

Removal of heavy metals from polluted waters using lignocellulosic agricultural waste products

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Abstract

Many agricultural wastes, including barks, manures, and composts, contain high levels of lignocellulosic materials. We hypothesized that the lignin fraction, which contains numerous reactive groups, would be highly effective in binding and removing heavy metal ions from contaminated water, and, further, that the absorptive capabilities of the materials would be strongly affected by the pH of the solution. A series of materials were tested, and, at pH levels above about 5.5, they were highly effective in removing heavy metal ions, generally as large or larger than nickel, but ineffective in removal of lighter ions such as sodium or magnesium. Various barks were generally the most effective and were capable of removing more than 90% of iron, copper, or lead from solutions in simple shake flask experiments. Materials that retain cellular structures and that have high lignin contents were highly effective; barks possess these properties. At alkaline pH levels, many heavy metal ions precipitate,

but three separate lines of evidence indicate that, in the work reported here, ions were removed from aqueous solutions by absorption to barks rather than by precipitation. At acidic pH levels, they also were partially effective in removal of the oxyanion chromate. However, a more efficient method of removal of chromate involved reduction to chromite in acidic solutions, adjusting pH levels in transit to columns packed with bark, and removal of chromite with hardwood bark. The bark was capable of binding the chromite to a level more than 3% by weight, and the resulting bark-chromite mixture passed toxicity characteristic leaching procedure (TCLP) tests. This system is expected to be deployed to remediate a site with chromate-polluted groundwater.

Introduction

Ground, surface, and processing waters frequently contain dissolved heavy metals that may arise from operations of mines, factories, and other industries. These metals are frequently difficult or expensive to remove, toxic to people, and damaging to the environment. Metal-contaminated waters may include ions of copper, zinc, nickel, lead, cadmium, mercury, chromium, and uranium, among others. All have toxicity to animals, plants, and other organisms or may deleteriously affect sensitive environments. In addition, even more innocuous materials may have low limits for discharge under certain conditions. For example, in some situations, the discharge limit for iron is 1 ppm. Mining operations may have as contaminants traces of gold, silver, or other precious metals, as well as cyanide conjugates of such metals. Frequently, they are mixed with other ions, including less toxic sodium, potassium, magnesium, and others. In many cases the pH is low, since some heavy metal ions are soluble only under acidic conditions. Acid mine drainage may be

particularly vexing because pH levels may be low (e.g., 1–2), and these acids themselves may be corrosive and toxic. Other contaminants may be present, such as organic compounds. Polluted water systems may be relatively simple, with predominately one or a few metals, or more complex.

Current methods for removal of such metals frequently depend upon precipitation of metal ions, as the hydroxide or other material, in the presence of flocculating agents, and then final removal of the resulting sludge. In some cases, prior to discharge, the water from which the metals were precipitated must be filtered through sand beds or other systems to remove the total precipitate.¹ Such systems are quite expensive; for chromium alone, the yearly costs exceed \$3 billion.¹ Further, they require use of considerable amounts of flocculants that are expensive. Also, sand beds may plug, especially if organic materials are present, and result in biomass accumulation.

Certain natural substances, such as peat and humic acids, can bind heavy metals² and also absorb apolar compounds.³ In some cases, addition of composts and municipal waste biosolids to soil has resulted in reduced phytotoxicity and reduced bioavailability of heavy metals such as copper, nickel, lead, zinc, and cadmium.^{4–6} Thus, plants can be established in soils that are otherwise toxic due to heavy metal contamination.^{5,7} However, insofar as we can determine, solid peats, biosolids, or the like have rarely been used directly to decontaminate polluted water, although composts plus other ingredients have been used to ameliorate acid mine drainage waters.⁸

Lignocelluloses are plant cell wall materials that include cellulose, hemicellulose, and lignins. Lignocelluloses are the most abundant polymeric renewable resource in the US, and probably in the world. Large quantities of lignocellulosic materials are primary constituents of plants. Such materials are readily available as residual plant parts after harvests, but also are perhaps available in larger quantities following various common transformations of the materials. One such transformation is animal digestion. For example, ruminant animals can digest some lignocellulosic plant materials to a fairly high extent, ranging from about 82% for timothy grass to only 6% for ground lodgepole pinewood. The complex lignin fraction is basically unavailable to ruminants. The limit of digestion for each material is the “digestion ceiling”;⁹ that is, the level of lignin determines this ceiling. Thus, animal digestion decreases the cellulose and hemicelluloses to provide an enriched level of humic substances. Another material that is useful is tree bark, which also has a high level of humic substances. Digested plant materials in the form of manures, as well as tree barks, are very abundant and available and usually are considered low-value materials or even wastes that must be disposed of.

Composts themselves may be produced from diverse materials,

including food plant wastes, manures, mixed or monolithic organic waste streams from cities or towns, or, less commonly, from animal or fish wastes or flesh. Also, composts frequently are formed from biosolids from sewages; in this case, anaerobic digestion may be followed by composting of the separated solids, as is the case with animal composts. Typically, composting is an aerobic process and is typified by rapid microbial growth, with turning or other aerating steps within established moisture ranges. Thermal composting consists of three phases. In the first phase, temperatures in the compost materials begin to rise due to microbial degradation. In the second phase, temperatures reach 40°C to 65°C due to degradation of more-resistant compounds such as cellulose; at this temperature, most microorganisms die. During this time, the composts must be turned, aerated, or otherwise handled in order to expose all parts to the high temperatures to ensure microbial breakdown of available substrates and to ensure a homogenous product. Once temperatures decline due to depletion of substrates, then the third, or curing, phase begins; microbial recolonization occurs and humic substances increase. Typical composts are dark and consist largely of lignins, humic substances, and microbial biomass.¹⁰

In addition, there are widely used processes that do not degrade materials to the extent that aerobic composting does. Landscaping companies prepare “aged bark” mulches. In this process, bark particles are placed in large piles (usually tens of meters high), where aeration is minimal. This results in a largely anaerobic microbial process that retains the basic cell and fiber structure of the bark. Similarly, a commercial process introduces manure solids into an aerated rotating digester. This unit uses microbial processes to heat the manures sufficiently to kill bacterial pathogens of animals and humans and partially dries the materials. The result is a material that is relatively fluffy and composed primarily of plant fibers. The microbially accessible materials are removed, which is an advantage since these mostly water soluble materials would leach into waters causing undesirable coloration and potentially increasing biological oxygen demand to an unsuitable level. These materials are also produced in large quantities. Some of the materials, especially manure solids and wood or bark waste materials, have few uses and cost very little (typically \$10–\$20 per cubic yard).

With this background, we constructed three hypotheses: (1) that lignocellulosic agricultural wastes would effectively remove heavy metal cations or oxyanions from aqueous solution; (2) that the lignin portion of agricultural wastes would be the active portion of the materials; and (3) that the efficacy of removal would be dependent upon pH since ionization of reactive groups would be necessary for removal of either type of species. Further, it was expected that ligno-

cellulosic materials would be more effective than others, and that properties that result in greater efficacy could be identified.

It was the goal of the research reported here to determine whether the vast and inexpensive resource represented by plant waste products provides a reasonable method to remove heavy metal ions from polluted water. If proven possible, then a secondary goal was to investigate which materials were most effective, both chemically and economically, and to develop protocols for their use.

Materials and methods

Several materials were tested in this research, as follows.

ARKPORT SANDY LOAM CONTROL: A sandy loam soil with less than 1% organic matter, and therefore a low level of humic substances, was used as a control.

ANDRE COMPOST: This material was prepared by Andre Farms, (Wauseon, Ohio) by thermal composting of mixed yard and food plant wastes.

GENEVA MUNICIPAL SLUDGE COMPOST: This material was prepared by the city of Geneva, New York. The process consists of the dewatering of sewage sludge from an anaerobic fermentation, mixing it with hardwood sawdust, and then thermal composting, with aeration, first in a silo and secondarily in piles that are turned periodically.

MILORGANITE: Milorganite® is an eponymous commercial product (Milorganite; Milwaukee, Wisconsin) for home garden and golf course use as a soil conditioner, prepared from Milwaukee, Wisconsin, sewage sludge. The process, described at Milorganite's website (http://www.milorganite.com/docs/about/how_milorganite_is_made.pdf), has similarities to that of Geneva municipal sludge compost.

MUSHROOM COMPOST: Mushroom compost is the material that remains after the culturing and harvesting of mushrooms, mostly *Agaricus* spp. The mushroom growing procedure is itself a composting process; the starting materials for commercial mushroom production are commonly animal manure and straw.

DEWATERED DAIRY COW MANURE: Large dairy farms and other contained animal facilities must deal with copious quantities of manure. One method of handling this is to suspend the manure and urine in water and then to separate the solids and the liquids. The solids are separated from the liquids by appropriate compression equipment, and the dewatered manure is conveyed to another location for disposal or processing. This material is light tan in color, free of objectionable odors and retains the particulate, fibrous nature of the feed plants and bedding from which it was derived. The material used in these tests was obtained from the Fessenden Dairy, LLC (King's Ferry, New York).

COW MANURE COMPOST: The same dewatered manure described above was subjected to standard thermal composting to give a product that is primarily used as a horticultural soil amendment. This material was also obtained from the Fessenden Dairy. This dark brown, finely particulate material no longer resembles the plant materials from which it was derived.

AGED HARDWOOD BARK: Hardwood bark was obtained from local sawmills by Sensenig's Mulch and Landscaping (Geneva, New York). This material was placed in large piles and allowed to age for several months. The resulting dark brown material can be ground to any desired size and is sold as a mulch for plants.

AGED GROUND WOOD: Similar to the aged bark described above, this mixture composed of the entire biomass from forest clearing operations was produced by grinding the stumps and stems of trees and then aging. This material was also obtained from Sensenig's Mulch and Landscaping.

These materials were chosen because they are examples of lignocellulosic materials that are widely available and that are all considered as plant waste materials. We did not consider other materials, such as fresh plant products that are useful (and therefore costly) or those that would be available only seasonally. Many other lignocellulosic materials exist, but the ones we chose are available in large quantities and, because they are inexpensive, are reasonable starting materials for cost-effective removal of heavy metals. We also were interested primarily in materials expected to have high lignin contents, since we hypothesized that lignin would be the active portion of the materials.

In addition, for studies pertaining to comparative evaluation of efficacy, we tested additional materials chosen for their specific properties. These included silage and haylage, which are feeds for dairy animals that are prepared by a lactic acid fermentation of maize and alfalfa, respectively. These are the starting materials for manures, and dairy animals utilize this material through a complex process that removes cellulose. These materials also are representative of the plant materials that go into many composting products. Their use, however, is not reasonable for direct heavy metal removal, since they are valuable and probably too expensive for the processes we describe here.

The experimental protocols for early experiments were similar. The metals tested in initial experiments were copper (as copper sulfate), nickel (as nickel sulfate), magnesium (as magnesium sulfate), potassium (as potassium sulfate), iron (as ferrous sulfate), and lead (as lead nitrate). Thirty ml of these solutions, or mixtures of them, was added to 125 ml Erlenmeyer flasks, and 5 g (dry weight) of the composts or soil was added to each. The mixtures were placed on a rotary shaker overnight. The solid and liquid fractions were then sep-

arated, and the level of metals remaining in the liquid phase of the mixtures was assayed using atomic absorption spectroscopy. The pH proved to be a critical parameter, and it was adjusted to various levels using $\text{Ca}(\text{CO}_3)$. In further experiments, CoCl_2 at 5,400 $\mu\text{g}/\text{ml}$ was used in similarly designed experiments with aged hardwood bark, and the pH was adjusted to levels indicated with Na_2CO_3 .

This protocol was considered unsuitable for metals present as

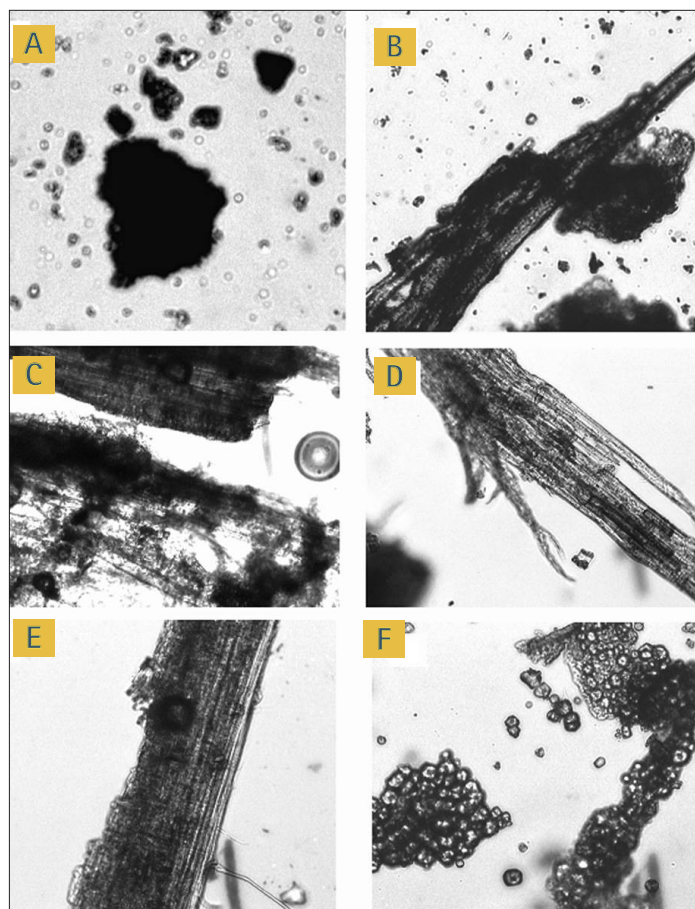


Figure 1. Photomicrographs of materials tested for heavy-metal removal from contaminated waters. (A) Andre composts, no cellular structures visible. (B) Aged hardwood bark, cellular structures, primarily fibers, visible. (C) Dried manure, degraded cells visible. (D) Hardwood bark chips, fibers evident. (E) Haylage, cellular structure evident. (F) Filage, cellular structures, primarily cells from pith of stems, visible. To give ideas of scale, all pictures were taken with similar magnification and individual plant cells are approximately 15–20 μm in width, although they may be much longer than wide.

oxyanions, e.g., chromate at pH levels near neutrality, since at least a major part of the abilities of these humic substances to remove metal ions from solution is based on charge, and it was assumed that negatively charged oxyanions would not bind to the materials except at low pH values. An alternative process for chromium is to reduce the chromium present as Cr^{+6} in the form of chromate to Cr^{3+} using reducing agents such as Fe^{2+} or metabisulfite. The solution can then be adjusted to a higher pH that permits binding of the Cr^{3+} to the lignocellulosic matrix. Consequently, for chromate, we developed a process that permits binding to lignocellulosic matrices but minimizes or eliminates precipitation of Cr^{3+} as the hydroxide.

To define properties that provide highly effective removal of heavy metals, we determined the level of lignin in specific test materials. To accomplish this, we washed the test materials with deionized water until no more colored material was released. This was done in order to simulate the processes that would be involved in actual heavy metal remediation. Once this was complete, the materials were dried and their dry weights determined. The materials were ground and sieved through a 40 mesh screen, and Klausen lignin contents were determined by the methods of Theander and Westerlund¹¹. Cellular structure or lack thereof was determined by microscopic observations (Figure 1).

Results

The first experiment evaluated the abilities of the lignocellulosic materials described to remove individual heavy metal ions from solution. In many cases, pH values of the test solutions were relatively low (pH 4 or below); CaCO_3 was thus added to adjust the pH upward (Table 1), as we anticipated that active sites capable of binding cations would be poorly ionized at low pH levels.

In no cases did the Arkport sandy loam control soil, which was deficient in organic matter, give a reduction of the heavy metal ion concentrations in the solutions, and in several cases, there was a significant increase due to leaching of some metal ions from the soil (Table 1).

Further, in no cases did any of the test materials remove significant amounts of Mg^{2+} or K^+ from solution. However, most of the materials had some abilities to remove heavy metal ions (Ni^{2+} , Fe^{2+} , Cu^{2+} , or Pb^{2+}). Generally, the greater the molecular mass of the ion, the greater the efficacy of removal; thus, for example, Pb^{2+} was removed more efficiently than Ni^{2+} . Solution pH was critical to efficient removal of the ions. Typically, increasing the pH level resulted in an increase of removal efficacy of one to two orders of magnitude. For copper and lead, when the pH was adjusted to values of 5.5 or above, more than 90% of the ions were removed by barks in these

simple shaking experiments. For nickel, only the Andre compost material gave more than 90% removal; mushroom compost removed 87% (Table 1).

Given the pH values employed, it was possible that some of the metal ions might have precipitated from solution rather than being removed by binding with bark. This was evaluated by a simple test: Solutions of the metal ions were adjusted to pH levels where precip-

itation would occur. In all instances, the precipitate was flocculant in nature and the particles sizes were small. Therefore, if filtered through a sieve with 2x2 mm holes, the precipitates flowed through. However, bark particles used in a comparative test were larger than this size and would not pass through the sieves. Therefore, if precipitate was present and a free-flowing slurry of the mixtures was prepared, then any precipitate would be readily apparent after the sieve

Table 1. Removal of individual metal ions from solution with organic media at various pH levels

MATERIAL	POTASSIUM			MAGNESIUM			NICKEL			IRON			COPPER			LEAD		
	pH	µg/ml	%	pH	µg/ml	%	pH	µg/ml	%	pH	µg/ml	%	pH	µg/ml	%	pH	µg/ml	%
Original solution	6.2	1100	—	7.1	760	—	7.2	1100	—	3.9	980	—	4.4	1250	—	5.0	1200	—
Sandy loam	6.6	1133	102	7.4	970	127	6.6	967	88	5.2	700	71	4.5	1333	107	6.1	1367	109
Hemlock bark	6.05	942	86	6.5	887	117	5.95	720	66	3.9	440	45	4.1	817	65	4.2	39	3.2
Hemlock bark, adjusted	7	not done	—	not done	not done	—	not done	not done	—	6.4	25	2.6	6.1	46	3.7	5.0	0	0
Aged pine bark	5.4	1016	92	4.3	826	109	4.2	767	70	3.8	327	34	3.2	833	67	4.2	17	1.4
Aged pine bark, adjusted	6.7	not done	—	6.7	813	107	6.6	330	30	6.2	0	0	5.9	53	4.2	5.0	21	1.7
Milorganite	6.3	1092	99	6.1	933	122	6.0	403	37	5.8	130	132	5.3	483	39	5.1	34	2.8
Sewage compost	5.9	1000	91	5.7	893	118	5.4	523	48	5.1	340	35	5.0	201	16	5.1	24	2.0
Sewage compost, adjusted	not done	not done	—	not done	not done	—	6.3	440	40	5.85	89	9	not done	not done	—	5.7	9	0.08
Andre compost, 1.5 g	7.35	1458	133	7.1	835	110	7	63	6	6.2	7.7	0.8	not done	not done	—	6.5	32	2.7
Andre compost, 3 g	—	not done	—	not done	not done	—	not done	not done	—	not done	not done	—	6.5	15	1.2	not done	not done	—
Aged hardwood bark	6.05	1058	96	6.3	810	107	6.2	310	28	5.1	85	8.7	5.0	67	5.4	5.5	20	1.7
Aged hardwood bark, adjusted	not done	not done	—	—	—	—	—	—	—	5.8	0	0	5.9	40	3.2	5.8	21	1.8
Manure	7.7	1442	131	6.9	816	107	6.6	417	38	6.3	51	5.2	6.1	64	5.1	7.0	79	6.3
Mushroom compost	7.1	2067	188	6.6	757	100	6.6	140	13	6.2	38	3.9	5.85	65	5.2	6.4	41	3.3

For each metal, the pH of the solution at the end of the experiment is provided, as is the mean amount of metal ion in the solution (µg/ml) at the end of the experiment, and the % of the original metal level remaining at the end of each treatment. In a few cases, the % values are greater than 100, since some of that particular metal ion solution was leached from the test material.

Solutions of the ions indicated were made using KCl, MgSO₄ x 7H₂O, NiSO₄ x 6H₂O, FeSO₄ x 7H₂O, CuSO₄, and Pb(NO₃)₂ in distilled water. Unless otherwise indicated, 3 g of the various materials was added to 50 ml of the solutions, and the mixtures were shaken at 85 rpm for 24 hr at room temperature. Subsequently, the particulate materials were removed by filtration through Whatman #4 filter paper, and the solution concentrations determined after appropriate dilution using atomic absorption spectrophotometry. For tests noted as adjusted, pH was changed to the value indicated by addition of 0.3 to 1 g of CaCO₃ to the system at the start of the experiment. Based on preliminary experiments, we attempted to raise the pH levels to greater than 5.5. Materials used are described in the *Materials and methods* section. Columns labeled pH contain the values at the end of the 24 hr shaking period. The µg/ml column is the concentration of the ion species determined in the filtrate. Each value is the mean of three separate replicates for each treatment. The 95% confidence interval around each mean was determined using Statistica 7.1 (StatSoft; Tulsa, Oklahoma). Values in italics are significantly different from the concentration in the starting solution, i.e., the 95% confidence range around each mean did not include the starting solution concentration. Further, the levels of the ions were compared in all combinations using a post-hoc LSD procedure. For every material where the pH was adjusted, the levels of Ni, Fe, and Cu were significantly less at the higher pH level. The % column indicates percentage of amount of each ion remaining in solution at end of experiment. Values on darker yellow background are those where 10% or less of the ion in question remained, i.e., where 90% or more of the ion was removed.

separation. In no cases where bark was present did any precipitates form that would pass through the sieves. We thus concluded that the removal of heavy metals from the solutions tested was due to binding to the lignocellulosic material. Secondly, insoluble hydroxides of heavy metals are flocculant and rather slimy, and, in all cases, clearly visible. If heavy metal hydroxides were present, it was very easy to see these even in the presence of the bark, as noted below for chromium. In no cases in the results reported in *Table 1* were precipitates visible. In addition, we conducted experiments with CoCl_2 . Solutions of this salt do not precipitate at pH levels up to 9.6. The loading rates of aged hardwood bark, as percentage cobalt in the final bark-metal mixture after reactions as in *Figure 1*, were 2.5%, 4.1%, and 5.9% at pH levels of 6.0, 7.4, and 9.6, respectively. These mean values (3 replicates) are all significantly different from each other at $p=0.02$. This confirmed that the barks were highly effective in absorption of the metals, and removal was not due to precipitation and filtration.

We then conducted similar tests on a mixture of metal ions (K^+ , Mg^{2+} , Fe^{2+} , and Cu^{2+}) in solution (*Table 2*). We compared aged pine bark, hardwood bark, and manure at two pH levels. As with our ear-

lier experiments on single ions in solution, K^+ and Mg^{2+} were not effectively removed, but Fe^{2+} and Cu^{2+} were. The pH had a significant effect: With Fe^{2+} in a solution at pH values of 3.6 to 5.9, depending on the absorbent material, removal was about 75% effective, but at pH values around 7, the removal was totally effective.

These systems were not expected to be effective with oxyanions, which have negative charges, especially at higher pH levels. Any functional groups on the test materials having positive charges would be expected to be effective at low pH values rather than high. Hardwood bark, manure, and sewage compost were evaluated to test this hypothesis (*Table 3*). Indeed, at a solution pH 3.0, chromate ions were relatively effectively removed, with the greatest value being almost 90% (*Table 3*). However, use of such a system would result in low pH effluents. In practice, a higher-efficacy system would be desired.

We therefore investigated the conversion of chromate (CrO_4^{2-}) to chromite (Cr^{3+}) and removal of cationic chromite ions with barks. In order to accomplish this, several experiments were designed. In the first, a sample of polluted groundwater was obtained that contained about 35 ppm chromate. The pH was adjusted to 3.3–3.5 with nitric

Table 2. Removal of metal ions from mixtures in solution at different pH levels

MATERIAL	pH	POTASSIUM		MAGNESIUM		IRON		COPPER	
		$\mu\text{g/ml}$	%	$\mu\text{g/ml}$	%	$\mu\text{g/ml}$	%	$\mu\text{g/ml}$	%
Original Solution	–	1100	–	1020	–	990	–	1050	–
Aged pine bark	3.6	1100	100	960	94	240	24	593	56
Aged pine bark	6.8	<i>1166</i>	106	<i>943</i>	92	0	0	48	4.5
Aged hardwood bark	3.8	1167	106	986	97	345	35	460	44
Aged hardwood bark	6.8	<i>1133</i>	103	<i>953</i>	93	0	0	97	9.2
Manure	5.9	<i>1533</i>	140	<i>983</i>	96	218	22	62	5.9
Manure	7.1	<i>1646</i>	150	993	97	0	0	37	3.5

Values for each metal are as in *Table 1*. Mixtures of solutions of the ions indicated were made using KCl , $\text{MgSO}_4 \times 7\text{H}_2\text{O}$, CuSO_4 , and $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ in distilled water. Three g of the various materials was added to 50 ml of the solutions, and the mixtures shaken at 85 rpm for 24 hr at room temperature. Subsequently, the particulate materials were removed by filtration through Whatman #4 filter paper and concentrations determined after appropriate dilution using atomic absorption spectrophotometry. The pH was changed to a higher value by addition of 0.2–0.4 g of CaCO_3 to the materials at the start of the experiment. The materials used are described in *Materials and methods*. The column labeled pH contains levels measured at the end of the 24 hr shaking period. The $\mu\text{g/ml}$ column is the concentration of the ion species determined in the filtrate after the 24 hr shaking period. Each value is the mean of three separate replicates for each treatment. The 95% confidence interval around each mean was determined using Statistica 7.1 (StatSoft; Tulsa, Oklahoma). Values in italics are significantly different from the concentration in the starting solution, i.e., the 95% confidence range around each mean did not include the starting solution concentration. Further, the levels of the ions were compared in all combinations using a post-hoc LSD procedure, and the levels of Fe and Cu were significantly lower at the higher pH level. The % column indicates the percentage of amount of each ion remaining in solution at the end of the experiment. Values on dark yellow background are those where 10% or less of the ion in question remained, i.e., 90% or more of the ion was removed.

acid, and chromate was reduced by the addition of 0.85 g $\text{Na}_2\text{S}_2\text{O}_5$ (sodium metabisulfate) per liter. The reduced and acidified material was pumped at a rate of 8–10 ml/min, with Na_2CO_3 added in-line to adjust the pH of the stream to 6.9 ± 0.2 . This stream was introduced into the base of a column (5×25 cm, 500 ml total volume) that was filled with 151 cm^3 of aged hardwood bark on a 3 mm deep crushed limestone bed. The aged hardwood bark size ranged between 8 mesh (2.35 mm opening) and 35 mesh (0.5 mm opening). This particle size provided a packing with relatively large void spaces. The matrix does not swell appreciably when moistened so there is essentially no back pressure. The bark matrix was moistened by pumping water into it by reverse flow until water emerged from the column.

The column was run at 8–10 ml/min (9 ml average) with the reduced and pH-adjusted chromite solution. Assuming a void volume of approximately 50%, the transit time was about 28 minutes. The total volume that passed through the column without breakthrough was 38 L of solution, for a total amount of Cr absorbed onto the matrix of 1.22 g. Cr levels in the effluent were consistently below 1 ppm. After the 38 L of solution passed through the column, the column was rinsed with two volumes of water and drained, and the matrix recovered. The resulting matrix material was dried, then subjected to TCLP analysis, which it passed.

A second trial was conducted to determine total column loading capacity. A column containing aged hardwood bark was prepared as noted above except that the bed support was glass beads rather than crushed limestone. A solution of $\text{CCl}_3 \times 6 \text{H}_2\text{O}$ was prepared to contain 135 ppm Cr, and 0.14 g $\text{Na}_2\text{S}_2\text{O}_5$ was added per liter. This was done in order to provide a reducing solution similar to what would be present in actual reduced samples, and because in the absence of the bisulfite ions, the Cr^{3+} precipitated even at relatively low pH values. The Cr solution was pumped onto the column, with the pH adjusted in transit with sodium bicarbonate to between 6.9 and 7.1. (The pH of the original chromium chloride solution was 3.8.)

The column was run in reverse flow at 3 ml/min; total transit time was about 83 minutes. Cr levels in the effluent were consistently below 1 ppm. When flow rate was increased to 5 ml/min, there were 3–4 ppm of Cr in the effluent. Total volume of 135 ppm Cr solution applied to the column was 38.8 L, containing a total of about 5.2 g of Cr, which gave an average loading of about 3.9% by weight of Cr on the matrix. However, after about 35 L of Cr solution passed into the column, a gray precipitate typical of $\text{Cr}(\text{OH})_3$ (or perhaps $\text{Cr}(\text{HCO}_3)_3$) appeared at the bottom of the column. This indicates that at this lower layer, the matrix became saturated, and at the slow flow rate of the column, at pH 7, the excess Cr precipitated. The column was taken down as above, and both the precipitate layer and upper

nonprecipitated layer were subjected to TCLP analysis; both passed.

Another process for chromite removal was also investigated. Fe^{2+} is an efficient reducing agent. This ion is efficiently bound to aged

Table 3. Removal of chromate from solution by various materials at different pH levels

MATERIAL	pH	$\mu\text{g/ml}$	%
Manure	7.8	12	34
Manure	2.9	4.3	12.3
Sewage compost	6.5	13	37
Sewage compost	3.0	4.9	14
Aged hardwood bark	6.9	11	31
Aged hardwood bark	3.0	3.6	11

Values in the column labeled pH, $\mu\text{g/ml}$, and % are as described for Table 1. A solution of Na_2CrO_4 was prepared to give a solution containing 35 mg/ml chromium. Three g of sewage compost or hardwood bark or 2 ml of manure was added to 50 ml of chromate solution, and assays were conducted at two pH values. Higher values (uppermost in each data-set pair) for each material are the ambient pH of the mixture; the lower values (second line, each data-set pair) were obtained by addition of HCl. Samples were shaken for 24 hr at room temperature, the solutions filtered through Whatman #4 filter paper, and the levels of Cr determined in the solutions. Each variable was run in triplicate. The $\mu\text{g/ml}$ values are means of the three determinations. With every material, the difference between the amount remaining in solution at high pH is significantly different ($p < 0.05$) from that at low pH. Statistica 7.1 (StatSoft; Tulsa, Oklahoma) was used with the one-way Anova test post-hoc Fisher's LSD.

Table 4. Lignin contents of several lignocellulosic materials

MATERIAL	KLAUSEN LIGNIN (g lignin/g material)
Andre compost	0.66 a
Mushroom compost	0.54 b
Aged pine bark	0.52 bc
Aged hardwood bark	0.49 bc
Manure	0.40 c
Wood mulch	0.28 de
Haylage	0.26 e
Silage	0.16 f

Mean values (from three replicates) followed by dissimilar letters are significantly different at $p = 0.05$ according to LSD tests.

hardwood bark and other media (Tables 2, 3). A column of 20 cm³ (11.3 g) was thus packed with aged hardwood bark as in the previously described trials, and a solution of FeSO₄ (100 mM) pumped onto the column with reverse flow until water emerged from the top of the column. A chromate solution (25 ppm Cr), obtained from a polluted water source, was then pumped onto the iron-charged column at 1 ml/min. In addition, a solution of 10 ppm of FeSO₄ was added concurrently with the chromium solution to the bottom of the column. About 3.3 L was added; chromate breakthrough in the effluent was not detected. The amount of Cr that was bound to the column was about 0.7%, which is less than in the other two trials.

Moreover, this system has two other disadvantages; the Fe²⁺ in the column oxidizes to insoluble Fe³⁺ and creates problems of column plugging and fouling. In addition, while Cr is effectively removed from polluted water, Fe does exit the column, and in some applications this is objectionable. Thus, the use of Fe²⁺ as an in-column reducing medium was not as efficient as the metabisulfite reducing system.

Finally, as indicated in Table 1, the test materials differed substantially in their abilities to remove heavy metals. Composts, manures, and barks were generally quite effective. We originally expected that lignins would be the most effective part of the lignocellulosic materials, and this was consistent with the results obtained. To confirm that lignin contents were correlated with efficacy, we determined the lignin contents of several materials (Table 4). The materials with the highest lignin concentrations were composts; vegetative material composts (Andre) were higher than mushroom (primarily manure) composts. The composts were followed closely by barks and then by manures. Lignin contents of wood chips were significantly lower than any of the materials above; the lightly processed cattle feed silages had the lowest contents. The silage materials can be used as indicators of the starting materials for both the Andre composts and the manures. Clearly, the processing that goes on during composting and in digestive processes leading to manure leads to increased lignin levels. Microscopic observations demonstrated that the silage-type materials and manure retained cellular plant structures, but these were totally lacking in Andre composts. Mushroom composts had some cellular structure remaining, but much of the material was amorphous and undifferentiated (Figure 1).

Discussion

A number of lignocellulosic substances were shown in this work to efficiently bind heavy metal ions from solution but not lighter metal ions, especially at pH values above ~5.5. The preferential binding of heavy metals probably occurs via chelation rather than simple

ionic binding. In comparative experiments, Bio Rex 70 (Bio-Rad Laboratories; Hercules, California), a simple ion-exchange resin, and Chelex 100 (Bio-Rad Laboratories), which has positively and negatively charged groups on the same molecule, were tested under conditions similar to the barks. As the manufacturer indicates, the behavior of the Chelex resin, but not the Bio Rex 70 resin, is similar to our results here. The ability of Bio Rex 70 to remove Cu²⁺ ions was about two orders of magnitude less than that of Chelex 100, but under similar conditions, Bio Rex 70 was more effective in removing K⁺ ions than was Chelex. This preferential ability of the lignocellulosic materials to remove heavy metals while having little affinity for lighter ones is a big advantage of agricultural waste products. As such, they can be used in the presence of small metal ions, such as sodium, permitting their use in salty waters without reduction in efficacy or binding capacity for heavier metals.

The ability of the substances tested to remove heavy metals, apparently due to their chelating abilities, is to be expected since such substances contain a hydrophobic framework of aromatic rings linked by more flexible carbon chains, with alcohol, carboxylic, carbonyl, phenolic, amine and imine, and quinone functional groups. They also contain a high level of bound free radicals, which increases their reactivity. Thus, depending on pH and other parameters, they can be made to efficiently bind particular ions¹². This array of charges and reactivities is similar in general configurations to commercial chelating resins.

The natural materials differed substantially, however, in their properties and capabilities. In general, the various barks were effective and satisfactory for the applications tested. The manures removed heavy metals effectively but (as indicated by their leaching of potassium and magnesium, together with observations and tests revealing their leaching of colored organic compounds) demonstrated a potential pollution issue, which would obviate their use. Composts, with the exception of nickel absorption, generally were less effective than the barks in removing heavy metals, with Milorganite being quite ineffective. Based on these results, we suggest that the most successful materials need to retain their cellular structure, and, hence, surface area, for absorption, and to have a high ratio of lignin to cellulose. The data presented in Table 4 and Figure 1 supports this contention. As expected, composting or animal digestion increases the percentage of lignins by removal of the more readily available cellulose. These results are to be expected from the literature.¹⁰ The barks fit this profile well.

The efficiencies of many of the materials tested are quite high, especially considering that the removal occurred by gentle shaking in solution. If the same materials were used in columns or towers with

the solution to be purified passed through the material, then much higher efficiencies could be obtained, as demonstrated by the abilities of bark columns to remove chromite.

Absorptive capacity of the various materials was strongly affected by pH, as was expected. The reactive groups in the lignin molecule no doubt depend upon ionization to be effective, and ionization is affected by pH. Generally, for cations, a pH level above at least 5.5 is required, and higher pH levels are more effective, so long as this does not result in precipitation of the heavy metal ion in question. Thus, for each specific heavy metal cation, some work is required to obtain the proper pH level and timing to permit absorption but to minimize or eliminate precipitation. For the oxycations, efficient absorption occurs at acidic pH levels and probably are too low for standard discharge methods. The absorption of heavy metals, at least Cr^{3+} , was highly effective and the binding level sufficient for the bark-metal complex to pass TCLP; the mixture, therefore, can be disposed of in a standard landfill. We do not know if this will be the case for all metals.

Commercial methods of removal of heavy metals from solution usually involve precipitation of the heavy metal ions by raising the pH until the metals precipitate or by adding phenolic or other residues. Typically, then, a flocculating agent is added and the result is a rather slimy precipitate that must be harvested in some fashion. Even after removal of precipitates, the resulting water frequently has to be filtered through a sand bed or other medium.¹ This causes difficulties of plugging and, if the medium contains organic materials, biofouling.

Our processes, as evidenced here, overcome many of these difficulties. The absorptive medium, since it is an agricultural waste product, is inexpensive. The overall system is certainly less costly than those requiring the addition of flocculating agents plus special settling tanks to collect the precipitates. These are "green," resource-efficient processes, usually using locally produced agricultural waste products, and, at least for chromite collection, the binding between the bark or other medium and the metal ion is sufficiently strong to pass TCLP tests. We do not yet know if this result will be obtained with all metals; should this prove to be the case, another advantage of the process described here is that the metal-bark mixtures can be disposed of in standard-waste, not toxic-waste, landfills. Filtration through the bark can remove a reasonable amount of precipitate with no increase in back pressure.

A first commercial program using the chromate remediation concepts demonstrated here will begin soon at a considerable cost savings over standard precipitation methods.

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