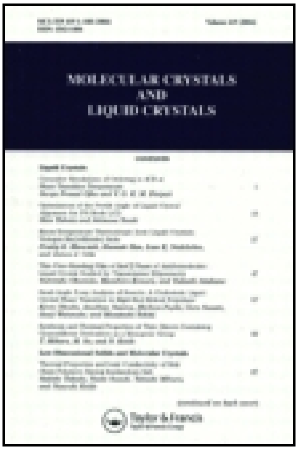

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Effectiveness of Wood and Bark in Removing Organic and Inorganic Contaminates from Aqueous Solution

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Effectiveness of Wood and Bark in Removing Organic and Inorganic Contaminates from Aqueous Solution

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The focus of this study was on aspen wood and other lignocellulosic materials for removing organic and inorganic contaminants typically present in stormwater runoff. The study demonstrated that aspen wood fibers remove PAHs from the aqueous solution. Removal increased with increasing molecular weight of the PAH, but did not seem to be related to the lignin content of the wood. In addition, bark from trees and other agricultural residues have been investigated as a non-competitive sorbent for copper II ion. It has been found that barks that are high in tannins are the most effective filtration media from all of the agricultural residues tested. These results suggest that filters made from wood or bark could find applications in wastewater treatment and control of roadway runoff pollutants.

Keywords: bark; copper; PAH; runoff; treatment; water contamination; wood fibers

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.

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TABLE 1 Categories of Typical Contaminants in Stormwater Runoff

Category	Examples
Organic compounds	Petroleum hydrocarbons including polycyclic aromatic hydrocarbons (PAH), pesticides
Metals	Copper, zinc, nickel, chromium
Nutrients	Nitrogen, phosphorous
Pathogens	Bacteria, viruses, protozoa
Salts, deicing chemicals	Sodium chloride, calcium chloride, magnesium chloride
Biological oxygen demand (BOD)	Human and animal waste, decaying leaves and grass clippings
Sediment	Silt and sand, soil

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. Table 1 shows the contaminates that are usually found in storm water runoff. Other conditions to be considered for clean water include pH, temperature, habitat, and noxious plants.

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 macrofiltration) will increase from $17 billion in 1998 to $75 billion by 2020. The fastest-growing nonindustrial application area for filter media is for the generation of clean water.

Toxic Organics in Water

Many polycyclic aromatic hydrocarbons (PAH) are suspected carcinogens and have been detected in numerous surface- and ground-water bodies at levels threatening human health. PAHs originate from numerous pyrogenic and petrogenic sources. Increasing use of cleaner heating fuels and enhanced combustion efficiency in concert with stricter emission controls applying to power and heat generating plants have led to decreasing PAH fluxes from these sources. On the other hand, PAH pollution associated with roadway runoff have remained a significant environmental problem. In 1997, the US highway vehicle fleet consisted of about 212 million vehicles compared to approximately 160 million in 1980 and the total amount of emitted particulate matter increased by 25% (i.e., 0.29 million tons) from 1980 through 1991 [1].

PAHs tend to accumulate on roads, parking lots, rooftops, and other impermeable surfaces. During rainstorms, the accumulated PAHs wash off these surfaces and may enter drainage structures such as sewage pipes or ditches. PAHs in stormwater runoff have received great attention. For example, in a study of the chemical composition of stormwater runoff in the Upper Narragansett Bay watershed in Rhode Island [2], the authors distinguished between runoff originating from predominantly residential, commercial, industrial, and highway areas. Their findings indicated that stormwater runoff contributed over 50% of the total pollutant input (including PAHs and heavy metals, such as lead and zinc) into the Pawtuxed River. The total annual PAH discharge (i.e., the sum of dissolved and PAHs adsorbed to suspended matter) in the study area was approximately 2.2 kg km^{-2} drainage area or 1.0 g $capita^{-1}$ $year^{-1}$.

In many places, roadway runoff still enters rivers, lakes, the ocean, or other water bodies without receiving adequate treatment. The implementation of best management practices (BMP) has improved water quality to some extent. Structural BMPs, such as retention ponds, operate by physically trapping runoff until contaminants settle out or are filtered through the underlying soils. However, even sophisticated BMPs appear to be inefficient for removing dissolved PAHs [3].

Metal Ions in 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 aqueous solution containing only one type of metal ion. The amount of metal ion removed by noncompetitive adsorption is about twice of that can be achieved by competitive adsorption.

In the second group, the metal ion 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 [4–10]. 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 $0.4\,\mathrm{g\,cm^{-3}}$, has a surface area of $1.4\,\mathrm{m}^2$. However, it has been shown that particle size is very important on the ability of a lignocellulosic to sorb contaminates from water. The purpose of this research was to determine the effectiveness of different types of lignocellulosic resources to remove selected PAH and metal ions from aqueous solutions in laboratory tests.

EXPERIMENTAL

PAH Removal

Aspen wood (*Populus tremula*) was studied to remove three selected PAHs (pyrene, anthracene, and fluorene) dissolved in water at concentrations similar to those found in stormwater runoff. These PAHs were selected based on their relative importance in stormwater runoff environments. Aspen wood fibers were obtained from ACE Hardware in Tucson, AZ. A series of batch and column experiments were carried out to investigate PAH interaction with the wood. The equilibrium wood-water partition coefficient K_{ww} ($\mu g_{sorbed}\, g_{wood}{}^{-1}/\mu g\, L^{-1}$) was calculated Eq. (1) from the batch experiment data.

$$K_{ww} = \frac{C_s}{C_w} \tag{1}$$

where C_w is the dissolved PAH concentration and C_s is the mass of sorbed PAH per dry unit weight of aspen wood, was obtained from the final data set. The K_{ww} is related to the lignin mass of wood, f_{lignin} ($g_{lignin}\, g_{wood}{}^{-1}$) according to Eq. (2):

$$K_{ww} = f_{lignin} K_{lignin} \tag{2}$$

where K_{lignin}($\mu g\, g_{lignin}{}^{-1}/\mu g\, L^{-1}$) is the lignin-water partition coefficient [11]. In this study, the K_{lignin} was calculated based on an aspen wood lignin content of $f_{lignin-aspen} = 21\%$ [12].

Column experiments were carried out to study the uptake (sorption) and release (desorption) of dissolved pyrene, anthracene, and fluorene under dynamic, i.e., flow-through conditions. Water saturated, leached aspen wood was packed into a stainless steel column (HPLC preparatory column, ID: 2.2 cm, length: 7 cm, volume: 26.6 cm^{-3}, Alltech Inc.). Based on dry weight, between 2.25 g and 3.43 g wood fibers were used. Porosity values ranged from 68% to 75%. The pore volume, PV, of each column was determined from the breakthrough curve of a conservative tracer, potassium bromide, prior to pumping contaminant solution.

Aqueous solutions containing approximately 50 $\mu g\,L^{-1}$ of a single PAH were pumped through each column using a precision piston pump (Acuflow Series I HPLC pump) and stainless steel tubing. The flow velocity was held constant at 0.5 $cm^3\,min^{-1}$. After flushing contaminant solution through the column for some time (i.e., several weeks), deionized water was pumped into the column to study the PAH desorption from the wood. During the column experiments, flow interruption experiments were performed to study possible nonideal contaminant transport. Flow interruptions lasted for approximately 24 to 72 h. A desorption experiment was terminated when the effluent concentration reached 0.1 C/Co or if further concentration decrease was very slow. Column experiments lasted up to 3 months.

Aqueous concentration of pyrene, anthracene, and fluorene was determined with a fluorescence spectrophotometer (Shimadzu RF-1601). The detection limit was 1 $\mu g\,L^{-1}$. The excitation wavelength was 247 nm, 350 nm, and 358 nm for pyrene, anthracene, and fluorene, respectively. The emission wavelength was 350 nm (pyrene), 400 nm (anthracene), and 430 nm (fluorene). Duplicates, blanks, and standards were analyzed regularly to assure quality control. Effluent concentrations are reported as relative concentrations, C/Co, where Co is the concentration of the solution entering the column and C is the effluent concentration. Duplicates and controls containing no wood or no PAHs were prepared following the same procedures.

Metal Ion Removal

To determine the efficiency of different agricultural residues to remove a single metal ions 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 was placed in a known concentration of Cu^{++} solution and after equilibrium was reached, the concentration of the remaining soluble Cu^{++} was determined. The results are reported either as a percent of Cu^{++} removed or as equilibrium equitant (q_e) calculated as Eq. (3):

$$q_e = [\text{concentration before} - \text{concentration after}] \times \text{solution volume} \quad (3)$$

RESULTS AND DISCUSSION

PAH Removal

The results of the PAH-aspen wood column experiment are exemplified by the anthracene-aspen wood sorption and desorption experiments shown in Figure 1. Similar results were obtained for pyrene and fluorene. The anthracene concentration in the solution flowing from the column, C, increased in a nonlinear fashion (best described by $C/Co = 0.162t^{0.535}$, where Co is the concentration in the column influent and t is the time in days). After 7 days or 300 pore volumes of flushing, C/Co was approx. 0.45. At this point, the flow was interrupted for 72 h to investigate rate limited sorption. The results of the flow interruption experiment indicate that immediately after the flow resumed, anthracene concentrations were lower than before the flow interruption. This indicates that its sorption is rate limited, i.e., the anthracene residence time in the column under flow conditions was too short to reach equilibrium between the aqueous solution and the wood. After the flow interruption experiment, the anthracene

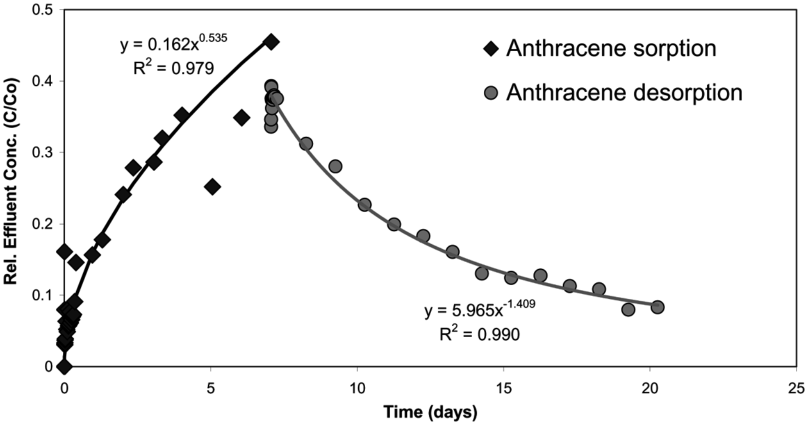

FIGURE 1 Results of the anthracene sorption and desorption experiments with aspen wood fibers. During the sorption experiment, a solution containing 50 µg L^{-1} PAH was flushed through the column. Afterwards, deionized water was flushed to desorb the PAH from the aspen wood fibers.

TABLE 2 Molecular Weights and the Measured Aspen-Wood Water Sorption Coefficients, K_{ww}, for all PAH Compounds Used in this Study. The K_{lignin} was Calculated Based on an Aspen Wood Lignin Content of 21% [12]

Compound	Mol. weight g mol^{-1}	K_{ww} ($\mu g\ kg^{-1}$) ($\mu g\ L^{-1})^{-1}$	K_{lignin} ($\mu g\ g_{lignin}{}^{-1}$) ($\mu g\ L^{-1})^{-1}$
Fluorene	166.2	333 ± 14.0	1.59
Anthracene	178.2	264 ± 9.05	1.26
Pyrene	202.3	462 ± 7.9	2.20

concentration decreased exponentially ($C/Co = 5.965\,t^{-1.409}$). It is noteworthy that the rate of desorption was much slower than the sorption rate.

The isotherm experiments confirmed that the PAH uptake by aspen wood was rate limited. Common to all three PAH studies, the initial uptake of PAH by the wood was rapid over the first hours of the experiment. This fast uptake was then followed by a period lasting up to 250 h before equilibrium was established between the aqueous and wood phase. It is assumed that after initially fast uptake of PAH to easily accessible sorption sites on the wood surface, slower diffusion transport processes into the wood matrix caused the long equilibration time, i.e., was the reason for the observed rate limited transport of PAH into the wood. The K_{ww} as well as the K_{lignin} for all three PAHs

TABLE 3 Effectiveness of Bark and Wood in Removing Copper II from Solution

	q_e	
	Bark	Wood
Eastern Black Walnut	9.7	2.1
Osage Orange	8.7	2.8
American Sycamore	6.9	2.7
Eastern Red Cedar	6.8	1.5
Burr Oak	6.8	2.3
Eastern Cottonwood	5.3	2.6
Green Ash	5.1	1.1
Silver Maple	5.0	2.2
Shagbark Hickory	4.9	4.3
Utah Juniper	−5.0	2.1
Honey Locust	4.3	3.1
Hackberry	3.4	4.0
Longleaf	2.8	1.2

TABLE 4 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	3.5
Southern pine needles	2.8

are summarized in Table 2. The K_{ww} data indicates that the affinity of PAHs to aspen wood increased with increasing molecular weight, namely fluorene $<$ anthracene $<$ pyrene. However, there was no clear relation between K_{lignin} and PAH removal. This indicates that the lignin content of the aspen wood by itself cannot be the sole factor explaining the observed PAH removal.

Metal Ion Removal

Table 3 shows the effectiveness of thirteen different types of tree fiber and the corresponding barks of 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 4 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 were the best sorbers of Cu^{++}.

CONCLUSIONS

The focus of this study was on aspen wood and other lignocellulosic materials for removing organic and inorganic contaminants typically present in stormwater runoff. The study demonstrated that aspen wood fibers remove PAHs from the aqueous solution. That is, even after flushing several hundred pore volumes of contaminated water, the aspen wood still removed a considerable fraction of the contaminants. Removal increased with increasing molecular weight of the PAH contaminants, but does not seem to be related to the lignin content of the wood. Wood filters could find applications in wastewater treatment and control of roadway runoff. For example, filters made from wood fibers could be placed in the wastewater stream. As the contaminated water flows through the filter, the wood removes – at least in part – dissolved PAHs, thereby reducing contaminant flux into surface or ground water. Currently, there are field tests under way to determine the feasibility of this filtration approach.

Bark from trees has 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 tannins seem to be the best. Tree bark is also effective as a competitive adsorbent removing substantial amounts of iron, aluminum and manganese from 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. These natural materials are available in many different forms, as fibers, dust, or chips, for example. Also, incineration in municipal incinerators appears to be the preferred way to dispose loaded filters. Further studies are needed to explore the full potential of these filter materials.

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