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Station

Strategic Environmental Research and Development Program

Low-Cost Sorbents: A Literature Summary

by   Susan Bailey, Trudy J. Olin, R. Mark Bricka

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Improving Mission Readiness through
Environmental Research

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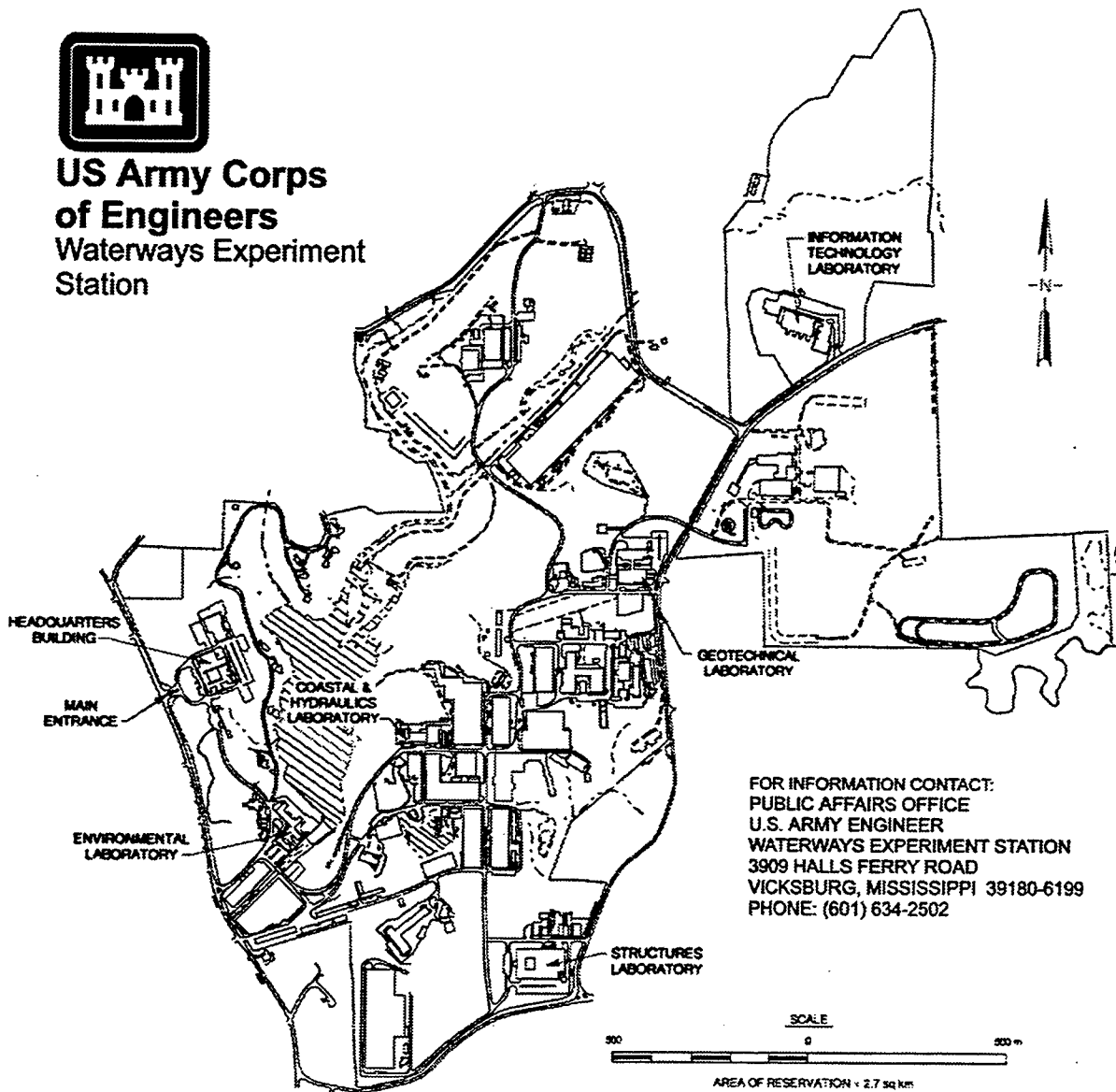
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500   0   500 m

AREA OF RESERVATION < 2.7 sq km

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Preface

The work reported herein was conducted by the Environmental Laboratory
(EL) of the U.S. Army Engineer Waterways Experiment Station (WES) for
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This report is one component of a work unit encompassing identification
and bench-scale testing of low-cost sorbents for treatment of metals-
contaminated water and waste streams. The report was prepared by Ms. Susan
Bailey and Mr. R. Mark Bricka, Environmental Restoration Branch (ERB), and
Ms. Trudy J. Olin, Environmental Resources Engineering Branch (EREB),
Environmental Engineering Division (EED), EL. Mr. Daniel E. Averett, ERB,
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1 Introduction

Heavy metal contamination is a problem for aqueous waste streams from many industries such as metal-plating facilities, mining operations, and tanneries. The soils surrounding many military bases also suffer from metal contamination, which pose a risk of leaching into the groundwater and transport in surface water. Metals associated with these activities include cadmium, chromium, lead, and mercury. Heavy metals are not biodegradable and tend to accumulate in living organisms, potentially causing various diseases and disorders.

Proven methods for removing heavy metals are expensive. Treatment processes for heavy metals-contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, and carbon adsorption. Activated carbon adsorption is frequently used to treat heavy metal-contaminated water. The carbon can be reused several times by regeneration with acid. However, for every dollar spent on adsorption, it is estimated that three dollars are spent on regeneration. Also, the regeneration step produces a hazardous waste stream of concentrated metals and acid that must be disposed, and treatment efficiency is not high. Higher efficiencies can be achieved with ion-exchange resins, but these are expensive both for the resin and for regeneration. Alternative technologies or sorbents for treatment of metals-contaminated waste streams are needed. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without regeneration. It is likely that disposal in a hazardous waste landfill would be required. An important part of the feasibility analysis then will include evaluation of the relative capital and disposal costs for low-cost sorbents versus capital, regeneration, and ultimate disposal costs for regenerable sorbents. A volume reduction analysis based on the sorbent capacity will also be important.

There is abundant information in the literature on low-cost sorption using a wide variety of sorbents. Most of this research appears to have been conducted at bench scale. A comprehensive summary of literature reviewed follows. The original keyword search included the following sets of keywords on Compendex*Plus, GeoRef, and FLUIDEX databases:

a. Set 1: wastewater.

   b. Set 2: metal or Cd or Cr or Pb or Hg.

   c. Set 3: sorption or adsorption or sorbent or starch or xanthate or ISX or crown ethers.

   d. Set 4: set 1 and set 2 and set 3.

A follow-up search was performed using sorbents generated from the first search. A wide variety of possible sorbents have been reported in the literature. These are as follows:

- Bark/tannin-rich materials.

- Lignin.

- Chitin/chitosan.

- Xanthate.

- Zeolite.

- Clay.

- Peat moss.

- Dead biomass.

- Seaweed/algae/alginate.

- Bone gelatin beads.

- Crown ethers.

- Leaf mold.

- Moss.

- Iron-oxide-coated sand.

- Modified wool.

- Modified cotton.

There is some difficulty encountered comparing different sorbents based on work by different researchers due to the varying experimental conditions and methods of reporting results. Some researchers used batch testing, which is typically easier and more straightforward, while others used continuous or

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column experiments, which are used more often in the field, as they are considered to be more efficient to operate than a batch process. Many researchers used both types of experiments. Solution concentrations and sorbent-to-liquid ratios also varied greatly. One important factor when conducting adsorption experiments is pH. If pH is not controlled, precipitation can occur, and measurements of the metal-removal efficiency will include that removed by precipitation as well as by adsorption. Furthermore, pH drastically affects adsorption, as it influences the competition of H^+ ions as well as the speciation of the metal ions in solution. Unfortunately, many sources do not report that this was taken into account.

Another aspect that makes it difficult to compare sorbents reported in the literature is the varying methods of quantifying results. Most articles report the effectiveness of the sorbents in terms of adsorption capacity. This parameter indicates the amount of metal that can be adsorbed per unit weight of sorbent. However, some researchers report efficiencies in terms of percent adsorption, or percent of the metal that is adsorbed from solution. This parameter is not a good basis for evaluation. Percent adsorption is dependent on the experimental conditions and does not really measure the efficiency of the sorbent. By varying the amount of sorbent used and/or the concentration of the metal in solution, any value can be achieved; using a large amount of sorbent with low concentrations of metals can easily give values near 100-percent adsorption. While percent removal is useful for examining the effectiveness of different sorbents under one specific condition, it is not an effective parameter for comparing the efficiencies of a variety of sorbents over a range of conditions or for determining maximum capacity. Adsorption capacity takes into account both the solution concentration and the ratio of solution to sorbent, and by increasing the solution concentration, a unique maximum adsorption capacity can be achieved that is independent of solution concentration and ratios. Most researchers did not attempt to determine the maximum capacity. One other factor that affects adsorption of metals is temperature. The sorption process can either be exothermic or endothermic. Lower temperatures favor exothermic adsorption, while higher temperatures improve endothermic adsorption.

Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the amount of modification required and local availability. For example, bark can be obtained relatively cheaply, but, if it must be treated before it can be used, the cost of the modified sorbent increases considerably. In general, a sorbent can be assumed to be "low cost" if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry.

2   Sorbent Literature

Bark and Other Tannin-Rich Materials

Much attention has been given to tree bark, a by-product of the timber industry. The effectiveness of bark stems from its high tannin content. It is suspected that the polyhydroxy polyphenol groups of tannin are the active species in the adsorption process. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups, forming a chelate (Randall et al. 1974; Vázquez et al. 1994). Hydrogen ions are apparently released as evidenced by alteration of pH. Several sources note an initial pH decrease as metal ions replace hydrogen ions; then the pH will increase as hydrogen ions become competitive with the heavy metal ions, as well as with light metals, which are natural constituents of the bark (Alves et al. 1993; Deshkar, Bokade, and Dara 1990; Teles de Vasconcelos and González Beça 1994; Randall, Hautala, and Waiss 1974).

One problem with tannin-containing materials is discoloration of the water from soluble phenols. Chemical pretreatment of bark has been shown to overcome this problem. A study by Vázquez et al. (1994) indicates that treatment with acidified formaldehyde eliminated the bleeding of colored compounds without appreciably affecting capacity. Also, Alves et al. (1993) tested several treatment methods using acid, base, or formaldehyde. Results showed several treatments decrease capacity, while acid treatment with formaldehyde or certain treatments with sodium or calcium, salts, or hydroxides improve bark capacity. However, treatment cost to control bleeding may outweigh incidental increases in capacity.

Bark species and origin may influence capacity. Among the best results are those for black oak with a demonstrated capacity of 400 mg Hg/g (Masri, Reuter, and Friedman 1974) and redwood (182 mg Pb/g and 32 mg Cd/g). Redwood bark studies reduced copper mine runoff with 6-ppm Cu to less than 0.1 ppm and outflow from a lead battery plant with 4.5-ppm Pb to less than 0.5 ppm (Randall, Hautala, and Waiss 1974).

Some other tannin-rich agricultural by-products have been examined for their use as metal sorbents. Randall et al. (1974) and Randall, Hautala, and Waiss (1974) compared bark adsorption with that of peanut skins, walnut

expeller meal, and coconut husks and showed their capacities to be comparable. Randall, Hautala, and McDonald (1978) also did a study specifically with formaldehyde-polymerized peanut skins. The formaldehyde was used to prevent leaching of color and disintegration upon prolonged contact with water. Orhan and Büyükgüngör (1993) compared nut and walnut shell, waste tea, and coffee with activated carbon and observed the capacities of the tannin-containing products to be only slightly less than that of activated carbon. The reported capacities for bark and these materials are given in Table 1. While bark is the most likely choice due to its wide availability, other low-cost by-products containing tannin show promise for an economical replacement for activated carbon as well.

Table 1 Reported Adsorption Capacities for Tannin-Containing Materials						
Material	Source	mg Cd/g	mg Cr (III)/g	mg Cr (VI)/g	mg Hg/g	mg Pb/g
Hardwickia binata bark	Deshkar, Bokade, and Dara 1990				34	
Redwood bark	Randall et al. 1974	27.6				6.8
Redwood bark	Randall, Hautala, and Waiss 1974	32				182
Formaldehyde-polymerized peanut skins	Randall, Hautala, and McDonald 1978	74				205
Pinus pinaster bark	Vázquez et al. 1994					1.59
Pinus pinaster bark	Teles de Vasconcelos and González Beca 1993	8.00	19.45			
Pinus pinaster bark	Teles de Vasconcelos and González Beca 1994					3.33
Activated carbon	Teles de Vasconcelos and González Beca 1994					2.95
Treated pinus sylvestris bark	Alves et al. 1993		9.77			
Untreated pinus sylvestris bark	Alves et al. 1993		8.69			
Douglas fir bark	Masri, Reuter, and Friedman 1974				100	
Redwood bark	Masri, Reuter, and Friedman 1974				250	
Black oak bark	Masri, Reuter, and Friedman 1974	25.9			400	153.3
Nut shell	Orhan and Büyükgüngör 1993	1.3		1.47		
Walnut shell	Orhan and Büyükgüngör 1993	1.5		1.33		
Waste tea	Orhan and Büyükgüngör 1993	1.63		1.55		
Exhausted coffee	Orhan and Büyükgüngör 1993	1.48		1.42		
Turkish coffee	Orhan and Büyükgüngör 1993	1.17		1.63		
Sawdust	Bryant et al. 1992			10.1		
Sawdust	Dikshit 1989			16.05		
Sawdust	Zarraa 1995			4.44		

Another waste product from the timber industry is sawdust. Sawdust has a smaller particle size than bark as processed from the lumber mill and would not require size reduction. Bryant et al. (1992) tested red fir sawdust for adsorption of copper and hexavalent chromium and tested α-cellulose to determine if the metal was being sorbed onto the cellulose backbone of the sawdust. Results showed adsorption onto the α-cellulose to be one or two orders of magnitude less than that onto the sawdust, suggesting the metals are primarily sorbed onto other components of the wood such as lignin or tannin. Adsorption was found to increase with temperature, but above 60 °C sorption of copper decreased due to solubilization of wood extracts such as tannins. Chromium adsorption did not decrease, suggesting that the chromium either forms insoluble complexes with the bark or the Cr (VI) binding sites are not solubilized. Maximum adsorption capacities were found to be 10.1 mg Cr^{6+}/g and 7.09 mg Cu^{2+}/g sawdust. Dikshit (1989) also observed hexavalent chromium adsorption onto sawdust and found the process to be exothermic. The maximum adsorption capacity was 16.05 mg Cr^{6+}/g. Experiments by Zarraa (1995) demonstrated a maximum adsorption capacity of 4.44 mg Cr^{6+}/g sawdust. Further studies by Sabadell and Krack (1975) investigated several wood types for adsorption of Pb, Cd, Cu, and Ni. The following average capacities for the woods were given: oak sawdust: 0.0982 meq metal/g; ash shavings: 0.0721 meq metal/g; cedar sawdust: 0.0683 meq metal/g.

Lignin

Srivastava, Singh, and Sharma (1994) studied adsorption of lead and zinc onto lignin. The lignin used was extracted from black liquor, a waste product of the paper industry. Waste black liquor can be purchased for $1.00/ton, and the lignin can be processed for approximately $60/ton, as compared with activated carbon at $100/ton. The adsorption capacity for lignin at 30 °C was found to be 1,587 mg Pb/g and 73 mg Zn/g, and increased to 1,865 mg Pb/g and 95 mg Zn/g at 40 °C (Table 2). The high adsorption capacity of lignin is due in part to polyhydric phenols and other functional groups on the surface. Ion exchange may also play a role in the adsorption of metals by lignin. The surface area of the lignin used was 1,440 m^2/g. Srivastava et al. found the adsorption process to be endothermic and to increase with increasing pH. Masri, Reuter, and Friedman (1974) found uptake of mercury by sulfuric acid lignin to be 150 mg/g (Table 2).

Table 2
Reported Adsorption Capacities for Lignin

Material	Source	mg Hg/g	mg Pb/g	mg Zn/g
Lignin	Srivastava, Singh, and Sharma 1994		1,865	95
Sulfuric acid lignin	Masri, Reuter, and Friedman 1974	150		

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Chitosan and Seafood Processing Wastes

Another material shown to adsorb metals is chitin. Chitin is second only to cellulose in terms of abundance in nature and is found in the exoskeletons of crabs and other arthropods and in the cell wall of some fungi (Berkeley 1979; Rorrer, Hsien, and Way 1993). Chitin is also a waste product of the crab meat canning industry. It is estimated that more than 36 million kilograms of chitin is available from the fisheries of crustaceans annually (Onsøyen and Skaugrund 1990). However, more important than chitin is its deacetylated derivative, glucosamine, or chitosan. Chitosan can be produced chemically from chitin and is found naturally in some fungal cell walls. It is estimated that up to 1.8 million kilograms of chitosan could be produced at a market price under $1.00 per/kilogram (Berkeley 1979).

Not only is chitosan inexpensive and abundant, it is highly adsorbent for heavy metals. Yang and Zall (1984a) report chitosan chelates five to six times greater amounts of metals than chitin due to the free amino groups exposed during deacetylation. This study also compares chitosan with fish scales. While the fish scales did show some ability to remove metals, they were not as effective as chitosan. Kurita, Sannan, and Iwakura (1979) note that the adsorption capacity of chitosan varies with crystallinity, affinity for water, percent deacetylation, and amino group content. Polysaccharides with about 50-percent deacetylation seem to be most effective for adsorption although their high solubility in water presents difficulties for practical use. To make the 50-percent deacetylated chitosan insoluble, Kurita, Koyama, and Taniguchi (1986) suggest loose cross-linking the polymer with glutaraldehyde. Experiments with the cross-linked chitosan showed 80-percent copper removal in 1 hr and 100-percent removal in 24 hr. Cross-linking did somewhat reduce the adsorption capacity of the chitosan. Table 3 presents a summary of the chitosan capacities reported in the literature for Cd, Cr, Hg, and Pb.

Another experiment by Yang and Zall (1984b) demonstrated the usefulness of chitosan columns for the removal of metals from sludge. The sludge, which was obtained at a sewage treatment plant and contaminated with Cu, Zn, Cr, Cd, and Pb, was first acidified to leach the metals. The pH was then adjusted to 6.0, and the liquid stream was subjected to a column containing powdered chitosan. Results showed that Cu has a strong affinity for chitosan, and Cu competition decreased removal efficiency of the other metals. Ershov et al. (1992) found capacities for Cu to be 15.9 mg Cu/g chitin and 222.4 mg Cu/g chitosan.

Chitosan was compared with bark, activated sludge and poly (p-aminostyrene), and other materials by Masri, Reuter, and Friedman (1974). Results showed chitosan to possess exceptional binding capacity, greater than 1 mmol metal/g for most metals (except for chromium). Also, for all metals tested except mercury, chitosan showed greater adsorption capacities than did polyaminostyrene, the constituent of expensive

Table 3
Reported Adsorption Capacities for Chitosan

Material	Source	mg Cd/g	mg Cr (III)/g	mg Cr (VI)/g	mg Hg/g	mg Pb/g
N-acylated cross-linked chitosan beads	Hsien and Rorrer 1995	136				
N-acylated chitosan beads	Hsien and Rorrer 1995	216				
Chitosan	Jha, Iyengar, and Prabhakara Rao 1988	6.4				
Chitosan	McKay, Blair, and Findon 1989				815	
Chitosan	Masri, Reuter, and Friedman 1974	558	92		1,123	796
Chitin	Masri, Reuter, and Friedman 1974				100	
Chitosan (from lobster shell)	Peniche-Covas, Alvarez, and Argüelles-Monal 1992				430	
Chitosan powder	Rorrer, Hsien, and Way 1993	420				
Chitosan beads	Rorrer, Hsien, and Way 1993	518				
Chitosan	Udaybhaskar, Iyengar, and Abhakara Rao 1990			27.3		

ion-exchange resins. As shown in Table 2, Masri et al. achieved extremely high adsorption capacities with chitosan.

The usefulness of chitosan beads is noted by Rorrer, Hsien, and Way (1993). Chitosan beads were cross-linked with glutaraldehyde and had magnetite added to incorporate a magnetic component that could be useful for site cleanup. Cross-linking of the chitosan renders the bead insoluble in low-pH solutions, whereas uncross-linked chitosan is soluble to some extent in slightly acidic solutions. The beads also possessed a surface area 100 times higher than that of chitosan flakes. A comparison of the beads and powder showed a maximum capacity of 420 mg Cd/g chitosan powder and 518 mg Cd/g chitosan bead. An increase in pH was noted during adsorption, which rules out ion exchange as the mechanism of sorption. Mitani et al. (1995) also experimented with swollen chitosan beads and found that increasing the ionic

strength of solution improved the ability of the beads to adsorb nickel and cobalt ions. Chitosan beads could have advantages over other forms, such as greater capacity, faster kinetics, and increased ease of operation.

Two limitations of chitosan are that it is nonporous and it is soluble in acidic solution. As mentioned above, cross-linking can be used to overcome solubilization. Also, Hsien and Rorrer (1995) suggest N-acylation as a means of increasing porosity. They N-acylated chitosan, cast it into beads, then cross-linked the beads with glutaric dialdehyde to overcome these problems. Analysis of the internal surface area showed the beads to have higher surface area (223.6 m^2/g) than uncross-linked N-acylated beads (192.4 m^2/g) and nonacylated cross-linked beads (42.6 m^2/g). The solubility of the beads was also tested. The solubility of N-acylated cross-linked beads (0.3 percent) was much lower than that of uncross-linked chitosan powder or beads ($\geq$ 99 percent). N-acylation improved the adsorption capacity for cadmium over non-acylated beads from 169 mg Cd/g to 216 mg/g. However, cross-linking the N-acylated beads at 0.75 wt percent glutaraldehyde reduced the capacity to 136 mg Cd/g bead. This loss of capacity may be necessary to ensure stability of the beads.

Even though chitosan is highly sorptive in its natural state, its adsorption capacity could also be improved by the substitution of various functional groups, such as organic acids, onto the chitosan backbone. Substitution of carboxylic groups changes the number and nature of the adsorption sites. For example, Guibal et al. (1994) investigated the sorptive potential of chitosan modified by grafting of oxo-2-glutaric acid. The modification takes place by dissolving chitosan in the organic acid to form a ketoimine, then hydrogenating it using sodium cyanoborohydride to form glutamate glucan. The modification increases the porosity of the polymer and enhances the ability of the solute to diffuse. Also, the time to reach equilibrium is drastically reduced for the glutamate glucan over chitosan. The modified chitosan was used to adsorb uranium and vanadium, and results showed that it could adsorb as much as 450 mg metal/g sorbent in a batch reactor. An alternative experiment by Jansson-Charrier et al. (1996) for vanadium removal used unmodified chitosan and obtained capacities as high as 400 mg V/g chitosan. This study showed that chitosan sorption is mainly a surface exchange affected by particle size and sorbent porosity. Other functional groups grafted to chitosan to improve capacity are amino acid esters (Ishii et al. 1995), pyridyl (Baba and Hirakawa 1992), substituted pyridine rings (Tong et al. 1991), and polyethylenimine (Kawamura et al. 1993).
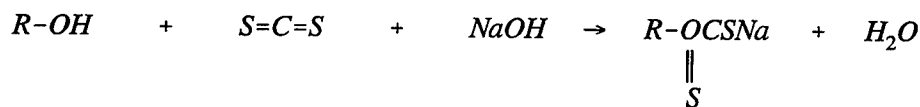
Xanthate

Adsorbents containing sulfur-bearing groups have a high affinity for heavy metals but a low affinity for lighter metals. Some sulfur-bearing compounds include sulfides, thiols, dithiocarbamates, dithiophosphates, and xanthates. Xanthates are the most prominent because they are easy to prepare, highly

insoluble, and the reagents used are relatively inexpensive (Flynn, Carnahan, and Lindstrom 1980). Reported adsorption capacities are given in Table 4.

Table 4
Reported Adsorption Capacities for Xanthate

Material	Source	mg Cd/g	mg Cr (III)/g	mg Cr (VI)/g	mg Hg/g	mg Pb/g
Cellulose xanthate	Bricka and Hill 1989	19.88	19.67		0.6367	
ISX	Bricka and Hill 1989	33.27	17.57		1.1487	
Xanthated sawdust	Flynn, Carnahan, and Lindstrom 1980	21.4			30.1-40.1	31.1-41.4

Xanthates are formed by reacting an organic hydroxyl-containing substrate with carbon disulfide:

$$R\text{-}OH \quad + \quad S\text{=}C\text{=}S \quad + \quad NaOH \quad \rightarrow \quad R\text{-}OCSNa \quad + \quad H_2O$$
$$\overset{\|}{S}$$

Organic Substrate   Carbon Disulfide   Caustic   Xanthate   Water

Heavy metal removal by xanthate takes place by an ion-exchange reaction much like hydroxide precipitation. A report by Bricka and Hill (1989) examines solidification of both cellulose and starch xanthate sludges. The amounts of metal loaded onto the cellulose xanthate were 19.67 mg Cr/g, 19.88 mg Cd/g, and 0.6367 mg Hg/g. Starch xanthate sludges adsorbed 17.57, 33.27, and 1.1487 mg/g of Cr, Cd, and Hg, respectively.

Flynn, Carnahan, and Lindstrom (1980) studied the sorptive capabilities of xanthated sawdust. Aside from reactions with xanthate, some of the sorptive capacity of xanthated sawdust is due to entrained carbonate and hydroxide and alkalized cellulose and lignin. The adsorption capacity varied randomly due to variation in the particle porosity and size. The capacity of the xanthate also decreased with age (18 percent in 47 days) due to decomposition and air oxidation of sulfur-containing species. Although xanthates are quite selective for heavy metals, high concentrations of light metals decrease the heavy metal capacity significantly. Column experiments exhibited the following order of metal selectivity: Na $<<$ Ca=Mg=Mn $<$ Zn $<$ Ni $<$ Cd $<$ Pb=Cu. The adsorption capacity for cadmium batch testing ranged from 0.28-0.38 meq/g (15.7-21.4 mg/g). For Mn^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Zn^{2+}, Hg^{2+}, and Pb^{2+}, the adsorption capacity ranged from 0.3 to 0.4 meq/g.

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Other literature looked specifically at starch xanthates. Two articles (Tare, Chaudhari, and Jawed 1992; Jawed and Tare 1991) compared soluble (SSX) and insoluble starch xanthate (ISX). Both forms are produced from corn starch, but an extra cross-linking step was employed to make the xanthate insoluble. The reports note that the experiments with ISX are classified as sorption since solute molecules from an aqueous phase are transferred to an already existing solid phase. Soluble xanthate reactions are considered precipitation, rather than adsorption, as the solid phase is formed after the interaction between xanthate and the metal ions. The article showed that ISX is better than SSX in terms of metal-removal capacity, reliability, and ease of operation. However, SSX is much less expensive. The cost data presented report that ISX costs $7.61/100 g ISX and requires 90-110 hr for preparation, and SSX costs only $0.10/100 g viscose and takes only 3-4 hr to make.

A preliminary cost estimate from Wing and Rayford (1977) reports only $0.30/lb for ISX production. This article presents several case studies in which ISX was used to remove heavy metals from plating rinse waters. Also, ISX was shown to be effective as a precoat to a filter. Several other case studies are presented by Wing (1983) showing ISX effectiveness.

Zeolites

A study by Leppert (1990) reports that zeolites, clinoptilolite in particular, demonstrate strong affinity for lead and other heavy metals. Zeolites are naturally occurring silicate minerals that can also be produced synthetically. Clinoptilolite is probably the most abundant of more than 40 natural zeolite species (Ming and Dixon 1987). Deposits of this mineral occur in abundance throughout the western United States, making it readily available and inexpensive. The adsorption properties of zeolites result from their ion-exchange capabilities. The three-dimensional structure of zeolite possesses large channels containing negatively charged sites resulting from Al^{3+} replacement of Si^{4+} in the tetrahedra. Sodium, calcium, potassium, and other positively charged exchangeable ions occupy the channels within the structure and can be replaced with heavy metals. Table 5 presents some of the reported adsorption capacities for zeolite.

Table 5
Reported Adsorption Capacities for Zeolite

Material	Source	mg Cd/g	mg Cr (III)/g	mg Cr (VI)/g	mg Hg/g	mg Pb/g
Zeolite	Leppert 1990	84.3	26.0		150.4	155.4
CETYL-amended zeolite	Santiago et al. 1992			0.65		
EHDDMA-amended zeolite	Santiago et al. 1992			0.42		

Research has been conducted at several Superfund sites showing the effectiveness of clinoptilolite. At the Bunker Hill Superfund site, clinoptilolite adsorbed large amounts of lead even when competing ions were present. Laboratory testing was conducted in which spiked water samples containing 750 ppb lead were treated in zeolite ion-exchange columns. The effluent concentration ranged from 12 to 27 ppb lead. The overall adsorption capacity for zeolites is reported to vary for different zeolites, but tends to be around 1.5 meq/g (155.4 mg Pb/g zeolite) (Leppert 1990). A preliminary report by Desborough (1995) states that clinoptilolite-rich rocks (CRRs) have preferential affinity for Pb over other cations. An investigation was done on the leachability of Pb from CRRs to determine if CRRs could be used for Pb removal from wastewater and subsequently disposed of as nonhazardous waste. The CRRs tested showed no significant leaching of Pb, suggesting that Pb-contaminated CRRs could be disposed of without leaching of Pb. Further research on CRRs by Desborough and Frishman (1995) demonstrated that the leachability of adsorbed Pb, Cu, and Zn varies depending on the local origin of the CRR. For example, South Dakota CRR showed much greater retention characteristics than other CRRs. Thus, CRRs and other types of zeolite appear to be an effective and inexpensive alternative for the adsorption of heavy metals.

A report by Santiago et al. (1992) reports unaltered zeolite to be ineffective for hexavalent chromium removal and investigates the use of zeolites tailored with the organic cations Ethylhexadecyldimethylammonium (EHDDMA) and Cetylpyridinium (CETYL). Tailoring of the zeolite results in a positively charged species, allowing for the mechanism of anion exchange in which CrO_4^{2-} attaches to the tailored zeolite. Results showed the CETYL-amended zeolite to perform better than that with EHDDMA. Reported adsorption capacities were 0.65 mg Cr/g zeolite with CETYL and 0.42 mg Cr/g zeolite with EHDDMA.

Clay

The adsorption capabilities of clay also result from a net negative charge on the structure of fine-grain silicate minerals. This negative charge is neutralized by the adsorption of positively charged species, giving clay the ability to attract and hold cations such as heavy metals. The large surface area of clays (up to 800 m²/g) also contributes to the high-adsorption capacity (Cadena, Rizvi, and Peters 1990). There are three basic classes of clays: kaolinite, micas (such as illite), and smectites (for example, montmorillonite). Of the three species, kaolinite clays have the largest crystals, the lowest surface area, and the lowest cation-exchange capacity. Montmorillonite clays have the smallest crystals, the largest surface area, and the highest cation-exchange capacity. Thus montmorillonite clays would be expected to have the highest sorptive capacity. A study by Griffin et al. (1977) found the removal of mercury by montmorillonite to be five times greater than that by kaolinite.

Viraraghaven and Kapoor (1994) note that the abundance and low cost of bentonite make it a strong candidate as an adsorbent for the removal of heavy metals from wastewaters. The composition of bentonite varies, though it consists mainly of montmorillonite. In batch adsorption studies on bentonite by Farrah and Pickering (1978) with an initial concentration of 1 mg/L Hg, only 34.2 percent of the mercury was adsorbed by the bentonite. The adsorption of mercury was found to be endothermic. A study by Khan, Riaz-ur-Rehman, and Khan (1995) found the adsorption of Ag^+ and Cr^{3+} to be exothermic and adsorption of Cr^{6+} to be endothermic. The amphoteric oxides of bentonite favor anion adsorption at low pH and cation adsorption at higher pH. Newton, Ellis, and Paulsen (1976) found mercury adsorption by bentonite to be greatest at pH 4.5-5.5. Some of the reported capacities for clay are shown in Table 6.

Table 6 Reported Adsorption Capacities for Clays						
Material	Source	mg Cd/g	mg Cr (III)/g	mg Cr (VI)/g	mg Hg/g	mg Pb/g
Bentonite	Khan, Riaz-ur-Rehman, and Khan 1995			0.512		
Bentonite	Cadena, Rizvi, and Peters 1990			55		6
Tailored bentonite	Cadena, Rizvi, and Peters 1990			57		58
Acid-treated bentonite	Pradas et al. 1994	4.11				
Heat-treated bentonite	Pradas et al. 1994	16.50				
China clay	Yadava, Tyagi, and Singh 1991					0.289
Wollastonite	Yadava, Tyagi, and Singh 1991					0.217
Wollastonite-fly ash mixture	Panday, Prasad, and Singh 1984			0.271		

Another type of clay, wollastonite, was used in batch experiments by Sharma et al. (1990). This clay showed a Langmuir maximum adsorption capacity, q_{max} of 6.52 mg/g for nickel. A study by Sharma (1995) used wollastonite for cadmium adsorption. The study suggests that between pH 2.0 and 4.0, ion exchange takes place at planar sites on the clay particle, and at pH > 4.5, adsorption takes place at edge sites as shown below.

$$\textit{Planar site interaction: } Cd^{2+} + CaSiO_3 \Leftrightarrow Ca^{2+} + CdSiO_3$$

$$\textit{Possible edge site interactions: } SOH + Cd^{2+} \Leftrightarrow SO^-Cd^{2+} + H^+$$
$$SO^- + Cd^{2+} \Leftrightarrow SO^-Cd^{2+}$$
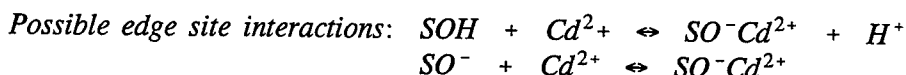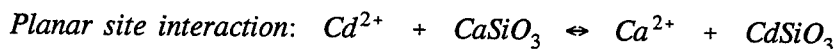
Because of the different reactions taking place at the two sites, the variation with pH is different as well. Between pH 2.0 and 4.0, pH does not significantly affect uptake, whereas above pH 4.5 adsorption increases with pH, with maximum uptake occurring around pH 9.5. The rate-limiting step for adsorption of cadmium onto wollastonite was attributed mostly to intraparticle diffusion, and adsorption was exothermic.

Another study investigated adsorption of lead onto wollastonite and china clay (Yadava, Tyagi, and Singh 1991). The wollastonite contained 48.52 percent SiO_2 and 48.48 percent CaO, and the china clay contained 46.22 percent SiO_2 and 38.40 percent Al_2O_3. Equilibrium times were found to be 90 min for the china clay and 120 min for wollastonite. Overall, the china clay showed a greater capacity to remove metals than wollastonite. For both clays the rate-limiting step appeared to be pore diffusion, and the process was exothermic.

Panday, Prasad, and Singh (1984) studied the adsorption of hexavalent chromium onto a 1:1 mixture of fly ash and wollastonite. The adsorption capacity of the mixture is the result of oxides in the fly ash and wollastonite. The wollastonite used was 48.52 percent SiO_2 and 48.48 percent CaO. Fly ash was 56.04 percent SiO_2 and 25.90 percent Al_2O_3. Since hexavalent chromium is adsorbed in the form of $HCrO_4^-$, a positive charge is needed to attract the metal ions. Most of the adsorption is attributed to alumina and CaO since above pH 2.5, SiO_2 possesses a negative charge. Removal of anions may be more effective at low pH. Adsorption of Cr (VI) onto the mixture was found to be exothermic, decreasing as temperature increases.

It is possible that clay could be modified to improve its sorption capacity. Cadena, Rizvi, and Peters (1990) used bentonite, tailored by replacing the natural exchangeable cations in the clay by the organophilic cation tetramethylammonium ion (TMA^+) to adsorb lead and hexavalent chromium. The TMA^+ makes the clay surface more hydrophobic, improving its adsorption capacity. Tailoring agents also affect the interlamellar spacing of the clay platelets. Natural bentonite gave adsorption capacities of approximately 6 mg Pb^{2+}/g and 55 mg Cr^{6+}/g, and tailored bentonite adsorbed approximately 58 mg Pb^{2+}/g and 57 mg Cr^{6+}/g. The tailoring significantly improved the capacity for lead, but only minimally increased hexavalent chromium adsorption. Other less complex treatments include heat treatments and acid treatments. Acid treatment is likely to decrease adsorption capacity because the acid neutralizes the negative charge of the clay surface or even generates a positive charge. Heat treatment, on the other hand, should improve adsorption capacity due to moisture loss, mostly from the interlayer, allowing the metal ions more adsorption sites. Pradas et al. (1994) examined both

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modifications with natural bentonite, adsorbing cadmium and zinc. Results showed that the acid-treatment decreased the adsorption capacity, with the 0.5 M sulfuric acid-treated sample adsorbing 4.91 mg Cd/g. The heat treatment did improve the adsorption capacity, with the 200 °C heated bentonite adsorbing 16.50 mg Cd/g. The adsorption of zinc was not as strong as that for cadmium.

Whether tailored or in their natural state, due to their abundance, low cost, and adsorption capabilities, montmorillonite clays are potentially a promising alternative to activated carbon for the adsorption of heavy metals. However, it is important to note that the low permeability of clays could be problematic for use in columns.

Fly Ash

Grover and Narayanaswamy (1982) observed that fly ash, a waste product from thermal power plants, has some adsorption capabilities for hexavalent chromium. Fly ash consists of carbon and oxides of silica, alumina, and iron. An adsorption capacity of 4.250 mg/g was observed at pH 2.0. Kapoor and Viraraghavan (1996) note that the properties of fly ash are extremely variable and the adsorption capacity varies with the lime content. Fly ash could easily be solidified after the metals are adsorbed since it contains pozzolanic particles that react with lime in the presence of water, forming cementitious calcium-silicate hydrates. It is important to note that fly ash may contain heavy metals and trace amounts of radioactive elements, although levels are such that fly ash not by definition classified as hazardous waste. The possible effects of these contaminants on the sorption process and at disposal should be considered and evaluated.

Peat Moss

Peat moss is a relatively inexpensive and widely available sorbent that has adsorption capabilities for a variety of metals. Reported adsorption capacities are given in Table 7. The Mineral Resources Institute Technical Report Series (1985) estimates that there are 7.3 billion kilograms of peat available on a dry basis in Alabama alone. Peat is mined and processed for fuel in Ireland and northern Europe and as a soil conditioner in the United States. Sphagnum moss peat is commercially available and has an average cost for a standard pack (50 L) of $7.75 (Ho, Wase, and Forster 1994). Peat is a rather complex soil material with organic matter in various stages of decomposition, containing lignin and cellulose as major constituents. These constituents, especially lignin, contain polar functional groups, such as alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers that can be involved in chemical bonding. Because of this, peat moss tends to have a high cation-exchange capacity and is an effective adsorbent for the removal of heavy metals. A study by Sharma and Forster (1993) indicates peat moss to be about six times more

Table 7
Reported Adsorption Capacities for Peat Moss

Material	Source	mg Cd/g	mg Cr (III)/g	mg Cr (VI)/g	mg Hg/g	mg Pb/g
Irish sphagnum moss peat	Sharma and Forster 1993			119.0		
Irish sphagnum moss peat	Sharma and Forster 1995			43.9		
Modified peat	Kertman, Kertman, and Chibrikova 1993		76			230
Sphagnum moss peat	McLelland and Rock 1988	5.8	29			40
Rastunsuo peat	Tummavuori and Aho 1980a		4.63		16.2	
Rastunsuo peat	Tummavuori and Aho 1980b	5.058				20.038
Milorganite (H_2O)	Masri, Reuter, and Friedman 1974	35.5	35.9		460	95.3

effective than coconut-shell-based carbon for Cr (VI) removal. Peat collects metals to such an extent that some bogs are actually mined for their metals content in other countries. For example, in Finland, peat bogs are sampled on a routine basis in prospecting for metal deposits (Mineral Resources Institute Technical Report Series 1985). The main chemical constituents of peat are humic and fulvic acids, which have high levels of anionic substituent groups. Huang and Yang (1995) studied the copper adsorption capabilities of humic- and fulvic acid-coated kaolin. Their study showed that the abundant carboxyl and phenolic groups in fulvic acid results in a greater capacity to adsorb protons. Peat also has a large specific-surface area (>200 m^2/g) and is highly porous (95 percent) (McLellan and Rock 1988).

Some research has been done to determine the mechanism of metal adsorption onto peat. Chen, Gosset, and Thévenot (1990) showed that the adsorption of Cu onto eutrophic and oligotrophic peat is due to both complexation and ion exchange. The study indicates that between Cu concentrations of 0 and 15 mmol/L, the cation-exchange sites were saturated at 308 and 101 mmol/kg (dry weight) for eutrophic and oligotrophic peat, respectively. The complexation sites, however, did not become saturated and attained up to 74 and 119 mmol Cu/kg (dry weight). The values for ion exchange and complexation are dependent on the type of peat as well as other conditions. For example, when the solution concentration is high, complexation becomes about 10 times as important as ion exchange (Chen, Gosset, and Thévenot 1990). Sharma and Forster (1993) also found both ion exchange and complexation to play a role in the adsorption mechanism of hexavalent chromium. Sharma and Forster (1995) propose that while there can be appreciable adsorption of hexavalent chromium at low pH, the most likely mechanism is

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reduction to trivalent chromium, then combination with phenoxyl and carboxyl groups, forming chromium humic acid complexes. Ho, Wase, and Forster (1996) determined that for Cu and Ni adsorption, both mass transfer and pore diffusion are important to adsorption rates.

Adsorption capacity and values for ion exchange and complexation are dependent on conditions such as pH, ionic strength, peat type, and concentration. There are many different types of peat available with varying chemical and physical properties. Significant differences in the sorption capabilities of peat suggest a great deal of variability in the composition of different peats. Peat can be eutrophic or oligotrophic. Eutrophic peat is formed in alluvial plains supplied by well-mineralized water and is poor in cellulose, but rich in humic substances. Oligotrophic peat is the sphagnum type, which is more acidic and contains more organic matter. Both peats contain about 75-85 percent humic acid and 15-25 percent fulvic acid. As shown by Chen, Gosset, and Thévenot (1990), the complexation and ion-exchange capabilities vary between the two peats. Peat type and composition vary for different locations. For example, Tummavuori and Aho (1980a) used two different peats for metal sorption: one from Rastunsuo and a peat from Jouttenisenneva. Significant differences were found in the adsorption capabilities of the two peats.

Metal removal by peat is largely affected by pH. Most researchers found that as pH increases, the capacity of peat to adsorb metal cations increases (Chen, Gosset, and Thévenot 1990; Sharma and Forster 1993; Ho, Wase, and Forster 1994). Ho, Wase, and Forster (1994) derived an expression to calculate the removal of copper by peat based on initial pH and initial Cu concentration and found the maximum adsorption of Cu to occur at pH 5.0. Sharma and Forster (1993) found Cr (VI) removal to be favored by lower pH values with the best results occurring at pH 1.5-3.0. However, at this low pH, conversion to Cr (III), which is poorly adsorbed at low pH, occurs. Furthermore, Sharma and Forster (1993) showed temperature to be a factor, as increasing the temperature from 25 °C to 40 °C nearly doubled the adsorption capacity of hexavalent chromium onto Irish moss peat.

As with many other sorbents, peat can be modified to improve its sorption capacity. Kertman, Kertman, and Chibrikova (1993) investigated modified peat to adsorb a variety of heavy metals. The type of modification was not reported, but they state that the modification involved fairly cheap and readily available reagents; it increased the number of ionogenic groups by the formation of sulfo groups. The modified peat exhibited a capacity of 90-230 mg Pb/g, which means 1,000 kg modified peat could sorb approximately 90-230 kg of lead. The modified peat was also tested in columns using storage-battery plant effluent (100 mg/L). The 25 g peat column was still effective after 10 L effluent had passed through the column. Testing with other metals showed exchange capacities of 104 mg Zn/g, 114 mg Cu/g, 76 mg Cr/g, and 132 mg Ni/g. Acid treatment can also improve the adsorption capacity of peat as shown by Viraraghavan and Rao (1993). Acid-treated peat was shown to have a higher adsorption capacity for cadmium and chromium than raw horticultural sphagnum peat.

The results from many of the studies for Cd, Cr, Hg, and Pb are shown in Table 7. However, it is important to mention some of the studies with other metals. Ho, Wase, and Forster (1994) examined copper removal with sphagnum moss peat. The maximum adsorption capacity demonstrated was 16.4 mg Cu/g peat. The peat demonstrated rapid initial uptake, with most removal being achieved within 30-40 min and equilibrium reached after 108 min. Also, Ho, Wase, and Forster (1996) tested peat for its ability to adsorb Cu and Ni ions. Batch testing with 100-mg/L solutions demonstrated adsorption capacities of 12.29 mg Cu/g and 7.15 mg Ni/g. Viraraghaven and Dronamraju (1993) showed that at pH 4.55, nearly all metals found in industrial wastewater can be adsorbed by peat.

McLellan and Rock (1988) investigated peat as an adsorbent for metals from landfill leachate. Batch testing at 500 mg/L gave the following adsorption capacities: 5.8 mg Cd/g, 29 mg Cr/g, 23 mg Cu/g, and 40 mg Pb/g. These results were not, however, duplicated in column testing. When desorption experiments were conducted, nearly 50 percent of the sorbed metals were removed. The study concluded that peat could be better used as a pretreatment since, by itself, it is incapable of removing sufficient metals for direct discharge. Previous experiments by Rock et al. (1985) confirmed the suitability of peat as a pretreatment for landfill leachate.

Kinetics are also favorable for peat adsorption as shown by Ho, Wase, and Forster (1994). Most of the copper removal by sphagnum moss peat was achieved within 30-40 min, and equilibrium was reached after 108 min. Sharma and Forster (1993) found regeneration of peat uneconomical since little desorption occurs in low-molarity caustic solutions and in high-molarity caustic solutions, the peat becomes unstable. Overall, however, low cost, availability, and high-adsorption capacity for a variety of metals make peat a promising material for adsorption of heavy metals.

Another highly organic material found to have high-adsorption capacity for heavy metals is Milorganite, activated sewage sludge residue. Masri, Reuter, and Friedman (1974) experimented with Milorganite and found the adsorption capacities reported in Table 4.

Dead Biomass

According to Matis and Zouboulis (1994), sorption of heavy metal ions such as Cd^{2+} by dead biomass has been demonstrated. Dead cells accumulate heavy metals to an equal or greater extent than living cells. The predominant mechanisms include binding to the cell surface, extracellular complexing, and subsequent accumulation. The bacterial cell surfaces are known to be anionic, due to the presence of ionized groups in the cell wall polymers, causing the cell to attract metal cations. Jansson-Charrier et al. (1996) report that the cell wall of fungal biomasses consists of glycoproteins, glucans, and chitin or chitosan, which contain amino functions useful in metal-ion removal. Large

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quantities of waste microbial biomass are produced in many industries such as citric acid biosynthesis and penicillin production, making it an economical metal-adsorbent material. It is estimated that fermentation industries produce some 790,000 tonnes of microbial waste each year, with 41,000 tonnes resulting from citric acid production by *Aspergillus niger* (Berkeley 1979). The use of dead rather than live biomass eliminates the problems of waste toxicity and nutrient requirements. Table 8 shows some of the adsorption capacities reported in the literature.

Table 8
Reported Adsorption Capacities for Dead Biomass

Material	Source	mg Cd/g	mg Cr (III)/g	mg Cr (VI)/g	mg Hg/g	mg Pb/g
Streptomyces griseus	Matis and Zouboulis 1994	28				
Penicillium chrysogenum	Niu, Xu, and Wang 1993					116
Chlorella minutissima	Roy, Greenlaw, and Shane 1993	11.14		162.23		9.74
Rice hulls	Roy, Greenlaw, and Shane 1993	21.36		164.31		11.40

In a study by Matis and Zouboulis (1994), two bacterial strains, *Streptomyces griseus* and *S. clavuligerus*, were used for the biosorption of cadmium. Maximum adsorption appeared to be approximately 28 mg Cd/g biomass. In other experiments by Niu, Xu, and Wang (1993), dead *Penicillium chrysogenum* biomass was used for removal of lead. This species demonstrated uptake of 116 mg Pb/g biomass. Other species of biomass (*Bacullus mycoide, Penicillium sp., and S. longwoodensis*) were employed in the study but were not as effective as the *Penicillium* biomass. Roy, Greenlaw, and Shane (1993) investigated heavy metal uptake by biomasses of green algae, *Chlorella minutissima*, and rice hulls. Rice hulls have a structure similar to that of the green algae and are a by-product from the commercial harvesting of rice. Algal uptake was 11.14 mg Cd/g and 9.74 mg Pb/g cell mass. Experimental results showed rice hulls to possess adsorption capacities similar to that of algae for As, Cr (VI), and Pb, but for Cd adsorption, the capacity of rice hulls was twice as high as that of algae (21.36 mg Cd/g).

Seaweed and Alginate

Seaweed is an abundant source of metal-sorbing biomass. Some seaweeds have been identified for their ion-exchange properties associated with their polysaccharide content. These properties are particularly pronounced in brown algae. The polysaccharide content of the brown marine algae

Ascophyllum nodosum consists of 25 percent L-fucose, 26 percent D-xylose, 19 percent D-glucuronic acid, 13 percent sulfate groups, and 12 percent proteins, classifying the mixture as alginates or glucuronoxylofucanprotein (Holan, Volesky, and Prasetyo 1993). This composition varies depending on the age of the algae and the season. Experiments by Volesky and Prasetyo (1994) used *A. nodosum* in sorption columns to remove cadmium. The procedure reduced 10 mg/L of cadmium to 1.5-ppb levels, representing 99.985-percent removal. The maximum adsorption capacity for the seaweed was shown to be approximately 67 mg Cd/g seaweed. In an experiment by Wilson and Edyvean (1994), the brown seaweeds *Fucus serratus* and *Laminaria digitata* outperformed other biological materials such as fungi, green seaweed, and unicellular green algae for cadmium and mercury removal. The green seaweed *Ulva lactuca* was just slightly less effective than the two brown seaweeds.

Although seaweed has demonstrated extremely high-sorption capacities, Holan, Volesky, and Prasetyo (1993) note that the biomass has a tendency to disintegrate and swell, which does not allow it to be effectively used in columns. Modifications, such as cross-linking, can improve the stability and mechanical properties of the algae. Holan et al. investigated several types of cross-linking of *A. nodosum* for cadmium uptake. The best cross-linking results were obtained using divinyl sulfone and formaldehyde under acidic conditions. While the cross-linking slightly reduced capacity, the procedure reduced swelling so that the material would be amenable to column adsorption. The maximum capacity of *A. nodosum* was found to be 215 mg Cd/g raw seaweed and 149 mg Cd/g formaldehyde-cross-linked seaweed. *Asocphyllum nodosum* was more effective than the other seaweeds tested, *Sargassum natans* (135 mg Cd/g) and *Fucus vesiculosus* (73 mg Cd/g).

Leusch, Holan, and Volesky (1995) also investigated different modifications of *A. nodosum* and *Sargassum fluitans*. The modifications included formaldehyde cross-linking (FA), glutaraldehyde cross-linking (GA), and polyethylenimine embedding (PEI). As shown in Table 9, *S. fluitans* is generally more effective than *A. nodosum*, although the most effective modification varies for each metal. Besides adsorption capacity, sorbent stability should also be considered. *Asocphyllum nodosum* is more easily modified, and the modification of *A. nodosum* exhibited a greater decrease in swelling, with glutaraldehyde cross-linking being most effective. Some modifications to *S. fluitans* actually increased swelling. The effect of particle size was also determined to be a factor, as larger particles were shown to outperform the smaller particles.

A material derived from the processing of brown seaweed is algin, a high-molecular-weight polymer. Alginate, a polysaccharide-based biosorbent is formed from algin by replacing protons in the carboxylic groups with metal ions. In the adsorption process, it appears that heavy metal ions exchange with calcium ions to form a metal alginate. One study shows that 23.5 mg/L Ca-alginate beads adsorbed 47 g Cd/dm^3 (Apel and Torma 1993). This

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Table 9 Langmuir q_{max} for Uptake of Five Metals by Modified Biomass of Marine Algae					
Sorbent Type	Cd, mg/g	Cu, mg/g	Ni, mg/g	Pb, mg/g	Zn, mg/g
S. fluitans, PEI	109	129	75	304	49
S. fluitans, FA	107	114	117	378	63
S. fluitans, GA	120	100	80	344	65
A. nodosum, PEI	98	87	113	244	58
A. nodosum, FA	96	91	84	285	57
A. nodosum, GA	52	54	54	169	24
Note: Leusch, Holan, and Volesky 1995.					

equates to 2 mg Cd/g Ca-alginate. Jang, Nguyen, Geesy (1995) report the theoretical maximum binding capacity of sodium alginate to be 138.3 mg Cu/g, and a capacity of 107 mg Cu/g was determined experimentally. Another study (Sag et al. 1995) compared the copper adsorption of Ca-alginate beads with that of immobilized *Zoogloea ramigera* in packed columns. *Zoogloea ramigera* is an activated-sludge bacterium that produces extracellular polysaccharides. The adsorption onto the Ca-alginate beads was more rapid than onto *Z. ramigera*, but *Z. ramigera* demonstrated higher sorptive capacity. In a second part of the study, *Z. ramigera* was immobilized onto the Ca-alginate beads for higher capacity. Ca-alginate immobilized *Z. ramigera* was also examined by Kuhn and Pfister (1989). The addition of *Z. ramigera* greatly increased the capacity of the alginate beads. The material adsorbed a variety of metals from both dilute and concentrated solutions. The method of immobilizing cells onto Ca-alginate beads provides an effective adsorbent material amenable to continuous flow column adsorption.

Bone Gelatin Beads

Bone gelatin beads have been studied as a heavy metal sorbent although little information is available on them. An experiment by Petersen et al. (1991) indicates that there is a size change associated with metal adsorption onto modified bone gelatin beads. The diameter of the bead was found to be a function of the solution pH and the ion concentration in the solution. This size change could be advantageous in the design of separators for the recovery and concentration of contaminated waters. The study suggests that a fluidized bed separator can be operated such that natural segregation of loaded beads occurs. The report states that significant quantities of heavy metals will adsorb onto the beads, measuring 35 mg Cu/g bead at pH 5.5.

Crown Ethers

Several studies have been conducted using crown ethers to remove heavy metals from solution. Crown ethers have a ring formation with a negative charge constituting the center of the ring, which attracts metal cations. However, it is important that the metal radii be just the right size to fit in the ring cavity, making crown ethers highly selective. Many crown ethers present a variety of problems. For example, most (mono) crown ethers are highly soluble in water, and it is time-consuming to prepare polycrown ethers that are not soluble. Also, some crown ether precipitates have been shown to undergo hydrolysis at pH > 2.

Ion et al. (1994) used dibenzo-18-crown-6-phosphomolybdic acid (PMA)/ polystyrene supported on glass balls for adsorption of lead, silver, and cadmium. This crown ether did not hydrolyze at pH > 7 and demonstrated adsorption of 14.60 mg Pb/g and 0.62 mg Cd/g. Although crown ethers have shown some effectiveness in complexing heavy metal ions, their high cost of preparation suggests their use is not economically feasible except for cases in which selectivity is important.

Leaf Mold

In a study by Sharma and Forster (1994), leaf mold, which is a natural waste by-product found in deciduous woodland areas, was used for the removal of hexavalent chromium ions from aqueous solution. The study found a maximum removal capacity of 43.0 mg Cr (VI)/g at pH 2.0. However, removal at low pH is apparently not all due to adsorption, as some of the chromium is reduced to the trivalent form and therefore not detected. At pH values >3.0, hexavalent chromium was not reduced, and the adsorption capacity was 8.9 mg/g. Part of the adsorption capabilities of leaf mold are attributed to oxo groups (C_xO and C_xO_2) on the sorbent surface:

$$C_xO \ + \ 2H_2O \ + \ HCrO_4^- \ \Leftrightarrow \ C_xO_2H_3O_3Cr^+ \ 2OH^-$$
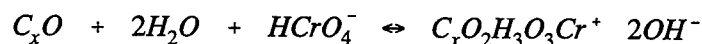
The adsorption process causes an increase in pH since hydroxide ions are released. Hexavalent chromium removal is more efficient at lower pH, as hydroxide ions are in competition with the bichromate and dichromate ions. Chromate ions do not participate in the adsorption reaction. The adsorption capacity and kinetics of leaf mold adsorption are inferior to other sorbents such as activated carbon and peat moss, but the availability of the material could be important to wastewater treatment in developing countries.

Moss

Experimental results from Low and Lee (1991) indicate that the moss *Calymperes delessertii* is an efficient sorbent for cadmium. The cost of this moss is minimal, and generally no pretreatment is required. The maximum adsorption capacity is approximately 46.65 mg Cd/g. Further studies by Low et al. (1993) examined copper adsorption by dye-coated moss. The dyes tested were Reactive Yellow 2 and Reactive Orange 16. The capacities for the dye-coated moss were higher than for untreated moss. This is because the sulphonic acid groups on the dyes have greater binding capacity than the unesterified polyuronic acids on the untreated moss. The Reactive Orange dye was slightly more effective than the Reactive Yellow, and no leaching of the dye was observed during the experiment. The Reactive Orange dye-coated moss demonstrated adsorption of 18.68 mg Cu/g.

Iron-Oxide-Coated Sand

A study by Bailey, Bennett, and Benjamin (1992) investigated the adsorptive capacity of iron-oxide-coated sand surfaces. Ferrihydrite, an amorphous iron oxide, is formed in conventional waste treatment by precipitation of iron salts, which are added to coagulate metal precipitates. During this process, some metals are removed by adsorption onto the ferrihydrite. Iron oxide is an excellent regenerable adsorbent and can be used in a column when applied as a coating to sand surfaces. The sand is coated by adding ferric salt and base and heating. Coating sand with iron salts minimizes the total amount of iron oxide used and reduces the amount of sludge produced in the system, thereby minimizing cost. Ferric chloride showed better results than ferric nitrate and is quite inexpensive since it is a by-product of many industries, such as steel pickling. Furthermore, depending on the solution pH, the media can be made to adsorb either cationic or anionic metals. This is important since Cr(VI) is typically in the anionic form. The study indicates greater than 99-percent removal of Cr(VI) from a 20-mg/L solution was consistently achieved.

Modified Wool

Masri and Friedman (1974) have investigated the potential of wool for removing metal ions from aqueous media. In their study, raw wool is modified by the addition of various functional groups such as sulfhydryl to increase the adsorption capacity. It is suggested that the sulfhydryl groups bind with the metal ions to form metal mercaptides. Numerous metal ions were tested, including Hg, Ag, Au, Cu, U, Sb, Sn, Pb, Pt, Zn, Bi, Cd, Pd, Fe, Ce, Cr, Ni, Co, Th, As, Zr, Tl, and Ti. Some of the results are given in Table 10.

Table 10
Metal Ion Uptake (24 hr) by Raw Wool and Modified Wools[a] (in mmole metal/g wool and (mg/g))

Metal Ion	Native	WSH	2-PEW	NPEW	NTW	ATW
Hg(II)	2.25(451)	3.15(632)	2.49(499)	2.10(421)	1.92(385)	1.94(389)
Pb(II)	0.58(120)	0.65(135)	0.20(41)	0.23(48)	0.32(66)	0.14(29)
Cd(II)	0.30(34)	0.77(87)	0.72[b](81)	0.25(28)	0.01(1.1)	0.05(5.6)
Cr(III)	0.11(5.7)	0.18(9.4)	0.33(17)	N/A	N/A	N/A

[a] Modified wools are reduced (WSH), S-β-(2-Pyridylethyl) wool (2-PEW), S-(p-nitrophenylethyl) wool (NPEW), 3-nitrotyrosyl wool (NTW), and 3-aminotyrosyl wool (ATW).
[b] 1-hr value.

Among the different modifications, the maximum adsorption capacities reported for Hg, Pb, Cd, and Cr are 632, 135, 87, and 17 mg/g, respectively, which are some of the highest capacities reported for these metals. Only chitosan demonstrated higher capacities for Hg. High adsorption capacity and relatively low cost make wool a viable material for heavy metal adsorption. While modifications can improve the capacity of the wool, the native (raw) wool alone is still quite efficient. Also, it is important to note that the majority of the adsorption takes place in the first hour. Rapid adsorption is especially important in the case of column operation. Freeland, Hoskinson, and Mayfield (1974) studied wool modified with polethylenimine for mercury adsorption. A capacity of 330.97 mg Hg/g was achieved for the PEI-wool.

Modified Cotton

The removal of mercury using modified cotton has been studied by Roberts and Rowland (1973). Cotton fibers are 90-percent cellulose. In this study, cotton is chemically modified with four amine units including cross-linked polyethylenimine (CPEI), polyethylenimine (PEI), O-(2-diethylamino)ethyl (DEAE), and O-(2-aminoethyl) (AE). CPEI cotton displayed the best results when cottons were compared on a weight-to-weight basis, with adsorption varying from 1,000 to 60 mg mercury sorbed per gram of cotton. The order of effectiveness, which appears to be proportional to the amine content, is CPEI cellulose > AE cellulose > PEI cellulose > DEAE cellulose. Unmodified cellulose was ineffective. Although cotton in chopped form performed better than cotton fabric, the fabric could be more suitable for continuous, automated operations.

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Miscellaneous Sorbents

Other miscellaneous materials have been studied less extensively as low-cost sorbents. Limited data are available for rice husks and bambara nut husks (Said, Shalmor, and Egila 1993). Masri, Reuter, and Friedman (1974) present mercury adsorption capacities for several natural materials although no other information is given as to the sorption mechanisms of these materials or their chemical constituents. Shukla and Sakhardande (1992) also report adsorption capacities for several cellulosic materials dyed with C. I. Reagent Orange, a reactive dye of the monochlorotriazine type. No insight is given as to how the dye improves metal sorption. The adsorption capacities of some of these materials are given in Table 11.

Table 11
Reported Adsorption Capacities for Several Miscellaneous Sorbents

Material	Source	mg Hg/g	mg Pb/g
Orange peel (white inner skin)	Masri, Reuter, and Friedman 1974	125	
Orange peel (outer skin)	Masri, Reuter, and Friedman 1974	275	
Dry pine needles	Masri, Reuter, and Freidman 1974	175	
Senna leaves	Masri, Reuter, and Friedman 1974	250	
Dry redwood leaves	Masri, Reuter, and Friedman 1974	175	
Undyed bamboo pulp	Shukla and Sakhardande 1992	9.2	8.4
Dyed bamboo pulp (C. I. Reactive Orange 13)	Shukla and Sakhardande 1992	15.6	15.0
Undyed jute	Shukla and Sakhardande 1992	7.6	7.9
Dyed jute (C. I. Reactive Orange 13)	Shukla and Sakhardande 1992	13.7	14.1
Undyed sawdust	Shukla and Sakhardande 1992	8.5	7.3
Dyed sawdust (C. I. Reactive Orange 13)	Shukla and Sakhardande 1992	18.0	24.0

3 Conclusions

Inexpensive, effective, readily available materials exist that can be used in place of activated carbon or ion-exchange resins for the removal of heavy metals from solution. A wide range of low-cost sorbents have been presented although the list is by no means comprehensive. Due to inconsistencies in data presentation, it is difficult to make conclusive comparisons of the sorbents. However, Table 12 presents a summary of the materials demonstrating the highest adsorption capacities reported in the literature. Cost and availability were also considered in selecting materials for further testing. Very little cost information was given in the literature, however, and a somewhat subjective judgment regarding both cost and availability was necessary. It was assumed that materials requiring modification would ultimately be more expensive than those that could be used in an unmodified form.

On the basis of these considerations, and previous experience with certain of the sorbents, 11 sorbents were selected for testing in batch studies for adsorption of Cd, Cr, Pb, and Hg. They were bark, clay, chitosan, crown ether, cellulose xanthate, ISX, peat moss, seaweed, zeolite, corn cob, and lignin. Although corn cob was not mentioned in the literature, its high porosity would suggest potential as a sorbent. Of the sorbents selected, the best will be further evaluated in column studies to determine kinetic, hydraulic, and engineering properties.

	Table 12 Summary Table of Maximum Reported Adsorption Capacities in the Literature					
Sorbent	Source (Cd, Cr(III), Cr(VI), Hg, Pb)	mg Cd/g	mg Cr (III)/g	mg Cr (VI)/g	mg Hg/g	mg Pb/g
Bark	Randall et al. 1974; Teles de Vasconcelos and González Beça 1993; Masri, Reuter, and Friedman 1974; Randall et al. 1974a	32	19.45		400	182
Sawdust	Dikshit 1989			16.05		
Lignin	Masri, Reuter, and Friedman 1974; Srivastava, Singh, and Sharma 1994				150	1,587
Chitin	Masri, Reuter, and Friedman 1974				100	
Chitosan	Masri, Reuter, and Friedman 1974 (Cd, Cr, Hg, Pb)	558	92		1,123	796
Xanthate	Bricka and Hill 1989; Bricka and Hill 1989; Bricka and Hill 1989; Flynn, Carnahan, and Lindstrom 1980	33.27	19.67		1.149	18
Zeolite	Santiago et al. 1992; Leppert 1990			0.65		155.4
Clay	Pradas et al. 1994; Cadena, Rizvi, and Peters 1990; Cadena, Rizvi, and Peters 1990	16.50		57		58
Peat	Tummavuori and Aho 1980a; Kertman, Kertman, and Chibrikova 1993; Tummavuori and Aho 1980b; Tummavuori and Aho 1980b; Kertman, Kertman, and Chibrikova 1993	5.058	76	43.9	16.2	230
Dead biomass	Matis and Zouboulis 1994; Niu, Xu, and Wang 1993	28				116
Seaweed	Holan, Volesky, and Prasetyo 1993; Leusch, Holan, and Volesky 1995	215				344
Leaf mold	Sharma and Forster 1994			43.0		
Moss	Low and Lee 1991	46.65				
Modified wool	Masri and Friedman 1974 (Cd, Cr, Hg, and Pb)	87	17		632	135
CPEI cotton	Roberts and Rowland 1973				1,000	

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The capital and regeneration costs of activated carbon and ion exchange media suggest that better process economics may be achieved with disposable sorbents for the treatment of metals-contaminated water and waste streams. An extensive literature search was conducted to identify potentially inexpensive sorbents that could be disposed, rather than regenerated, after use. The literature indicates that many materials with this potential are readily available, either as process by-products or in their natural form. The most promising sorbents iden-tified in this literature search will be tested at bench scale with synthetic metals solutions. The best of these will be further evaluated in characterization and column studies.

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