REMOVAL OF METAL IONS FROM CONTAMINATED WATER USING AGRICULTURAL RESIDUES

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SUMMARY

As the world population grows, there is a growing awareness that our environment is getting more polluted. Clean water is becoming a critical issue for many parts of the world for human, animal and agricultural use. Filtration systems to clean our air and water are a growing industry. There are many approaches to removing contaminates from our water supply ranging from reverse osmosis to simple sand filters. Agricultural residues represent a low cost, renewable, available, and sustainable resource that can remove metal ions from water.

INTRODUCTION

Seventy percent of the earth's surface is covered with water, however, most of this water, 97.5%, is in the oceans and seas and is too salty to drink or grow crops. Of the remaining 2.5%, 1.73% is in the form of glaciers and icecaps leaving only about 0.77% available for our fresh water supply. Of the total water on earth, only 0.0008% is available and renewable in rivers and lakes for human and agricultural use. It is the water that falls as rain or snow or that has been accumulated and stored as groundwater that we depend on for our "clean" water resource.

For 1.5 to 2.5 billion people in the world, clean water is a critical issue. It is estimated that by the year 2025, there will be an additional 2.5 billion people on the earth that will live in regions already lacking sufficient clean water. In the United States, it is estimated that 90% of all Americans live within 10 miles of a body of contaminated water. Contaminates in water include sediments, nutrients, pathogens, dissolved oxygen, heavy metal ions, suspended solids, pesticides, turbidity, fish contamination and ammonia. Other conditions to be considered for clean water include pH, temperature, habitat, and noxious plants.

About 80% of the fresh water in the United States originates on the 650 million acres of forestlands that cover about 113 of the Nation's land area. The nearly 192 million acres of National Forest and Grasslands are the largest single source of fresh water in the United States. In many cases, the headwaters of large river basins originate in our National forests. In 1999, the EPA estimated that 3,400 public drinking-water systems

were located in watersheds contained in national forests and about 60 million people lived in these 3,400 communities.

The development of filters to clean our water supply is big business. It is estimated that global spending on filtration (including dust collectors, air filtration, liquid cartridges, membranes and liquid macro-filtration) will increase from $17 billion in 1998 to $75 billion by 2020. The fastest-growing non-industrial application area for filter media is for the generation of clean water.

One of the prevalent contaminates in our water are metal ions that come from a wide variety of sources including abandoned hard rock and coal mines, highways and large parking lot runoff, and natural erosion of minerals.

Studies of metal ion removal reported in the literature can be classified into two groups: noncompetitive or single adsorbers and competitive adsorbers. Noncompetitive adsorption is used to describe the behavior of metal ion removal from an aqueous solution containing only one type of metal ion. The amount of metal ion removed by noncompetitive adsorption is about twice which can be achieved by competitive adsorption.

In the second group, the metal ions come into contact with an adsorbent and all the metal ions are adsorbed simultaneously with varying degrees of success depending on their affinities for the functional groups on the adsorbent.

Forest and agricultural by-products constitute the most abundant renewable resources available worldwide. Among these products, bark accounts for a significant proportion of wood by-products generated by the timber industry.

Most methods to remove metal ions from solution are expensive. It has been shown, however, that wood, bark and other agricultural residues remove metal ions from solution with varying efficiencies.

Laszlo and Dintzis have shown that lignocellulosics have ion-exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. These are adsorbents for a wide range of solutes, particularly divalent metal cations (Laszlo and Dintzis 1994). Lignocellulosic resources all contain, as a common property, polyphenolic compounds, such as tannin and lignin, which are believed to be the active sites for attachment of heavy metal cations (Waiss et al. 1973, Masri et al. 1974, Randall et al. 1974, Bhattacharyya and Venkobachar 1984, Phalman and Khalafalla 1988, Verma et al. 1990, Shukla and Sakhardande 1991, Maranon and Sastre 1992, Lalvani et al. 1997, Vaughan et al. 2001, Shin and Rowell 2005). Sawdust or wood fiber has been used to remove cadmium, nickel or copper (Ajmalet al. 1998, Bryant et al. 1992, Basso et al. 2002, Lee and Rowell 2004, Min et al. 2004) from water. Several types of barks have been used to remove cadmium, copper, lead, zinc, nickel, or cobalt (Randall et

al. 1974, Kumar and Dara 1980, Pawan and Dara 1980, Deshkar et al. 1990, Aoyama et al. 1993, Al-Asheh and Duvnjak 1997, Gloaguen and Morvan 1997, Seki et al. 1997, Tiwari et al. 1997, Gaballah and Kilbertus 1998, Kmiecik et al.2005) from aqueous solution. Cellulose can also sorb heavy metals from solution (Acemioglu and Alma 2001. Isolated kraft lignin has been used to remove copper and cadmium (Verma et al. 1990, Cang et al. 1998) and organosolv lignin has been used to remove copper (Acemioglu et al. Unpublished data) from aqueous solutions.

Corn cobs (Vaughan et al. 2001), soybean hulls (Laszlo and Dintzis 1994), sugar beet pulp Laszol and Dintzis 1994, Reddad et al. 2002) and tea leaves (Tiwari et al. 1997) have also been used to remove metal ions from water.

Acemioglu et al. postulate that metal ions compete with hydrogen ions for the active sorption sites on the lignin molecule (Acemioglu et al. Unpublished data). They also conclude that metal sorption onto lignin is dependent on both sorption time and metal concentration.

Basso et al. studied the correlation between lignin content of several lignocellulosics and their ability to remove heavy metals from aqueous solutions (Basso et al. 2002). Brazil nut shell, sugarcane bagasse, *Prosopis ruscifolia* wood sawdust, and stems of *Arundo donax*, were used with lignin contents of 57%, 28%, 28%, and 23% respectively. The efficiency of removing Cd(II) and Ni(II) from aqueous solutions was measured and they found a direct correlation between heavy metal sorption and lignin content. They also noted that the cell wall structures and compositions were different for the different lignocellulosics selected which may have also influenced heavy metal sorption. In a later study, Lee and Rowell (2004) did not find a correlation between lignin content and metal ion sorption.

It is difficult to compare data from different literature sources since sorption of heavy metals is very dependent on temperature, heavy metal concentration and contact time and no two researchers use identical conditions. However, it is interesting to note that under similar experimental conditions, Vaughan et al. (2001) using corncobs with a lignin content of 9.1% and Acemioglu et al. (Unpublished data) using isolated organosolv lignin found about the same efficiency in removing Cu(II) from aqueous solutions.

Lignocellulosic materials are very porous and have a very high free surface volume that allows accessibility of aqueous solutions to the cell wall components. One cubic inch of a lignocellulosic material, for example, with a specific gravity of 0.4, has a surface area of 15 square feet. Even when the lignocellulosic material is ground, the adsorptive surface increases only slightly. Thus, the sorption of heavy metal ions by lignocellulosic materials does not depend on particle size.

Lignocellulosics are hygroscopic and have an affinity for water. Water is able to permeate the non-crystalline portion of cellulose and all of the hemicellulose and lignin.

Thus, through absorption and adsorption, aqueous solution comes into contact with a very large surface area of different cell wall components.

Extracting fibers with different solvents will change both the chemical and physical properties of the fibers. It is known, for example, that during the hot water and 1% sodium hydroxide extraction of fibers, the cell walls delaminate (Kubinsky 1971). At the same time, some of the amorphous matrix and part of the extractives, which have a bulking effect, are removed (Kubinsky and Ifju 1973), so that the individual microfibrils become more closely packed and shrunken (Kubinsky and IfJu 1974). Therefore, delamination and shrinkage may also change the amount of exposed lignin and other cell wall components that may affect the heavy metal ions sorption capacities of the fibers.

Each different extraction chemical will swell lignocellulosics to a different extent thus removing different amounts and types of extractives as well as cell wall components. The relative swelling, for example, of diethyl ether, ethyl alcohol and water is 3, 83 and 100, respectively. Fats, unsaturated fatty acids, such as oleic acid and linoleic acid, saturated fatty acids, resins, resin acids, waxes, oils and sterols in lignocellulosics are soluble in diethyl ether. Ethyl alcohol can dissolve coloring matter, such as flavonoids and anthocyanins, tannins, phlobaphenes, some water soluble and stilbenes from lignocellulosics. Carbohydrates, such as parts of the hemicelluloses, starch and pectic material, proteins, alkaloids, inorganic materials, such as Ca, K, Mg, Na and Fe, some phenolic substances, oxalate, citrates, humic acid-like substances, mucilages, gums, uronic acids are extractable by hot water. One percent sodium hydroxide can extract major amounts of the hemicelluloses and part of the lignin along with a major portion of the extractives (Browing 1967). Extracting lignocellulosic fibers with different solvents will also change the accessibility of heavy metal solutions to cell wall components.

EXPERIMENTAL

Laboratory Tests - Noncompetitive or Single Adsorbent

To determine the efficiency of different agricultural residues to remove a single metal ion from water, a simple copper II probe was developed so that comparisons between residues can be made. Copper II ion was selected for this test because it is soluble over a wide pH range. A small sample of the residue is placed in a known concentration of Cu^{++} solution and after equilibrium is reached, the concentration of the remaining soluble Cu^{++} is determined. The results are reported either as a percent of Cu^{++} removed or as equilibrium equitant (q_e) calculated as:

$$q_e = \frac{[\text{concentration before} - \text{concentration after}] \times \text{solution volume}}{\text{weight of sample}}$$

Field Tests - Competitive Adsorbent

To determine the efficiency of pine bark to remove metal ions in a competitive experiment, a demonstration filtration unit was set up in an abandoned coal mine in Ohio. The Addis mine is located in the Wayne National Forest near Ironton, Ohio. Thermophilic bacteria convert the sulfur in the remaining underground coal to sulfuric acid and the acidic water leaches metals as the pH drops converting them to soluble metal ions. Therefore, drainage from this abandoned coal mine has a low pH, variable flow rate (depending on rain fall) and is high in metal ions and sulfur.

Ponderosa pine bark was hammer milled and a fraction of 2 to 6 mm collected. It was then steam extracted to remove soluble components, washed with dilute sodium hydroxide and air-dried. The bark was placed in nylon bags that were inserted into stainless steel frames and placed in a filtration box. Water from the mine was piped into the filtration system. Water samples were taken at the inlet of the filtration box and at the outlet everyday for 25 days and analyzed for iron, aluminum and manganese. Samples were analyzed using a Jobin Yvon, Ultima, inductively coupled plasma - atomic emission spectrometer.

RESULTS AND DISCUSSION

Laboratory Tests - Noncompetitive or Single Adsorbent

Table 1 shows the effectiveness of thirteen different types of tree fiber and the corresponding barks in removing Cu^{++} from aqueous solutions. Wood fibers are not as effective in removing Cu^{++} from solution as compared to the corresponding bark. This may be due to the chemistry of the phenolic extractives in the bark. Table 2 shows the effectiveness of many other types of agricultural residues in removing Cu^{++} from aqueous solutions.

Tree barks, pine needles, peanut skins, sugar beet pulp, and corn husks are among the best sorbers of Cu^{++}. It would be interesting to determine the mechanism of effectiveness in biomaterials to capture metal ions. Once that was known, it would be possible to predict the effectiveness of a given biomaterial knowing its composition without having to test it.

Table 1 - Effectiveness of bark and wood in removing copper II from solution.

Wood q_e	Bark q_e
Eastern Black Walnut 21	
Osage Orange 2.8	8.7
American Sycamore 2.1	6.9
Eastern Red Cedar 1.5	6.8
Burr Oak 2.3	6.8
Eastern Cottonwood 2.6	5.3
Green Ash 1.1	5.1
Silver Maple 2.2	5.0
Shagbark Hickory 4.3	4.9
Utah Juniper 2.1	5.0
Honey Locust 3.1	4.3
Hackberry 4.0	3.4
Longleaf 1.2	2.8

Field Tests - Competitive Adsorbent

Table 3 shows the analysis of the water taken over a 20 day period from the Addis mine. The pH range is from 2 to 3.1 and the flow rate is 1 to 8.5 gallons per minute. The flow rate varies from day to day depending on the rain that feeds the mine. If there is no rain for 5 to 7 days, the flow rate drops to less than 1 gallon per minute. The metal ion analysis shows a wide variation of the amount of ions found in the water at any given time.

Table 2 - Effectiveness of other agricultural residues in removing copper II from solution.

Species q_e
Loblolly needles 6.7
Soybean Hulls 6.1
Peanut Skins 5.9
Slash pine needles 5.5
Sugar Beat Pulp 5.5
Corn Husks 5.0
Honysuckle 4.5
Loblolly cones 4.1
Sweet Gum Seeds 3.8
Slash pine cones 3.8
Kudzu 3.7
Pecan Shells 3.5
Rice Hulls
Southern pine needles 2.8

PH	Flow rate from mine G/min	Fe ppm	Al ppm	Mn ppm	S ppm
2–3.1	1–8.5	170 - 230	35 - 52	160 - 270	370 - 430

Table 4 shows the removal of iron, aluminum and manganese from the mine water over a 25-day period. At day 1, the iron content at the inlet of the filter box was 225 ppm and the outlet concentration was 50 ppm. Over the 25 days of filtering the water, the efficiency of the bark filter is reduced until on day 25 the inlet iron concentration was 210 ppm and the outlet iron concentration was 130 ppm.

Table 4 - Removal of iron, aluminum and manganese from acid coal mine drainage.

Day	Inlet Fe ppm	Outlet Fe ppm	Inlet Al ppm	Outlet Al ppm	Inlet Mn ppm	Outlet Mn ppm
1	225	50	37	16	230	105
5	180	50	43	20	160	110
10	190	100	45	30	270	70
15	170	130	40	35	250	120
20	180	120	46	42	230	220
25	210	130	44	44	230	220

A similar pattern was observed for aluminum and manganese except the efficiency of the bark filter is reduced in a shorter time. At the end of day 25, the inlet and outlet aluminum and manganese concentration were about the same.

CONCLUSIONS

Some tree barks have been found to be the most effective filtration media from all of the agricultural residues tested as a noncompetitive sorbent for copper II ion. Barks that are high in extractives seem to be the best. Tree barks are also effective as a competitive adsorbent removing substantial amounts of iron, aluminum and manganese from an acidic coalmine drainage. Filters made of agricultural residues are low cost, renewable, and widely available making them a logical choice to remove particles, oil/grease and metal ions from contaminated water.

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