. with HNO_3	Kapoor et al. 1999
Aspergillus niger		Hg(II), CH_3Hg^+	No eval	No eval	Sorption not sensitive to other ions; esterification of substrate defeated sorption; regenerable	Karunasagar et al. 2003
Undaria pinnatfida		Pb	350		Best pH 3-4; acid site binding	Kim et al. 1995
Rhizopus nigric.	Pelleted growth	Li(I), Ag(I), Pb(II), Cd(II), Ni(II), Zn(II), Cu(II), Sr(II), Fe(II), Fe(III), Al(III)	1.2, 49, 83, 33, 12, 16, 23, 25, 26, 23, 4	0.18, 0.45, 0.40, 0.30, 0.20, 0.24, 0.36, 0.28, 0.47, 0.41, 0.16	$Fe^{2+} > Ag^+ > Fe^{3+} > Pb^{2+} > Cu^{2+} > Cd^{2+} > Sr^{2+} > Zn^{2+} > Ni^{2+} > Li^+ > Al^{3+}$; Diverse binding sites; binding correlated with covalent index of the metal ions; Langmuir fits	Kogej & Pavko 2001
Aspergillus niger, A. s.; Penicillium j.		Cr(VI)	1-2	0.019	Best pH 2; Langmuir fit	Kumar et al. 2008
Trichoderma k.; Fusarium c		Cd(II)	9-102; 12-50	.08-.91, .11-.44	Difference between the two fungal biomass samples disappeared upon autoclaving	Kurek & Majewska 2004
Aspergillus niger		Co, Au, U	95, 200 27	1.6,1.0, 0.11	Higher pH favored; competition demonstrated	Kuyucak & Volesky 1989
Phanerochaete c		Cd(II), Pb(II)	15, 12	.13,.06	Best pHs 4.5; competition; Freundlich fits	Li et al. 2004

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Penicillium simp.		Pb(II), Cu(II)	153, 112	0.74, 1.76	Pseudo 2nd order rate; Langmuir fit; regeneration with HCl	Li et al. 2008
Mucro rouxii		Pb(II)	769	3.7	Best pH 6; Pb wins exchange competition	Lo et al. 1999
Aspergillus niger, Penicillium chrys., Claviceps paspali	NaOH	Zn(II)	800, 640, 320	12, 9.8, 4.9	Higher pH favorable to 9; regen. w HCl	Luef et al. 1991
Saccharomyces c		Cu(II)	10	0.16		Mattuschka et al. 1993
Aspergillus n.	On wheat bran	Cu(II), Zn(II)	__	__	Higher pH favored to 6; Langmuir fits; competition	Modak et al. 1996
Aspergillus n.	CTAB	Cr	11-14	.21-.27	2nd order rate; Freundlich fit; exothermic; amino groups participate	Mungasavalli et al. 2007
Ganoderma lucid.		Cu	24	0.38		Muraleedharan & Venkobachar 1990
Penicillium c.		Pb(II), Cd(II), Cu(II), Zn(II), As(III)	116,11, 9, 6.5, -	.56,.05, .09,.10 -	Best pH 4-5; moderate competition	Niu et al. 1993
Rhizopus arrhizus		Cr	36	.69		Nourbakhsh et al. 1994
Rhizopus arrhizus		Cr	11	.17	Best pH 4.5	Omar et al. 1996
Rhizopus arrhizus		Fe(III), Pb(II), Cd(II)	68, 55, 52	1.2,.26, .46	Langmuir fits	Ozer et al. 1997
Saccharomyces c.		Pb(II), Ni(II), Cr(VI)	270,46, 33	1.3,.78, .63	Langmuir fits; exothermic	Ozer & Ozer 2003
Aspergillus n.		Cr(VI)	No eval	No eval	Cr(VI) removed, Cr(III) appears in solution and as the bound species	Park et al. 2005b
Four strains	Dead	Cr(VI)	No eval	No eval	Reduction on contact	Park et al. 2005c
Fungal	Fe oxide coated	As(III), As(V)	No eval	No eval		Pokhrel & Viraraghavan 2006
Aspergillus n.	Fe oxide coated	As(III), As(V)	81, 93	1.08, 1.24	Best pH 6; pseudo 2nd order rate; Langmuir fit for As(V); Redlich-Peterson fit for As(III)	Pokhrel & Viraraghavan 2008
Rhizopus arrhizus	Immob.	Cr(VI)	9-11	.11-.21	Tests at pH 2; immobilization yielded moderately lower uptake; Freundlich fit	Prakasham et al. 1999
Aspergillus foetid.		Cr(VI)	2	0.04	Best pH 7	Prasanjit & Sumathi 2005
Rhizopus arrhizus		Zn(II)	__	__	98% removal; 2nd order rate; Langmuir fit	Preetha & Dubay 2005

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Rhizopus arrhizus		Cu(II)	—	—		Preetha & Viruthagiri 2007a
Rhizopus arrhizus		Cr(VI)	No eval	No eval	Kinetic study; Freundlich fit	Preetha & Viruthagiri 2007b
Aspergillus n.		Cu(II), Zn(II)	0.6-2.6, 0.1-0.2	.01-.04, 0-.003	Living fungus effective	Price et al. 2001
Rhizopus arrhizus		Cr*VI), Fe(III)	58	1.1	Tests at pH 2; competition; Langmuir fit	Sag & Kutsal 1996
Inonotus hispidus		As(III), As(V)	52, 60	0.69	Best pH As(III) was 6 & for As(V) 2; pseudo 2nd order rate; Langmuir fit; ion exchange; regen. with acids	Sari & Tuzen 2009a
Amanita rubesc.		Pb(II), Cd(II)	38, 27	0.18, 0.24	Pseudo 2nd order rates; Langmuir fit; ion exchange; regen. with acids	Sari & Tuzen 2009d
Aspergillus niger, Rhizopus arrhizus Saccharomyces		Co, U; Co, Co	2.4, 29; 2.9, 5.8	.04,.12, .05, .10		Sakaguchi & Nakajima 1991
Phanerochaete c		Pb(II), Cd(II), Cu(II)	2	0.01	Best pH 6; Langmuir fits	Say et al. 2001
Penicillium p		Hg(II), Cd(II), Pb(II), As(III)	70,110, 253,36	.34,.98, 1.2,.48	Higher pH favored to 5; Langmuir fits; competition; regen. with HCl	Say et al. 2003a
Penicillium c		Hg(II), Cd(II), Pb(II), As(III)	55, 12, 213,26	.27,.11, 1.0,.35	Higher pH favored to 5; competition; regen. with HCl	Say et al. 2003b
Penicillium p		Cr(VI)	36	0.69	Higher pH favored to 6 (!); Langmuir fit; regen. with HCl	Say et al. 2003c
Waste fungal	Dead	Ca(II), Fe, Ni(II), Cr(III), Cr(VI)	_, _, _, 16, 24	__, -, .31, .46	Uptake Ca > Cr(III) > Ni > Fe > Cr(VI); competition, Ni did not compete well	Sekhar et al. 1998
Penicillium c		Cd(II), Zn(II), Cu(II), Pb(II)	22, 13, 12, 96	.20,.25, .19,.46	Langmuir fits; tolerant of Ca	Skowronski et al. 2001
Aspergillus niger	NaOH	Pb(II)	93	0.45	Langmuir fit	Spanelova et al. 2003
Aspergillus niger		Cr(VI)	9	0.17	Study at pH 6	Srivastava & Thakur 2006
Rhizopus nigric.	Polymer matrices	Cr(VI)	45-119	.86-2.3	Immobilized systems had less capacity per unit mass; regen. with NaOH, carbonate, or biocarbonate; Freundlich fit	Sudha & Abraham 2003

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Aureobasidium p. Saccharomyces c.		Pb(II)	57	0.27	Dead cells had higher capacity, slower uptake	Suh et al. 1998
Penicillium oxal. Tolypocladium sp.		Cd(II), Pb(II), Hg(II)	-, -270	__ 1.34	Langmuir fit	Svecova et al. 2006
Rhizopus arrh.		La(III), etc.	16 Cu	0.25	$UO_2^{2+} > Cr^{3+} > Pb^{2+} > Ag^+ > Ba^{2+} > La^{3+} > Zn^{2+} > Hg^{2+} > Cd^{2+} > Cu^{2+} > Mn^{2+} > Na^+, K^+, Rb^+, Cs^+ (=0)$; ionic radius governs	Tobin et al. 1984
Aspergillus niger ; Penicillium spin.		Cu(II), Zn	5; 0.4-2, 0.2	.08,.01-.03, 0	Best uptake in the lag phase of growth	Townsley & Ross 1986
Rhizopus arrhizus		U, Th	180, 22	.76,.09	Best pH 4-5	Tsezos & Volesky 1981
Aspergillus terre.		U, Th	10, 60	.04,.26		Tsezos & Volesky 1981
Penicillium chrys.		U, Th	70, 142	.29,.61		Tsezos & Volesky 1981
Rhizopus arrhizus		U	180	0.76	Interference by Fe(II) and Zn(II)	Tsezos & Volesky 1982
Neurospora cras.		Cr(VI)	0.4-16	.01-.31	Very strong enhancements by acidic acid, heat inactivation, and NaOH; Freundlich fits	Tunali et al. 2005
Xanthoparmelia c		Hg(II)	83	0.41	2nd order rate; Langmuir fit; ion exchange; exothermic; regen. with HCl	Tuzen et al. 2009
Parmelina tili.		Pb(II), Cr(III)	76, 52	.37,1.0	Langmuir fits ; ion exchange	Uluozlu et al. 2008
Saccharomyces c		Cu(II), U, Zn	17-40, 55-140, 14-40	.27-.63, .23-.59, .21-.61		Volesky & May-Phillips 1995
Aspergillus n.		Pb(II)	__	__	1st order rate ; Freundlich fit ; regen. HNO_3	Wang et al. 2001
Pleurotus sapidus		Cd(II), Hg(II)	127, 287	1.3, 1.4		Yalcinkaya et al. 2002
Mucor rouxii	Poly-sulfone immob.	Pb(II), Cd(II), Ni(II), Zn(II)	4, 4, 0.4, 1.4	.02,.08, .01,.02	Regen. with HCl	Yan & Viraraghavan 2001
Mucor rouxii		Pb(II), Zn(II), Cd(II), Ni(II)	54, 54, 20, 21	.26,.82, .38,.36	Similar performance living vs. dead; higher pH favored; 2nd order rate	Yan & Viraraghavan 2003
Fungal, various	Heating, Ca	Cd(II)	31-63	.60-1.2	Heating and Ca treatment improved uptake; Pb2+ > Cu2+ > Cd2+ > Zn2+	Yin et al. 1999
Rhizopus nigric	dead	Pb(II)	14	0.07	Langmuir fit	Zhang et al. 1998

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Rhizopus arrhizus other fungi		Zn(II)	14	0.21	Higher pH favored ; Langmuir fit ; mainly bound to the chitin	Zhou 1999
Rhizopus arrhizus	Immob. on foam	Cu(II)	15+	0.24+	Best pH 6.7-7; competition: $Mn^{2+} \gg Zn^{2+} > Cd^{2+} > Mg^{2+} > Ca^{2+}$; could be regenerated	Zhou & Kiff 1991
LIGNIN-RELATED						
Isolated lignin						
Organosolv lignin	-	Cu(II)	1.7	0.027	Increasing pH; decreasing temp.; 10 min.; regeneration by HCl successful	Acemioğlu et al. 2003
Lignin content		Cd(II)	48	0.76	The pure lignin sample showed higher uptake; Langmuir fit	Basso et al. 2004
Pulping lignin		Pb(II), Cd(II), Zn(II); Cu(II)	18, 8, 11, 20	.09,.07, .17,.31	Best pHs 4-5; ion exchange	Celik & Demirbas 2005
Kraft lignin		Cu(II), Pb(II)	6.4, 62	0.1, 0.3	Proton displacement/ion exchange; Pb(II)>Cu(II)>Zn(II)>Cd(II)>Ca(II)>Sr(II) ; higher pH preferred esp. low-affinity metals; biotic ligand model discussed	Crist et al. 2002
Kraft lignin		Pb(II)	104+	0.5+	Indulin AT; results as exchange constants; Pb(II)>Cu(II)>Zn(II)>Cd(II)>Ca(II)> Sr(II); exchange with protons; Langmuir fit	Crist et al. 2003
Kraft lignin	$Ca(OH)_2$, DMF, heat	Pb(II), Cd(II)	72, 52	0.35, 0.46	Ion exchange with Ca	Crist et al. 2004
Alkali glycerol lign.		Pb(II), Cd(II)	7-9	.03-.08	Higher pH favored to 5; Langmuir fit	Demirbas 2004
Alkali glycerol lign.		Cr(III), Cr(VI)	9, 25	.17,.48	Best pH for Cr(III) 4.5-5.5	Demirbas 2005
Alkali glycerol lign.		Co(II), Hg(II)	8, 5	.14,.02	Higher pH favored; Langmuir fits (batch)	Demirbas 2007
Acid hydrolysis	Quat.	Cu(II), Cr(III)	1.7-26, 0.8-12	.03-.41, .01-.23	Large enhancement by quaternization	Dizhbite et al. 1999
Wheat bran lignin		Cr(VI)	35	0.67	Oxidation of substrate consumes protons and reduces to Cr(III), also providing binding site	Dupont and Guillon 2003
Lignin model cpds		Fe(III)	No eval	No eval	Best pH 5; Stable complexes; Surface oxidation by Fe(III)	Guillon et al. 2001

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Black liquor		Pb(II), Cu(II), Cd(II), Zn(II), Ni(II)	62, 18, 18, 9, 6	.30,.28, .16,.14, .11	Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II); pseudo 2nd order rate; carboxylic and phenolic sites	Guo et al. 2008
Kraft & organosolv		Cu(II), Cd(II)	22, 81	.35, .72	Higher pH favored; Sips equation fit (varied affinities); competition; ion exchange	Harmita et al. 2009
Kraft lignin		Cr(VI), Cr(III)	__	__	Oxygen groups e.g. phenols sorb Cr(VI); regen. with acid	Lalvani et al. 1997
Commercial lignin		Cr(VI), Cr(III)	3.8, 7	0.07, 0.13	Tests at pH 2.5 for Cr(VI) and 3 for Cr(III); a commercial activated carbon was not able to adsorb the Cr(VI), just Cr(III)	Lalvani et al. 2000
Lignin model compounds		Fe(III), Mn(II), Cu(II)	__	__	Potentiometric titrations to determine complex stabilities	Merdy et al. 2000
Straw lignin		Cu(II)	4	0.065	Carboxylic and phenolic groups involved; relatively stable	Merdy et al. 2002
Straw lignin		Fe(III), Mn(II)	No eval	No eval	Carboxylic and phenolic groups involved; relatively stable complexes characterized	Merdy et al. 2003
Kraft lignin		Cu(II), Cd(II)	87, 137	1.4,1.2	Pseudo 2nd order rate; particle and film diffusion; Langmuir fit	Mohan et al. 2006
PA-, EN- lignins	Aminated HCl soln	Au(III), Pd(II), Pt(IV)	__	__	Langmuir fit; reductive adsorption of Au; but Cu(II), Fe(III), Ni(II), Zn(II) were *not* adsorbed;	Parajuli et al. 2006
Sugar bagasse	CH_2O	Cd(II), Pb(II)	31, 91	0.28, 0.44	Langmuir fit	Peternele et al. 1999
Oxidized lignins	Acidic media	Cd(II)	No eval	No eval	Oxidation increased capacity	Quintana et al. 2008
Kraft lignin		Cu(II)	__	__	Effective over wide concentration range	Sciban & Kalasnja 2004a
Kraft lignin		Pb(II), Zn(II)	__	__	Higher pH favored: Langmuir fit	Srivastava et al. 1994
Kraft lignin		Cr(III)	18	0.35	Pseudo 2nd order rate; Langmuir 2-surface fit; ion exchange	Wu et al. 2008
Olive stone lignin	Phenol-CH_2O, H_2SO_4	Co(II), Ni(II), Cu(II)	31, 28, 25	0.52, 0.48, 0.42	Sulfonated novolak resin made with lignin was more acidic and had higher metal uptake	Zoumpoulakis & Simitzis 2001

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Lignite, humic ac.						
Lignite humic ac		Cr(III)	9, 16	0.18-0.30	Best pH 4-5; ion exchange/complexation with carboxyl groups; Langmuir fit; 90% regeneration potential	Arslan & Pehlivan 2008
Wallnut expeller, Peanut skins, Rice straw, Plum pit shells, Peanut hulls Rice hulls Sugar bagasse		Hg(II)	880, 820, 280, 240, 220, 180, 180	4.4, 4.1, 1.4, 1.2, 1.1, 0.90 0.90	Ag products can be used for Hg uptake; tests at pH 3.4-3.7	Friedman & Waiss 1972
Paper mill waste, sewage, compost		Pb(II), Zn(II)	39, 8	0.19, 0.12	Compost improved uptake; Langmuir fits; regen with acid	Lister & Line 2001
Tannin gel		Cr(VI)	274	5.3	Tests at pH 3; Langmuir fit	Nakajima & Baba 2004
Tannins fr. bark		Cu(II), Pb(II)	9, 31	.14,.15	Pseudo 2nd order rate; Langmuir fit; ion exchange/complexation	Oo & el. 2009
Aquatic humic		Cd(II), Ni(II), Cu(II), Mn(II), Pb(II)	No eval	No eval	Slow first-order rate alter initial quick uptake; Cu > Pb > Mn > Ni > Cd	Rocha et al. 1997
Tannic acid, C	Immob.	Cu(II), Zn(II), Cd(II)	2.2,1.2, 1.5	.03,.02, 0.01		Ucer et al. 2006
Compost		Cu(II), Cd(II)	17, 18	0.26, 0.16	Langmuir fits; better performance than activated carbon, cellulose pulp, etc.	Ulmanu et al. 2003
Peat, peat moss						
Sphagnum peat	NaCl	Cr(III)	19	0.37	Ion exchange; 2nd order rate; Langmuir fit; regenerated with HCl	Balan et al. 2009
Peat		Pb(II), Cd(II), Zn(II)	—	—	Competition, binary & ternary; ion exchange/complexation	Balasubramanian et al. 2009
Milled peat		Cr(III), Cr(VI)	14, 31	.26,.60	Best pHs 4, 2, resp.	Dean & Tobin 1999
Humin	Immob.	Cu(II), Pb(II). Cd(II), Cr(III)	18, 31, 1.3, 8	.28,.15, .01,.15	Cr(III) > Pb(II) > Cu(II) > Cd(II) > Ni(II)	De la Rosa et al. 2003

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Peat, humic acids		Cu(II)	16-28	.25-.44	Best pH 4; regen. with HCl	Gardea-Torresdey et al. 1996a
Pleurozium schr.		Cu(II)	11	.17	Pseudo 2nd order rate; Langmuir fit; regenerated with HCl	Grimm et al. 2008
Moss peat		Ni(II)	9	.15	Best pH 4-7; Langmuir fit;	Ho et al. 1995
Moss peat		Cu(II), Ni(II)	__	__	Pseudo 2nd order rate; pore diffusion control; competition	Ho et al. 1996
Moss peat		Cu(II), Ni(II), Pb(II)	12, 8, 12	.19,.14, 0.06	Pseudo 2nd order rate	Ho & McKay 2000
Moss peat			__	__	Pseudo 2nd order rate; model derived	Ho et al. 2000a
Moss peat, pith		Cu(II)	13	0.20	Pseudo 2nd order rate; model	Ho & McKay 2003
Peat		Cr(III), Cu(II), Cd(II)	22-25	.42-.48	Extended Langmuir fit	Ma & Tobin 2004
Peat moss		Cd(II), Cr(III)	32, 42	.28,.81	Pseudo 2nd order rate; Langmuir fit	Sari et al. 2008
Peat moss		Pd(II)	37	0.18	2nd order rate; Langmuir fit; ion exchange; exothermic	Sari et al. 2008
Drepanocladus r		Hg(II)	94	0.47	Best pH 5.5; pseudo 2nd order rate; Langmuir fit; ion exchange; regen. with HCl	Sari et al. 2009c
Moss peat		Cr(VI)	119	2.3	Best pH 1.3 to 3; regen with NaOH (50%)	Sharma & Forster 1993
Moss peat		Cr(VI)	66	1.3	Best pH 2; reduction favored by flow	Sharma & Forster 1995a
Moss peat		Cr(VI)	36-44	.69-1.1	Tested at pH 2-2.5	Sharma & Forster 1995b
Sludge						
Activated sludge	Dried	Cr(VI)	577	11.1	Tests at pH 1, Langmuir fit	Aksu & Akpinar 2001
Activated sludge	Immob.	Cr(VI)	19	0.36	Best pH 1; Langmuir fit	Aksu et al. 2002a
Activated sludge		Cr(VI)	294	5.7	Best pH 1; Langmuir fit	Aksu et al. 2002b
Anaerobic sludge		Pb(II), Cd(II), Cu(II), Ni(II)	255,60, 55, 26	1.2,.53, .87,.44	Langmuir fit	Hawari & Mulligan 2006
Biogas residuals		Cr(VI)	6	0.11	Best pH 1.5; First order rate; Langmuir fit	Namasivayam & Yamuna 1995a
Biogas residuals		Pb(II)	28	0.14	Langmuir fit	Namasivayam & Yamuna 1995b
Biogas residuals		Cr(III)	5.2	0.10	Langmuir fit; endothermic	Namasivayam & Yamuna 1999
Distillary sludge		Cr(VI)	6	0.11	Langmuir fit	Selvaraj et al. 2003

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
CHEM. MODIFIED						
BASE TREATED						
Sugar bagasse	5N NaOH, EDTA	Cu(II), Cd(II), Pb(II)	39-93, 88-149, 192-333	.61-1.5, .78-1.3, .92-1.6	Mercerization greatly increased adsorption capacities.	Karnitz et al. 20009
Sugar bagasse	NaOH, EDTA dianhydr	Ca(II), Mg(II)	16-54, 14-43	.40-1.4, .58-1.8	Modified sugarcane bagasse showed higher adsorption than modified pure cellulose.	Karnitz et al. 2010
OXIDIZED						
Oxycellulose		Cd(II), Zn(II), Ni(II)	31, 17, 10	.28,.26, .17	Cd2+, Zn2+ > Ni2+ >> Ca2+ > Mg2+ >> Na+, behaved like ion exchange resin	Foglarova et al. 2009
Periodate oxidn		Ag(I), Mg(II), Ca(II), Sr(II), Ba(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Fe(III), Cr(III)	390, 87, 144, 270, 343, 198, 206, 188, 240, 216, 229, 135	3.6, 3.6, 3.6, 3.1, 2.5, 3.6, 3.5, 3.2, 3.8, 3.3, 4.1, 2.6	2,3-dicarboxycellulose up to 70% DS remained insoluble in water; gave viscous complexes with the metals that solidified in air	Maekawa & Koshijima 1984
Bagasse	Various COO Rx	Cu(II), Ni(II), Cr(III), Fe(III)	99-381, 80-470, 440, 84-469	1.6-6.0, 1.4-8.0, 8.5, 1.5-8.4	Carboxymethylated bagasse > periodote oxidized > succinylated .	Nada & Hassan 2006

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Cotton linters	TEMPO, CMC fib.	Mg(II), Al(III), Ca(II), Mn(II), Co(II), Ni(II), Cu(II), Sr(II), Ag(I), Cd(II), Ba(II), La(III), Pb(II)	3.9-5.6, 4.0-5.1, 13-18, 14-19, 16-24, 16-25, 17-23, 18-32, 35-53, 24-37, 27-44, 49-53, 99-108	.16-.23, .15-.19, .32-.45, .25-.34, .28-.41, .27-.42, .27-.37, .20-.36, .32-.49, .21-.33, .21-.32, .35-.38, .48-.52	HIgher pHs favored to 4; Pb^{2+} > La^{3+} > Al^{3+} > Cu^{2+} > Ba^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}, Sr^{2+}, Mn^{2+}, Ca^{2+} > Mg^{2+}; approx 1:1 molar uptake of Pb(II), Ca(II), Ag(I)	Saito & Isogai 2005
ADSORBED …						
POLYMER ADS.						
Porous cellulose	PEI cross linked	Hg(II)	288	1.43	PEI crosslinking restricts ligand mobility	Navarro et al. 1996
Chitosan, cellulose	Blend coagula.	Pb(II), Cd(II), Cu(II)	68, 36, 19	.33,.32, .30	Best pHs 4-5; competition: Pb^{2+} > Cd^{2+} > Cu^{2+}; regen. with HCl; complexation	Zhou et al. 2004
Dye adsorption						
Oil palm fibers	Dye use	Cu(II), Pb(II), Cr, Ni(II)	1.9,.08, .06,.50	.03,.00, .00,.01	Tests at pH 2.9 (electroplating); dye greatly increased uptake.	Low et al. 1993
Coconut husk	Dye mod	Cu(II)	__	__	Treatment enhanced uptake; Langmuir fit	Low et al. 1995b
Yeast	Cationic surfact.	Cr(VI)	94	1.80	Tests at pH 4.5-5.5; Langmuir fit	Bingol et al. 2004
DERIVATIZATION						
Succinylation						
Cellulose	Succin.	Cd(II)	180	1.60	Best at intermediate pH; regeneration with NaCl	Belhalfaoui et al. 2009
Cellulose	Mercer-ized first	Cu(II), Cd(II), Pb(II)	30, 86, 206	.47,.77, 0.99	Langmuir fits	Gurgel et al. 2008

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Alhagi	Tartaric & heat	Zn(II)	__	__	2nd order rate; Langmuir fit; exothermic	Hashem et al. 2008
Sugar bagasse	Succin.	Cu(II), Cd(II), Pb(II)			Polylamines anchored by the derivatized material adsorbed metal	Karnitz et al. 2007
Sugar beet, corn cob, oat hull	Succin., maleate, phthalate	Ca(II)	22-139	.55-3.5	Sugar beet pulp was easiest to derivatize;	Lehrfeld 1996
Coconut husk, moss	Nitrilotri-acetic ac.	Cr(III)	14-39	0.28-0.75	Enhanced uptake by 50%	Low et al. 1997
Cellulose	Hydrox-amic	Fe(III), Cu(II), Ag(I), Mn(II), Zn(II), Ni(II), Cr(III)	212, 165, 226, 5.5, 20, 2.3, 5	3.8, 2.6, 2.1, 0.1,0.3, .04,.09	Periodate oxidation; metal complexes were characterized	Maekawa & Koshijima 1990
Wood meal	Succinic anhydr	Cd(II)	200	1.8	Below theoretical due to di-ester formation	Marchetti et al. 2000a
Bagasse	Various COO Rx	Cu(II), Ni(II), Cr(III), Fe(III)	99-381, 80-470, 440, 84-469	1.6-6.0, 1.4-8.0, 8.5, 1.5-8.4	Carboxymethylated bagasse > periodote oxidized > succinylated .	Nada & Hassan 2006
Coir pith	Succinic anhydrid	Co(II)	24-33	.41,.56	Modification highly beneficial; pseudo 2nd order rate; Langmuir fit; regen. with HCl	Parab et al. 2008
Eichhornia c	Xantho-genate	Cu(II)	100-260	1.6-4.1	Xanthogenate of water hyacinth achieved the highest uptake; first order rate	Tan et al. 2008
Citric acid ester						
Sawdust	Esterif.	Zn(II)	0-270	0-4.1	Freundlich fit better	Hashem et al. 2006b
Wood	Citric ac.	Cu(II), Pb(II)	24, 83	.38,.40	Treatment increased adsorption by about 10X; 2nd order rate	Low et al. 2004
Corn fiber	Citric ac	Cu(II)	127	2.0		Wing 1996
Corn fiber	Citric ac	Cu(II)	83	1.31		Wing 1997
Rice husk	Tartaric	Cu(II), Pb(II)	32,120	.50,.58	Langmuir fit; regen. with HCl	Wong et al. 2003

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Carboxylated						
Beads	CMC	Ni(II), Co(II), Cu(II), Cd(II), Pb(II), Fe(III), Al(III)	19,14, 20,35, 71,26, 5	.32,.23, .32,.31, .34,.47, .21	Tested at pH 6; metal adsorption decreased water retention value, especially in the case of Al(III) adsorption	Heinz et al. 1993
Cyanoethylation		Cu(II), Ni(II), Co(II)	25,14, 15	0.4,.23, 0.26	Photografted amidozime groups increased metal adsorption; higher pH favored	Kubota & Shigehisa 1995
Spherical cotton cellulose	Acrylo-nitrile Carbox-ylated	Cr(III)	73-90	1.4-1.7	Tests at pH 5; carboxylated; Langmuir fit; endothermic; regeneration with either NaOH or HCl	Liu et al. 2001
Spherical cellulose	Carboxyl-ated	Cu(II)	64	1.00	Carboxylated; ion exchange/complexation; Langmuir fit; endothermic; regen. with NaOH	Liu et al. 2002
	CMC, phosphat oxycell	Cu(II) perchlorate	34, 81	0.53, 1.3	Carboxymethylation greatly improved uptake	Padilha et al. 1995
Wood pulp	CMC	Na(I), K(I), Ca(II), Mg(II)	—	—	Donnan ion exchange	Sundman & Ohman 2006
Wood pulp	CMC	Ca(II), Cu(II)	No eval	No eval	Donnan ion exchange & complexation, two carboxylate groups per ion	Sundman et al. 2008
Aminated, etc.						
Wood quat.	Quatern.	Cr(VI)	26-27	.50-.52	Suppressed by sulfate; Langmuir fit	Low et al. 2001
Beech sawdust	Quatern., cross-lnk		—	—	Nitrogen level correlated with capactiy	Simkovic 1999
Cotton	Aminated	Hg(II)	28-29	.14-.15	Amination was more effective than PEI adsorption	Roberts & Rowland 1973
Other						
Undaria pinnat.	Oxime	Cu(II)	900	9.5	Uptake of Cu(II) increased 4.5X by oxime; highly selective vs. Ca(II), Cd(II), Pb(II)	Kim et al. 1996

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Undaria pinnat.	Xanth-ated	Pb(II), Cu(II), Cd(II)	1200	9.8	Xanthation increased adsorption capacity 3X; selective adsorption possible (compared to Ni(II), Zn(II), and Co(II)	Kim et al. 1999
30 strains	H_3PO_4	Cd(II), Pb(II), Ni(II), Zn(II)	269, 600, 153, 163	2.4, 2.9, 2.6, 2.5	Langmuir fits; different selectivities, different optimum pHs; phosphorylation beneficial in some cases	Klimmek et al. 2001
Bagasse peroxy-acid, kraft pulping	phosphorrylation	Cr( ), Cu(II), Mn(II), Ni(II), Pb(II)	4.7,4.4, 3.8,2.9, 6.2	.09,.07, .07,.05, .03	Peroxyacid pulping lignin yielded higher level of phosphate groups, higher sorption capacity	Nada et al. 2008
Cellulose powder	Amidoxyl ated	Cu(II), Cr(III)	240, 203	3.8, 3.9	Stoichiometric complexes formed; desorption by EDTA	Saliba et al. 2000
Cellulose	Amidoxyl ated	Cd(II), Ni(II)	402, 106	3.6, 1.8	Stoichiometric complexes; desorption by EDTA	Saliba et al. 2001
Cellulose powder	Amidoxyl ated	Cu(II), Cr(III), Cd(II), Ni(II)	102,83, 180,47	1.6,1.6, 1.6,0.8	Simultaneous or sequential adsorption; stoichiometric; reversal by EDTA	Saliba et al. 2002a
Wood flour & sawdust	Amidoxyl ated	Cu(II), Cr(III), Cd(II), Ni(II)	__	__	Increased adsorption capacity; 1:1 or 2:1 complexes	Saliba et al. 2005
Chlorodeoxy-cellulose	Ethdiam, thiourea,	Hg(II)	1.5	0.007	Best results after reacting CDC with thiurea, then oxidizing the substrate	Tashiro and Shirmura 1982
Corn stalk	Acrylo-nitrile	Cd(II)	13	0.12	Four-fold increase due to derivatization; best pH 7; pseudo 2nd order rate; Freundlich fit	Zheng et al. 2010
Grafting						
Bead cellulose	Graft amidox PAM	Ag(I), Cu(II), Pb(II), Zn(II), Cd(II)	__	__	NaOH treatment increased uptake by the grafted cellulose beads; sulfuric acid regeneration (>90%)	Aoki et al. 1999b
Cellulose	PAM	Hg(II)	712	3.6	Other ions don't interfere; regeneration with hot acetic acid	Bicak et al. 1999
Pine needle cellulose	Glycidyl methacr.	Fe(II), Cu(II), Cr(VI)	2.1, 0.9, 1.0	0.038, 0.014, 0.019	Structures of the graft copolymers	Chauhan et al. 2005a

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Cellulose	Hydroxypropyl, etc	Fe(II), Cu(II), Cr(VI)	__	__	Functionalization greatly increased uptake.	Chauhan et al. 2005b
Cellulose	Acrylamide-based	Fe(II), Cu(II), Cr(VI)	__	__	NaOH treatment yielded Fe(II), Cu(II) uptake with complete rejection of Cr(VI)	Chauhan et al. 2006
Bacterial cellulose	PAM graft		No eval	No eval	Cation exchange material	Choi et al. 2004
Sawdust	PAA	Cu(II), Ni(II), Cd(II)	47-104, 40-97, 76-168	.74-1.6, .68-1.7, .68-1.5	15-40X higher binding due to grafting; regeneration with HCl	Geay et al. 2000
Cellulose	PAA,AM, sulfonic	Pb(II), Cu(II), Cd(II)	4-60, 1-18, 2-33	0.02-0.29 (each)	Pb>>Cu≈Cd; great increase vs. raw cellulose	Guclu et al. 2003
Sunflower stalks	Acrylo-nitrile	Cu(II)	33	0.52	Amidoxylated (grafted), Langmuir fit	Hashem 2006
Sunflower stalks	Acryl-amide	Hg(II)	625	3.1	Langmuir fit	Hashem et al. 2006a
Cyanoethyl cellulose	Acrylo-nitrile	Cu(II)	No eval	No eval	Cotton linter	Kamel et al. 2006
Carboxylate, phosphate	Textiles	Cu(II), Cd(II)	13-248, 22-427	0.2-3.9, 0.2-3.8	Best results with Na salt of the carboxylate product; regeneration	Lacour et al. 2001
Wood meal	Acrylic acid	Cu(II), Ni(II), Cd(II)	46-104, 40-97, 76-168	.74-1.6, .68-1.7, .68-1.5	Grafting increased capacity 40X; regeneration with HCl	Marchetti et al. 2000b
Acrylamide		Cr(II), Pb(II), Mn(II), Ni(II)	189, 180, 185, 165	3.6, 0.87, 3.4, 2.8	Hydrolysis increases affinity for water and for metal ions	Nada et al. 2007a
	Glycidyl methacr, PEI	Co(II), Cu(II), Zn(II)	2-16, 38-57, 12-24	.03-.27, .60-.90, .18-.37	Graft polymerization increased sorption	Navarro et al. 1999
	Glycidyl methacr, PEI	Co(II), Cu(II)	No eval	No eval	Anion interactions with substrate can be used to understand ion exchange interactions	Navarro et al. 2001

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Cellulose	Glycidyl methacr, imidazole	Cu(II)	70	1.10	Pseudo 2nd order rate; Langmuir fit; exothermic	O'Connell et al. 2006a
Cellulose	Glycidyl methacr, imidazole	Ni(II)	48	0.81	Pseudo 2nd order rate; Langmuir fit; endothermic	O'Connell et al. 2006b
Cellulose	Glycidyl methacr, imidazole	Pb(II)	72	0.35	Pseudo 2nd order rate; Langmuir fit; exothermic	O'Connell et al. 2006c
Cellulose	Glycidyl methacr, imidazole	Cu(II)	66-71	1.04-1.11	Copper sulfate hydroxide (antlerite) was present at the surface	O'Connell et al. 2010
Coconut coir pith		Cr(III)	12	.23	Langmuir fit	Parab et al. 2006b
Sawdust	PAM graft	Cr(VI)	6-12	.11-.23	Exothermic; not adversely affected by other ions; Freundlich fit; regen. with NaOH or NaCl	Raji & Anirudhan 1998
Pine needle	HEMA & copolym.	Fe(II), Cu(II), Cr(VI)	__	__	Enhanced uptake	Sharma & Chauhan 2009
Banana stalk	PAM	Hg(II)	138	0.69	Best pH 6-9; pseudo 2nd order rate; Langmuir fit; regen. with HCl	Shibi & Anirudhan 2002
Banana stalk	PAM	Co(II)	13-55	.22-.93	Best pH 6.5-9; Langmuir fit; higher uptake than commercial resin; regen. with HCl	Shibi & Anirudhan 2005
Banana stalk	PAM	Pb(II), Cd(II)	185, 66	0.89, 0.59	Best pH 5.5-8; repressed by salt; pseudo 2nd order rate; Langmuir fit; regen. by acid	Shibi & Anirudhan 2006
Fabric wastes	Glycidyl methacr	Co(II), Cr(VI)	14-18, 3.2	.24-.31, 0.06	Converstion of epoxy groups into various functional groups for binding; best chromate adsorption at pH 9	Sokker et al. 2009
Cellulose	Calix[4] arene	Co(II), Ni(II), Cu(II), Cd(II), Hg(II), Pb(II), Cr(VI)	4.7,7.6, 6.3,10, 16,17, 13-36	.08,.13, .10,.09, .08,.08, .25-.69	For Cr(VI) best pH 1.5; grafted cellulose was effective for updake	Tabakci et al. 2007

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Rubberwood dust		Cr(VI)	144-172	2.8-3.3	Tests at pH 3; higher temperature favored; Langmuir fits	Unnithan et al. 2001
Coconut coir pith	Graft amino-	Cr(VI)	12-127	.23-2.4	Tests at pH 3; 2nd order rate; Langmuir fit; alkali regeneration	Unnithan et al. 2004
Baker's yeast	Polyamic acid	Cd(II), Pb(II)	95, 210	0.84, 1.01	Grafting of carboxylic and amide groups greatly increased uptake; pseudo 2nd order rate; Langmuir fit; complexation	Yu et al. 2007
Cellulose	Acrylic ac acrylamid	Cu(II)	50	0.79	Freundlich fit; regen. with ammonia	Zhao et al. 2006
Solution-phase						
Solution	Mercap.	Ag(I), Cu(II), Pb(II), Cd(II)	No eval	No eval	6-Deoxy-6-mercaptocellulose and its S-substituted derivatives; uptake in the range of 0.1 to 1.5 moles per mole	Aoki et al. 1999a
ACTIVATED CARBON						
Granular		C(VI)	147	2.8	Best pH 1; Langmuir fit	Aksu et al. 2002
Tamarind wood	$ZnCl_2$	Pb(II)	44	0.21	Langmuir fit; pseudo 2nd order rate	Acharya et al. 2009
Carbon cloth	NaOH	Bi(III),Cd(II), Co(II), Ag(I), Cu(II), Ni(II), Fe(III),Sb(III), Sn(IV),Sr(II), Pb(II),Zn(II), Ti(I)	19, 19, 12,140, 8, 19, 30,113, 77, 26, 8, 26	.09,.17, .22,1.3, .13,.32, .54,.93, .65,.30, .04,.39, .30	NaOH treatment increased adsorption; uptake 0.1-2 mmole/g; Langmuir fits	Afkhami et al. 2007
Various	Oxidation	Cr(III), Cr(VI)	10-30, 10-70	.19-.58, .19-1.4	Oxidation with nitric acid, persultate, H_2O_2, or O_2 increased Cr(III) uptake but descreased that of Cr(VI); degassing had opposite effects; Langmuir fits.	Aggarwal et al. 1999
Coconut shell		Cr(VI)	2-16	.04-.31	Uptake depends on conc.; Freundlich fits; low pH adsorption attributed to reduction	Alaerts et al. 1989

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Coconut shell	Chitosan; phos-phoric ac	Zn(II)	45-60	.69-.92	Coating of activated carbon with chitosan increased uptake ; Langmuir fit ; regen. with NaOH	Amuda et al. 2007
Coir pith	H_3PO_4, NaOH	___	—	—	Phosphoric acid activation was effective	Ash et al. 2006
Coconut shell	Chitosan, oxidizing	Cr(VI)	2-15	.04-.29	Nitric acid was more effective than sulfuric; Langmuir fits	Babel & Kurniawan 2004
Olive waste	H_3PO_4, $KMnO_4$	Cu(II)	12-35	.19-.55	Permanganate treatment enchanced adsorption by 3X	Baccar et al. 2009
Pecan shell	H_3PO_4, Steam, CO_2	Cu(II), Pb(II), Zn(II)	No eval	No eval	Competition; acid-modification helped Pb & Zn uptake; steam activation helped Cu	Bansode et al. 2003
Activated carb.		Cr(VI)	__	__	Best pH 3.6 ; endothermic Langmuir fit	Barkat et al. 2009
Arundo donax	H_3PO_4,	Cd(II), Ni(II)	55, 29	.49,.49	Pseudo 2nd order rate; Langmuir fit	Basso et al. 2002b
Peach stone, eucalpytus	CO_2, steam	Cr(VI), Hg(II)	35-93, .37-.42	.67-1.8, .02-.002	Pore structure important, diffusion; CO_2 acti. Favored Hg(II) uptake , steam favored Cr(VI)	Bello et al. 1999
Coconut shell	KOH, $ZnCl_2$, CO_2 atm.	Cr(III), Cr(VI)	534-721	10.3-13.9	Activation was effective ; phenol and carbonyl groups important, electrostatic mechanism	Bendezu et al. 2005
Granular	Electro-chem		No eval	No eval	Both anodic and cathodic treatments increased surface oxygen; cathodic treatment increased pores in presence of oxygen	Berenquer et al. 2009
Rice husk		Cr(VI)	No eval	No eval	Best pH 2; not Langmuir fit	Bishnoi et al. 2004
Birch biomass	H_3PO_4 + steam	Hg(II)	160	0.80	Phosphoric acid followed by steam pyrolysis yielded 1360 m^2/g surface area, adsorption.	Budinova et al. 2006
Activated carbon	H_3PO_4 + steam	Pb(II)	69	0.33	Endothermic	Bueno & Carvalho 2007
Various biomass		Cr(VI)	300	5.8	Lower pH favored; physical activiation effective ; reduction dominant below pH 1	Candela et al. 1995
Bean husk	HNO_3 post	Cd(II)	180	1.6	Oxygen content governs uptake	Chavez-Guerrero et al. 2008

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Carbon	Citric ac.	Cu(II)	15	0.24	Citric acid mod increased Cu(II) uptake	Chen & Wu 2003
Carbon	HCl, HNO$_3$; NaOH	Cu(II)	5-15	.08-.24	NaOH increases OH groups; HCl increases C-O bonds; HNO$_3$ oxidation incr. Cu uptake	Chen & Wu 2004a
Carbon	Humic acid	Cu(II)	3-8	.05-.13	Low amounts of humic acid competed with Cu(II) adsorption; higher amounts helped.	Chen & Wu 2004b
Carbon fibers	Steam, ZnCl$_2$, H$_3$PO$_4$	Ag(I)	__	__	Reduction of Ag(I) on adsorption; graphitization helped reduction	Chen et al. 2002
Carbon fibers	Steam, ZnCl$_2$, H$_3$PO$_4$	Pt(IV)	200	1.0	Reductive adsorption; capacity increased with sp. surf. Area and lower electrode potential; some converted to Pt(II)	Chen et al. 2007
Sisal-based	ZnCl$_2$, H$_3$PO$_4$	Ag(I)	700	6.5	Reductive adsorption of Ag(I) and Au were enhanced by ZnCl$_2$ and H$_3$PO$_4$ activation, also by methylene blue; oxidants did the opposite.	Chen & Zeng 2003
Rayon-based	NaCl + H$_3$PO$_4$		No eval	No eval	Activation enhanced pores; fractals, BET	Chen et al. 2008
Charcoal		Ni(II), Al(III)	__	__	Rate law	Choksi & Joshi 2007
Hydrous act. C		Cu(II), Pb(II), Ni(II), Zn(II)	No eval	No eval	Surface complexation model; participation of free ions and their hydroxo species	Corapcioglu & Huang 1987
Varous carbons		Cr(III)	0.4-32		Tests at pH 3; Langmuir fits	Cordero et al. 2002
Flax shive	Hot sulfuric	Au(III), Pd(II), Ag(I), Pt(II)	__	__	Au(III) > Pd(II) > Ag(I) > Pt(II) $\approx$ Pt(IV); ion exchange; regeneration possible	Cox et al. 2005
Cow dung	Sulfuric post	Cr(VI)	11	0.21	Low pH favored ; first order rate ; Langmuir fit	Das et al. 2004
Pecan shell	Air, H$_3$PO$_4$	Cu(II)	41	1-2	Bound phosphorus important at high levels (complexation); ion exchange of protons	Dastgheib & Rockstraw 2001
Pecan shell	Air, H$_3$PO$_4$	Hg(II), Cr(III), Cu(II), Ni(II), Cd(II), Ca(II), Sr(II), Zn(II), Co(II), Mn(II), Mg(II), K(I)	360,78, 201,59, 112,32, 53, 33, 35, 33, 10, 12	1.8,1.5, 1.6,1.0, 1.0,0.8, 0.6,0.5, 0.6,0.6, 0.4,0.3	Ion exchange; Slips and Freundlich fits	Dastgheib & Rockstraw 2002a

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Pecan shell	Air, H_3PO_4	Cu(II), Mn(II)	51-102, 33	.8-1.6, 0.6	Site competition; charge buidup, speciation; models with more parameters fit better.	Dastgheib & Rockstraw 2002b
Carbon	HNO_3 oxidation		—	—	Oxidation increased acid groups with pKa<4, favoring uptake	De Mesquita et al. 2006
Olive bagasse		Cr(VI)	88-110	1.7-2.1	Best pH 2; Pseudo 2nd order rate; Langmuir fit	Demiral et al. 2008
Hazelnut shells		Ni(II)	6-12	.10-.20	Langmuir fit; exothermic	Demirbas et al. 2002
Apricot stone, almond shell		Cr(VI)	—	—	Best pH 1; pseudo 2nd order	Demirbas et al. 2004
Almond shells		Cr(VI)	190	3.6	Langmuir fit; endothermic	Demirbas et al. 2008
Hazelnut shells		Cu(II)	58	0.9	Best pH 6; pseudo 2nd order rate; Langmuir fit; endothermic; regeneration (74+%)	Demirbas et al. 2009
Pine cone	$ZnCl_2$, H_3PO_4	Cr(VI)	60-80	1.2-1.5	Best pH 2; activating agents decreased porosity; highest adsorption with phosphoric acid activation	Duman et al. 2009
Pomegran. peel		Pb(II), Cu(II)	—	—	2nd order rates; Langmuir fits	El-Ashtoukhy et al. 2008
Corn cob	H_3PO_4	Pb(II)	37-120	.18-.58	Activation increased area and sorption.	El-Hendawy et al. 2001
Corn cob	HNO_3	Pb(II)	130-440	.63-2.1	Nitric acid widened pores and decreased surface area; removal of phenol increased O functionalities; lead updake greatly enhanced	El-Hendawy 2003
Date pits	HNO_3	Pb(II), Cd(II)	100-160, 110-160	.48-.77, .98-1.4	Higher pH favored; Langmuir fits; oxidation led to high affinity sorption; importance of oxygen sites	El-Hendawy 2009
Date palm seed	H_2SO_4	Cr(VI)	120	2.3	Best pH 1; pseudo 2nd order rate; Langmuir fit (equilibrium data)	El Nemr et al. 2008
Rice husk	H_2SO_4	Cr(VI)	—	—	First order rate; reduction by the sorbent	El-Shafey & Canepa 2003
Rice husk	H_2SO_4	Zn(II), Hg(II)	11-12, 100-120	.17-.18, .50-.60	Pseudo 2nd order rates; Hg(II) reduced to Hg(I), as adsorbed;	El-Shafey 2010
Ulva lactuca		Cr(VI)	112	2.2	Best pH 1; not sensitive to salt; pseudo 2nd order rate; Langmuir fit	El-Sikaly et al. 2007

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Apricot waste	K_2CO_3	Ni(II)	17-101	.29-1.7	Best pH 5; Langmuir fit	Erdogan et al. 2005
Sugar waste		Cr(III)	27	0.52	Best pH 5; Langmuir fit	Fahim et al. 2006
Granular carbon	Quat poly	Cr(VI)	54	1.0	Best pH low; reversible 2nd order kinetics; much less reduction to Cr(III) if treated; ion exchange; reduction if pH<4	Fang et al. 2006
Act. C cloths		Cu(II), Ni(II), Pb(II)	11, 7, 33	0.18, 0.12, 0.16	Cu2+ > Ni2+ > Pb2+ ; results attributed to electronegativity, ionic radius ; adsorption occurred below precipitation pH	Faur-Brasquet et al. 2002
Granular carbon		Cd(II), Cu(II)	3.3,2.5	.03,.04	Higher pH favored	Gabaldón et al. 2000
Coconut shell		Cd(II)	No eval	No eval	HIgher pH favored to 6; Freundlich fit	Gaikwad 2004
Act. carbon	Diphenyl carbazid	Cr(VI)	1.7-2.6	-	Removal as complex is favored by oxidized state, not Cr(III); data as carbazide	Gajhate et al. 1992
Olive, apricot, peach stones	H_2SO_4, persulf.	Zn(II)	2-32	.03-.49	Surface complexes; both basic and acidic carbons were effective	Galiatsatou et al. 2002
Rosewood	H_2SO_4	Cr(VI)	15-25	.29-.48	Best pH 3; first-order rate	Garg et al. 2004
Peach stone	Atmosph, H_3PO_4	Pb(II)	65-204	.31-.98	External gases reduced porosity, except air and steam increased mesoporosity; acidic carbons removed Pb well (air addition)	Girgis et al. 2007
Cotton stalks	H_3PO_4	Pb(II)	__	__	No purging gases; effective uptake	Girgis et al. 2009
Act. carbon	Heated, sulfurized	Hg, Cd, Pb	360, 34, 83	1.3-1.8, 0.2-0.3, 0.2-0.4	Best for Hg, especially when sulfurized; pH effects	Gomez-Serrano et al. 1998
Evergreen oak	H_3PO_4 levels	Zn(II)	0.9-1.6	0.013-0.024	Phosphoric treatment reduced microporosity ; surface area was key	Gomez-Tamayo et al. 2008
Kraft black liquor	H_3PO_4 pyrolysis	Cr(VI)	80-93	1.5-1.8	Tests at pH 3; higher temperature widened the pores; favorable results	Gonzalez-Serrano et al. 2004
Rice husk	KOH, NaOH	Cr(VI)	38	0.73	Low pH favored; pore sizes important	Guo et al. 2003
Sawdust Waste tires Commercial		Cr(VI)	1.9-2.3, 48-58, 44-53	.03-.05, 0.9-1.1, .84-1.0	Sawdust carbon not nearly as effective as carbon from tiers; best pH 2; first-order reversible; Langmuir fit; endothermic	Hamadi et al. 2001

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Granular		Cr(VI)	20-60	0.4-1.2	Tested at pH 4; dissolved oxygen inhibited uptake; treatment with reductants did not help; regeration with K_2PO_4; reduction of Cr to Cr(III) acidic	Han et al. 2000
Act. C. cloth	Electroch reduction	Cr(VI)	198	3.8	Electroreduction of the carbon greatly increased Cr(VI) uptake; ion exchange	Harry et al. 2008
Almond husks	H_2SO_4	Zn(II)	5	.076	Best pH 5.5; Langmuir fit	Hasar et al. 2003
Several carbons		Cr(VI)	40-101	.96-1.9	Tests at pH 3; Langmuir & Freundlich fits in different cases	Hu et al. 2003
Filtrasorb 400		Cr(VI)	26	0.50	Best pH 5-6; Adsorption & reduction; Cr(III) is less adsorbable than Cr(VI), which is adsorbed in the 6-valent state	Huang & Wu 1977
Hazelnut husks	$ZnCl_2$	Cu(II), Pb(II)	__	__	Langmuir fit	Imamoglu & Tekir 2008
Terminalia cata.	H_2SO_4	Hg(II)	94	0.47	Best pH 5-6; Langmuir fit	Inbaraj et al. 2006
Jackfruit peel	H_2SO_4	Cd(II)	52	0.46	Second order rate; Sips fit; regenerated with HCl	Inbaraj & Sulochana 2004
Indian almond	H_2SO_4	Hg(II)	94	0.47	Best pH 5-6; Langmuir fit; KI could displace	Inbaraj & Sulochana 2006
Cherry stone	Air, CO_2, steam, O_3, H_2O_2, HNO_3,	Cu(II)	4-28	.06-.44	Oxidation greatly enhanced uptake; Langmuir fit; ion exchange/complexation	Jaramillo et al. 2009
Coconut shell	HNO_3	Au(III), Ag(I) cyanides	24-55, 14-30	.12-.28, .13-.28	Nitric acid treatment hurt Au-cyanide complex adsorption; free CN ion suppressed Ag uptake	Jia et al. 1998
Coconut shell	HNO_3	Cd(II)	2-38	.02-.34	Oxidation greatly enhanced Cd(II) uptake; ion exchange; binding to carboxylate was irreversible	Jia & Thomas 2000
Coconut shell	HNO_3, NH_3	Cd(II), Ni(II), Cu(II), Ca(II)	2-16, 1-5, 2-14, 0.4	.02-.14, .02-.08, .04-.22, .01	High-N carbons had higher adsorption; complexation	Jia et al. 2002

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Soft vs. hard lignocellulosics	CO_2, steam	Pb(II), Cu(II), Ni(II), Cd(II), Zn(II)	14-50, 13-51, 0-0.6 1-4, 0-5	.07-.24, 0.2-0.8, .00-.01, .01-.04, .00-.03	Oxidation helped metal adsorption for carbons from soybean hull, sugarcane bagasse, peanut shell, and rice straw	Johns et al. 1998
Granular		Cd(II), Pb(II)	__	__	Column breakthrough equation fits	Jusoh et al. 2007
2 activated Cs		Cu(II), Ni(II), Pb(II)	8-32, 2-45, 5-211	.13-.50, .03-.77, .02-1.0	Higher pH favored to two units below precipitation ; ion exchange	Kadirvelu et al. 2000
Act. carbon cloth		Cu(II), Ni(II), Pb(II)	No eval	No eval	Higher pH favored to 6 ; max adsorption pH zones 2 units; ion exchange; carboxylate involvement	Kadirvelu et al. 2001
Parthenium		Ni(II)	54	0.92	HIgher pH favored; Langmuir fit; regen. with HCl	Kadirvelu et al. 2002
Rubberwood	H_3PO_4	Cu(II)	4.8-5.7	.08-.09	Best pH 6; pseudo 2nd order rate; Langmuir fit best; film & particle diffusion control	Kalavathy et al. 2005
Paper mill sludge	KOH	Cu(II), Cd(II), Cr(III)	12, 10, 5	0.19, 0.09, 0.10	Tests at pH 6 ; char; monolayer metal adsorption	Kang et al. 2006
Straw, sawdust, date pit		Cd(II)	3.6-4.3	.03-.04	Smaller particle size better; salt interference; straw carbon was best	Kannan & Rengasamy 2005a
Straw, sawdust, date pit		Ni(II)	__	__	Higher pH favored to 6; Smaller particle size better; salt interferences; first order rate; Langmuir fit;	Kannan & Rengasamy 2005b
Rubberwood		Cr(VI)	44-66	.85-1.26	Best pH 2; pseudo 2nd order rate; diffusion control; Langmuir fit best; endothermic	Karthikeyan et al. 2005
Wood	KOH, H_3PO_4	Cr(VI)	33-316	.63-6.1	KOH activation best; lower pH best; diffusion control; Langmuir fit	Khezami & Capart 2005
Oxidized act. C	ZnO	Pb(II), Cu(II), Cd(II)	8-46, 4-15, 2-14	.04-.22, .06-.23, .02-.12	ZnO loading and oxidation both favored adsorption; carboxyl groups important	Kikuchi et al. 2006
Peach stone	H_3PO_4	Cd(II)	No eval	No eval	Phosphoric acid activation was effective.	Kim 2004
Hazelnut shells		Ni(II)	__	__	Pseudo 2nd order rate	Kobya et al. 2002

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Hazelnut shells		Cr(VI)	170	3.3	Best pH 1; pseudo 1st order rate; Langmuir	Kobya 2004a
Hazelnut shells		Cr(VI)	170	3.3	Best pH 1; Langmuir fit	Kobya 2004b
Hazelnut shells	H_2SO_4	Cr(VI)	__	__	Particle size important; Freundlich isotherm	Kobya et al. 2004
Apricot stone	H_2SO_4	Ni(II), Co(II), Cd(II), Cu(II), Pb(II), Cr(III), Cr(VI)	27,30, 34,24, 23,29, 35	.46,.51, .30,.38, .11,.56, .67	Cr(VI) > Cd(II) > Co(II) > Cr(III) > Ni(II) > Cu(II) > Pb(II); best pHs 3-6, except 1-2 for Cr(VI)	Kobya et al. 2005
Eucalyptus bark	H_3PO_4	Cu(II), Pb(II)	29, 110	.46,.53	Binary mixtures, competition; best pH 5; carboxylic, amine, & amide groups important	Kongsuwan et al. 2009
Deposit lignin	H_3PO_4	Cu(II)	__	__	Good uptake observed.	Kriaa et al. 2010
Bagasse pith	Steam, sulfur	Hg(II)	67-94	.33-.47	Best pH 4-9; lower ionic strength better; pseudo 2nd order rate; Langmuir fit; regenerable with HCl	Krishnan & Anirudhan 2002a
Bagasse pith	Sulfur	Pb(II), Hg(II), Cd(II), Co(II)	200,189 154,129	.97,.94, 1.4,2.2	Pb(II) > Hg(II) > Cd(II) > Co(II); higher pH favored; pseudo 2nd order rate; Langmuir fit; regeneration by HCl	Krishnan & Anirudhan 2002b
Bagasse pith	Steam, sulfur	Cd(II)	150	1.3	Sulfurization helped; best pH 5-9; low ionic strength best; Langmuir fit	Krishnan & Anirudhan 2003
Bagasse pith	Steam, sulfur	Co(II)	150-180	2.5-3.1	Best pH 4.5-8.5; Langmuir fit	Krishnan & Anirudhan 2008a
Olive stone	$ZnCl_2$	Cd(II)	0.75	0.007	Higher pH favored to 6; pseudo 2nd order rate; Langmuir fit	Kula et al. 2008
Olive stone	$ZnCl_2$	U( ), Th( )	40, 20	.17,.09	Pseudo 2nd order rate	Kutahyali & Eral 2010
Activated carbon	Graphite electrode	Cr(VI); Pb(II), Zn(II), Cr(III)	No eval	No eval	Graphite electrode method; only the specialized carbon removed the anion; commercial C removed Pb, Zn, Cr(II)	Lalvani et al. 1998
Activated carbon		Cr(VI), Cr(III)	__	__	A commercial activated carbon was not able to adsorb the Cr(VI), just Cr(III)	Lalvani et al. 2000
Activated carbon		Cr(VI)	16+	0.3+	Best pH 6; Freundlich fit; reduction	Leyva-Ramos et al. 1994
Activated carbon		Cr(III)	6-7	.12-.13	Best pH 5; hydroxide ppt above pH 6.4; Langmuir fit	Leyva-Ramos et al. 1995

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Activated carbon		Cd(II)	8.0	0.071	Higher pH favored, except hydroxide precipitates at pH>9; lower temperature favored; Langmuir fit best;	Leyva-Ramos et al. 1997
Activated carbon		Cd(II), Zn(II)	16, 18	0.14, 0.27	Langmuir fits including bi-solute isotherms; partial competition	Leyva-Ramos et al. 2001
Carbon cloth	HNO_3	Cd(II)	5-13	.04-.12	Oxidation increased uptake; best pH 8; regen. by decreasing pH	Leyva-Ramos et al. 2005
Spartina altern.		Pb(II)	99	0.48	Best pH 4.8-5.6; pseudo 2nd order; Freundlich fit	Li & Wang 2009
Rice husk	H_3PO_4, $ZnCl_2$		No eval	No eval	Base-leaching & acid washing enhanced uptake capacity, surface area	Liou & Wu 2009
Raw act. carbon	HNO_3 & NaOH	Cr(VI)	4-11	.08-.21	The treatment increased Cr(VI) uptake; effect attributed to acidic sites	Liu et al. 2007
Activated carbon		Hg(II)	24-40	.12-.20	Higher pH favored; reduction to Hg(I) was a key mechanism	Lloyd-Jones et al. 2004
Mixed wastes, Oxidized carbon		Cr(III)	26-57; 46-53	.50-1.1, .89-1.0	Langmuir fits	Lyubchik et al. 2004
Granular act. C		Pb(II)	14	.066 (.047 & .075)	A two-site model was proposed to account for fast & slow rates for both adsorption & desorption; 2-site Langmuir fit	Machida et al. 2004
Lab carbon	SO_2 at temps.	Cd(II)	34-48	.30-.43	Heating increased the carbon's capacity; the SO_2 treatment was unimportant	Macias-Garcia et al. 2003
Lab carbon	SO_2 at temps.	Pb(II)	33-81	.16-.39	Sulfur treatment slowed down the rate but increased the capacity for Pb(II) sorption	Macias-Garcia et al. 2004
Activated carbon	H_3PO_4	Pb(II), Cu(II)	116, 32	.15-.56, .26-.51	Continuous proton affinity distribution explains dissociation and uptake behavior	Malik et al. 2002
Coconut husk	Cu(II) impregn	As(III)	160	2.1	Best pH 12; Langmuir fit; regenerable with H_2O_2 and HNO_3	Manju et al. 1998
Flax shive	H_3PO_4, H_2SO_4	Cd(II), Cu(II), Ni(II), Zn(II)	664,97, 48, 53	5.9,1.5, .82,.81	Phosphoric treatment more effective than sulfuric acid	Marshall et al. 2007
Militia f. leaves		Pb(II)	3	0.015	First order rate; Freundlich fit	Mengistie et al. 2008
Haxelnut shells	Steam, ultrsound	Cu(II)	239	4.5	Ultrasound helped; diffusion control; Langmuir fit	Milenkovic et al. 2009

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Bagasse		Cr(VI)	__	__	Best pH 2; Langmuir fit	Mise & Shantha 1993
Bagasse		Cd(II), Zn(II)	30, 29	.27,.44	Film diffusion; Freundlich fits	Mohan & Singh 2002
Act. C cloth		Cr(VI)	1-117	.02-2.2	Tests at pH 2; pseudo 2nd order rate; Langmuir fits	Mohan et al. 2005
Act. C cloth, coconut shell		Cr(III)	40, 12	0.63, 0.23	Pseudo 2nd order rate; Langmuir fit	Mohan et al. 2006
Woody biomass; Pine, oak: Barks, wood	Char fr. bio-oil	Pb(II), As(III), Cd(II),	2-14, 1-12, 1-4	.01-.07, .01-.16, .01-.04	Best pHs 3-5; Langmuir fit	Mohan et al. 2007
Terminalia arj.	ZnCl$_2$	Cr(VI)	28	0.04	Chemical ratio, temperature, & time of preparation; best uptake pH 1; first-order rate; Langmuir fit	Mohanty et al. 2005
Activated carbon		Cr(VI)	1.0	0.02	Best pH 2; Langmuir fit	Mor et al. 2007
Dates stone	H$_2$SO$_4$	Pb(II), Zn(II)	20, 10	0.10, 0.15	Best pH 6; pseudo 2nd order rate; Langmuir fit	Mouni et al. 2010
Activated carbon	Na acetate	Cu(II)	20-33	0.31-0.52	Acetate treatment increased uptake by 2.2X ; regeneration with NaOH	Mugisidi et al. 2007
Spent grain lignin	H$_3$PO$_4$	Ni(II), Fe, Cr, Si	No eval	No eval	Performance comparable to commercial activated carbon	Mussatto et al. 2010
Agricultural wastes		Cr(VI)	9	.17	Oxidizing agents increased the surface area; in-situ reduction	Muthukumaran et al. 1995
Husk and pod	CTAB, H$_3$PO$_4$, H$_2$SO$_4$, HCl	Pb(II)	25-30	.13-.15	Pseudo-2nd order rate; Langmuir fit	Nadeem et al. 2006
Coir pith		Hg(II)	154	0.77	Higher pH favored to 5; Langmuir fit; regeneration with HCl or KI	Namasivayam & Kadirvelu 1997
Coir pith		Hg(II),	154	0.77	Higher pH favored to 4; First order rate; Langmuir fit	Namasivayam & Kadirvelu 1999
Peanut hull	NaHCO$_3$	Hg(II)	2-20	.01-.10	The bicarbonate-treated carbon was 6X more effective than the control; Langmuir fit	Namasivayam & Periassamy 1993
Activated carbon		Pb(II), Cu(II), Co(II)	No eval	No eval	Best pH just below formation of hydroxide for each metal; competition very important	Netzer & Hughes 1984

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Oil palm shell	Chitosan	Cr(VI), Cr(III)	0.45	0.009	Best pH 4-5; ionic interactions & complexation; adsorptive reduction; regeneration with NaOH	Nomanbhay & Palanisamy 2005
Activated carbon	Ag metal, acid treat	Na(I)	—	—	Sodium carbonate, bicarbonate, NaOH uptake	Oh 2005
Sugar beet pulp	H_3PO_4	Cd(II)	68-73	.60-.65	96% uptake; 2nd order rate; Langmuir fit	Ozer & Tumen 2003
Pitch-based C		Cr(VI)	24-25	.46-.48	Langmuir fits	Park et al. 2003
Activated carbon		Cr(VI)	No eval	No eval	Reduced to Cr(III) on contact/adsorption	Park et al. 2006a
Activated carbon	Anodic treatment	Cr(VI), Cu(II), Ni(II)	18-26, 7-17, 4-10	.35-.50, .11-.27, .07-.17	Oxidized carbons had higher adsorption	Park & Kim 2004
Peanut hulls		Cd(II)	2-20	.02-.17	Good pHs 3.5-9.3; Freundlich fit	Periasamy & Namasivayamm 1994
Peanut hulls		Ni(II)	0.7-20	.01-.34	Good pHs 4-10; Langmuir fit	Periasamy & Namasivayamm 1995a
Peanut hulls		Pb(II)	14-20	.07-.10	Good pHs 3-10; Langmuir fit	Periasamy & Namasivayamm 1995a
Peanut hulls		Cu(II)	3-32	.05-.50	Good pHs 4-10; Langmuir fit	Periasamy & Namasivayamm 1995a
Jute, coconut fibers	CO_2, H_3PO_4	Cu(II)	10-137	0.15-2.15	Acidic surface sites active in adsorption	Phan et al. 2006
Hymenaea shell	$ZnCl_2$, H_3PO_4, H_2SO_4, HNO_3, HCl	Cd(II)	—	—	Freundlich fit	Poleo et al. 2010
Activated carbon	H_3PO_4	Cu(II)	No eval	No eval	Key role of P-containing groups	Puziy et al. 2002
Activated carbon		Cd(II)	10	0.19	Vs. carbon nanotubes, magnetic particles ; higher pH favored; pseudo 2nd order; Langmuir fits	Pyrzynska 2010
Activated carbon		Th	No eval	No eval	Higher pH favored to 3; Langmuir fit; regen with HNO_3	Qadeer et al. 1992
Activated carbon		Sr	—	—	Diffusion into micropores controls rate	Qadeer et al. 1995a

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Activated carbon		Sr(II), Sm(III), Gd(III),Th(IV) UO_2^{2+}	__	__	Fast & slow processes; diffusion into fine pores controls rate	Qadeer et al. 1995b
Activated carbon		Dy(III),Gd(III), Eu(III),Sm(III)	__	__	Adsorption correlated with Z/r; Dy3+ > Gd3+ > Eu3+ > Sm3+	Qadeer et al. 1996
Parthenium w	H_2SO_4, NH_4 per-sulfate	Cr(VI), Hg(II), Fe(II)	> 1, > 1, > 1	> 0.02, > .005, > 0.02	Found to be effective	Rajeshwarisivaraj & Subburam 2002
Sawdust		Cr(VI)	50	0.10	Pore diffusion control; reduction at lower pH; Langmuir fit; regen. with NaOH	Raji & Anirudhan 1997
Sawdust	$NaHCO_3$	Pb(II), Hg(II), Cd(II)	__	__	Best pHs 4-9; Langmuir fit; regen. with HCl	Raji et al. 1997
Activated carbon		Cr(VI)	15-35	.29-.67	Tests at pH 3; Langmuir fit	Ranganathan 2000
Act. carbon cloth	HNO_3, O_3, elec. oxidation	Cd(II)	6-147	.05-1.3	Oxidation of activated carbon increased the ion exchange capacity by a factor of 3.5; higher pH favored	Rangel-Mendez and Streat 2002
Act. carbon fiber	$AlCl_3$, $ZnCl_2$	Zn(II), Cd(II)	__	__	Treatments affected pore sizes	Rincon et al. 2007
Activated carbon	Ozonized	Cr(III)	7-19	.13-.37	Tests at pH 6; Langmuir fits	Rivera-Utrilla et al. 2003a
Activated carbon	*E.coli* adsorp.	Pb(II), Cd(II), Cr(VI)	21-26, 5-8, 3-4	.10-.13, .04-.07, .06-.08	Bacteria in the solution enhanced adsorption of cations, but not Cr(VI)	Rivera-Utrilla et al. 2003b
Activated carbon		Ce(III),Sm(III) Eu(III), Gd(III)	18,19, 15,18	.13,.13, .10,.11	Adsorption controlled by effect of pH on dissoved metal species; best pH 8-9.5	Saleem et al. 1994
Activated carbon	Control Air ox'd " Nitric acid ox'd	Cu(II) Cu(II), Zn(II), Ni(II), Cd(II); Cu(II), Zn(II), Ni(II), Cd(II)	0.25; 3.2,8.5, 3.5,26; 27,10, 12,24	0.004; .05,.13, .06,.23; .42,.16, .20, .21	Oxidation by nitric acid increased Cu uptake by 100X; regeneration with 0.1 M HCl worked best for Cu	Saha et al. 2003
Coir pith	KOH	Cd(II), Cu(II), Zn(II)	No eval	No eval	Higher pH favored; 1st order rate; Freundlich fit; regen. by HCl	Santhy & Selvapathy 2004
Biomass mixture		Mn	3.0-3.4	.05-.06	Surface oxides play key role; ion exchange	Savova et al. 2003
Hazelnut	KOH, ultrason.	Cu(II)	40	0.63	Open pore structure	Sayan 2006

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Coconut shell		Pb(II)	26	.12	Best pH 4.5; Langmuir fit; exothermic	Sekar et al. 2004
Coconut tree		Cr(VI)	3.5	0.067	Adsorption at pH 3; Langmuir fit	Selvi et al. 2001
Various act. Cs		Cr(VI)	1.9-4.9	0.036-0.09	H-type (from coconut shell or coat) vs. L-type (from wood) performed differently; for L the Best pH for Cr was 2; for H it was 3-4; the H type can reduce Cr(VI) to Cr(III).	Selomulya et al. 1999
Activated carbon		Cr(VI)	76	1.46	Very little reduction took place when using leaf mold; activated carbon caused reduction	Sharma & Forster 1996a
Activated carbon		Cr(VI)	145	2.8	Best pH 2.5 to 3; Langmuir fit	Sharma & Forster 1996b
Pitch	HNO_3, NaOH	Cu(II), Ni(II)	9, 2	.14, .03	Post treatments; HNO_3 increased acid sites 3X, points of zero charge fell pH 6 to pH 4;	Shim et al. 2001
Lodgepole pine	Vacuum pyrolysis, steam, KOH	Cu(II), Cd(II), Mn(II), Ni(II), Pb(II), Zn(II)	50-400 (mixed)	0.5-10 approx.	The carbons outperformed commercial carbons for the metals mixture	Shin et al. 2008
Carbon slurry		Cr(VI)	24-26	.46-.50	Tests at pH 2.5; Langmuir fit; higher temperature favored	Singh & Tiwari 1997
Tamarind wood	H_2SO_4	Pb(II)	134	0.65	Best pH 6.5; Langmuir fit	Singh et al. 2007
Various ag wastes	H_3PO_4	Au	No eval	No eval	Heating temperature and time were critical	Soleimani & Kaghazchi 2007
Apricot stones		Au	__	__	Langmuir fit; regen. with base	Soleimani & Kaghazchi 2008
Sawdust		Pb(II)	41	0.20	Higher pH favored to 6; Citric acid lowered pH optimum; peudo 1st order rate; Langmuir fit	Sreejalekshmi et al. 2009
Coconut oilcake		Ni(II)	__	__	Pseudo 2nd order rate; Langmuir fit	Srinivasan & Hema 2009
Coconut		Cd(II), Ni(II), Zn(II)	__	__	Best pH 6; pseudo 2nd order rate	Srivastava et al. 2008b
Granular		Cr(VI)	__	__	Langmuir fit	Tandel & Oza 2005
Cashew nut		Cr(III)	14	0.27	Langmuir fit	Tangjuank et al. 2009
Kraft lignin	H_2O_2	Cr(VI)	76	1.46	Best pH 2; pseudo 2nd order rate; Langmuir fit; endothermic	Tazrouti & Amrani 2009

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Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Almond, pecan	H_3PO_4, CO_2 Air oxidn	Cu(II)	2-18	.03-.28	Oxidation increased uptake	Toles et al. 1997
Various nuts	H_3PO_4, Air oxidn	Cu(II)	17-18	.27-.29	Various oxidations increased uptake	Toles et al. 1998
Various nuts	H_3PO_4, Air oxidn	Cu(II)	6-60	0.1-0.9	Functional group abundance correlates with updake: carbonyl, phenols, lactones, carboxyl	Toles et al. 1999
Sunflower husk	H_3PO_4 in nitrogen	Cu(II), Cr(VI)	48, 19	.76,.36	Langmuir fit for Cu(II); Freundlich fit for Cr(VI); stoichiometric relationship to groups	Tupkanjana & Phalakornkule 2007
Activated carbon	Tannic acid	Fe(III)	__	__	Tannic acid enhanced metal uptake; Langmuir fit	Ucer et al. 2005
Olive stone	$ZnCl_2$	Ni(II)	.28-.66	0.005-0.01	Higher pH favored to 6; pseudo 2nd order rate	Ugurlu et al. 2009
Bagasse	Hetero atoms	Cr(VI)	3.4-10.1	.06-.20	Basicity of the carbon contributed to Cr(VI) uptake through heteroatoms	Valix et al. 2006
Bagasse		Cr(VI)	2-32	.04-.62	Reduction mechanism; uptake favored by mimimal oxygen and hydrogen contents	Valix et al. 2008
Granular act C		Co(II), Zn(II)	No eval	No eval	Higher flow beneficial	Wang et al. 2003
Activated carbon		Pb(II)	50	0.24	Breakthrough prediciton	Xiu & Li 2000
Peanut shell	HNO_3	Pb(II)	36	0.17	Langmuir fit; uptake enhanced by pore widening, oxygen groups, hydrophilicity	Xu & Liu 2008
Activated carbons	H_2SO_4 , $ZnCl_2$	Cd(II)	6-25	.05-.22	$ZnCl_2$ gave a high surface area; 1st order rate; ion exchange; competition; diffusion control	Youssef et al. 2004
Low cost	Low temp act.	Cr(VI)	8-40	.15-.77	High surface area, mesopores important	Yue et al. 2009
Activated carbons		Pb(II)	6.3-8.5	.03-.04	Adsorption accounted by surface area, pore size, and heteroatom concentrations	Zhang et al. 2005
Activated carbon	Zero-valent Fe	As(III), As(V)	18, 12	.24, .16	Arsenite and arsenate were taken up by the supported ZVI crystals; Langmuir fit; regen. with NaOH	Zhu et al. 2009b

Biomass type	Modifi-cation	Metals	Capac. (mg/g)	Capac. (mM/g)	Key findings	Citation
Ash						
Fly ash	Al, Fe	Cr(VI)	1.4-1.8	0.026-0.035	Tests at pH 2; Langmuir fit	Banarjee et al. 2004
Rice husk		Zn(II)	__	__	Langmuir fit	Chaves et al. 2009
Wood ash		Zn(II), Cd(II), Cu(II), Cr(III)	No eval	No eval	Pseudo 2nd order rate; Langmuir	Chojnacka & Michalak 2009
Oil palm waste		Zn(II)	11	0.17	Higher pH better; First order rate; Langmuir, other fits	Chu & Hashim 2002
Bagasse fly ash		Pb(II)	520	2.5	Best pH 3; Langmuir fit; treatment effective	Gupta et al. 1998
Bagasse fly ash		Cr(VI)	124-259	2.4-5.0	Tests at pH 1; Langmuir fits	Gupta et al. 1999
Bagasse fly ash		Cu(II), Zn(II)	__	__	Langmuir fit	Gupta & Ali 2000
Bagasse fly ash		Cd(II), Ni(II)	1.2,1.0	.01, .02	Best pH 6-6.5; Langmuir fit	Gupta et al. 2003
Bagasse fly ash		Pb(II), Cr(III)	3.9, 1.9	0.02, 0.036	Langmuir fit; exothermic	Gupta & Ali 2004
Sugar beet fly ash		Cu(II), Zn(II)	7, 8	.11, .12	60-97% uptake; best pHs 4-5; Langmuir fit	Pehlivan et al. 2006
Bagasse fly ash	NaOH, acetic ac	Cr(VI), Ni(II)	52, 4.4	1.0, 0.075	Activated carbon was more effective than fly ash or the starting mateiral	Rao et al. 2002
Bagasse fly ash		Cd(II), Ni(II)	2.3, 2.5	.02, .04	Higher pH favored to 6; Redlich-Peterson fit; competition; regen. with acid	Srivastava et al. 2006a
Bagasse fly ash		Cd(II), Zn(II)	6.2, 7.0	0.055, 0.11	Binary systems; best pH 6; Redlich-Peterson fit; competition	Srivastava et al. 2006b
Rice husk ash		Cd(II), Ni(II), Zn(II)	6.2, 4.2, 2.8	0.055, 0.072, 0.043	Higher pH favored to 6; pseudo 2nd order rate;	Srivastava et al. 2006c
Rice husk ash; bagasse fly ash		Cd(II), Ni(II), Zn(II)	20-25, 22-25, 25-26	.18-.22, .38-.43, .38-.40	Thermodynamics; heterogeneous sites	Srivastava et al. 2007
Rice husk ash		Cd(II), Zn(II)	2.9, 6.2	0.026, 0.095	Binary; higher pH favored to 6; Redlich-Peterson fit; competition	Srivastava et al. 2008a
Rice husk ash		Cd(II), Ni(II), Zn(II)	2.3,2.6, 3.1	.02,.04, .05	Ternary; Redlich-Peterson fit; competition	Srivastava et al. 2009a
Rice husk ash		Cd(II), Ni(II)	__	__	Competitive; Freundlich fit of binary	Srivastava et al. 2009b