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REMOVAL OF PHOSPHORUS USING CHEMICALLY MODIFIED LIGNOCELLULOSIC MATERIALS

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ABSTRACT

Heavy metals from an acid mine drainage (AMD) site were precipitated on the surface of juniper fiber. The modified fiber was tested in labscaled batch and column tests and in the field. Elemental analysis showed that soluble iron species deposited on the fiber act as an inorganic adsorbent for anions. Sorption capacity, determined by fitting results to a Langmuir isotherm model, was 2.18 mg/g of Q_{max} for phosphorus removal, which is similar or slightly higher to the sorption capacity of other conventional adsorbents. A pseudo second order kinetic model fitted well for sorption of phosphorus onto the modified filter medium. The kinetic constant was 8.09×10^{-2} g/mg/min at 10 ppm of phosphorus concentration. A column test showed a removal capacity of 3.5 mg/g of fiber. The modified fiber was used to remove phosphorus from wastewater from a dairy farm in New York. The fiber was installed inside a filter box, forming a non-woven mat. Phosphorus removal efficiency of the fiber filter is about 41 % at 59 ppm of inlet phosphorus concentration.

Keywords: Lignocellulosic material, acid mine drainage, iron species, phosphorus removal.

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1. INTRODUCTION

Phosphorus is the limiting nutrient in water systems because surface waters receiving excess input of nutrients through wastewater discharges may be susceptible to eutrophication [Hammer and Hammer 20011. The phosphorus removal processes that occur in natural, domestic, and industrial treatment systems are considered to be adsorption, chemical precipitation, and biological treatment [Morse et al. 1990]. Among industrial treatment technologies, adsorption on a fixed-bed filtration system is commonly used to purify wastewater with a low concentration of phosphorus [Hano et al. 19971. In adsorption processes, diverse adsorbents such as red mud, activated alumina, polymeric ligand exchangers, iron/aluminum-coated sand, and calcium-based adsorbents, have been studied as adsorbents for phosphate removal [Hano et al. 1997, Lo et al. 1997, Akay et al. 1998, Zhao and Sengupta 1998, Ayoub et al. 2001, Khadhraoui et al. 20021.

Lignocellulosic materials exhibit interesting capacities as pollutant adsorbents [Basso et al. 2002, Reddad et al. 20021, and chemical modification of lignocellulosic materials has been shown to improve their filtration performance. Saponification and phosphorylation of lignocellulosic materials enhance their sorption capacities for heavy cationic metals in water [Nada et al. 2002, Drake et al. 1996, Tiemann et al. 1999; Romero-Gonzalez et al. 2001]. For removal of anions such as phosphate, lignocellulosic materials have been cationized through hybridizing with inorganic chemicals as well as through grafting ammonium-type chemicals. Zghida et al. [2002] prepared lignocellulosic materials cationized by the reaction of epoxy propyltrimethylammonium chloride (EPTMAC) for removal of chromium oxy-anions. DeMarco et al. [2003] developed a polymeric/inorganic hybrid sorbent for arsenic removal. The hybrid sorbent was a polymeric cation exchanger containing agglomerates of nanoscale hydrated iron oxide. Likewise, iron (III)-loaded carboxylated polyacrylamide-grafted sawdust was prepared and tested for phosphate removal from aqueous solution [Unnithan et al. 2002]. The modification consisted of two steps: (1) graft copolymerization of acrylamid and *N,N'*-methylenebisacrylamide onto sawdust and (2) attachment of iron(III) to the carboxylic acid moiety of the adsorbent. However, to activate a lignocellulosic material for removing anion from water, chemical treatment was needed at least once.

Juniper (Juniperus monosperma) fiber is inexpensive and has relatively high heavy metal sorption capacity [Han 19991. Recently, juniper fibers were processed into a mat-type filter medium and used to restore the watershed affected by acid mine drainage (AMD) in the Wayne National Forest in Ohio. In general, AMD contains iron, sulfates, aluminum, manganese, and other dissolved and suspended solids because of its low pH [Drever 1997]. The juniper filter media were installed to remove dissolved metal ions from AMD. It was found that iron species was the primary metal deposited to the filter media, implying that the juniper filter can be a natural, novel, inorganic/lignocellulosic hybrid adsorbent.

Approximately 350 dairy and livestock farms and 90 other agricultural enterprises are operated in the Catskill/Delaware watershed. The various pollutants that originate from those farms and enterprises, such as *Cryptosporidium*, nutrients, pesticides, and sediment, can deteriorate the quality of water of the reservoirs in the Catskill/Delaware supply system. One potentially prevalent problem in the New York watershed is the eutrophication of the reservoirs due to excess nutrients, including phosphorus [NYCDEP 1999a,b; 2001].

The New York City Department of Environmental Protection (NYCDEP) operates several wastewater treatment plants to reduce phosphorus loadings into the watershed. The size of plants vanes from 4,200 to 5.6 million L/day, and the phosphorus removal process is based on precipitation techniques. The approach proposed by the Forest Products Laboratory is to decrease phosphorus loading by installing small filtration systems on dairy farms at the wastewater outlet.

The objective of the study reported here is to evaluate the effectiveness of juniper filter for removing phosphorus from water. Phosphate removal capacity was tested through adsorption and kinetic tests and a column test.

2. EXPERIMENTAL

2.1. Materials

The raw material for the filter medium was juniper (*Juniperus monosperma*), a small-diameter and underutilized (SDU) lignocellulosic species in the southern region of the United States. Juniper trees were shredded to small chips, refined (fiberized or pulped), and made into a Rando mat using 10% HC-105 binder. The fiber was chemically modified twice, after chipping and after mat formation. Mat density was 0.109 to 0.131 g/cm^3 and thickness was about 1.3 cm. Mats were cut into 61-by 61-cm pieces. The filter mats were initially used at the Wayne National Forest to reduce metal contents from water affected by AMD. After being used for 3 days, the filter mats were dried and shipped to the Forest Products Laboratory in Madison, Wisconsin. The filter mats were washed with water to remove water-soluble components and dried again. All the filter mats except for those used for the labscale tests were shipped to the field site in New York State to be reused for the removal of phosphorus from water.

Four types of filter mats—juniper, base-treated juniper, WNF01, and WNF02—were used for the isotherm, kinetic, and column laboratory tests. "Juniper"designates the original filter mats. Base-treated juniper mats were treated with NaOH to improve cation exchange. Detailed description of this chemical treatment can be found in Zghida et al. [2002]. WNF01 designates the mats used in the Wayne National Forest. WNF02 designates the WNF01 mats that were treated with water to remove soluble components. All the filter mats were ground with a Wiley mill and sieved with a 20-mesh sieve for adsorption tests.

2.2. Elemental Analysis and Adsorption Tests

Elemental analysis of inorganic components in the solid samples was conducted with an inductively coupled plasma atomic emission spectrometer (ICP-AES, ULTIMA, Jobin Yyon Inc.).

Phosphorus isotherms for all samples were acquired through batch experiments. Solid samples weighing between 0.1 and 1.0 g were placed in 125-mL bottles with 50 mL of solution having 10 ppm phosphorus concentration. The ionic strength of the solutions was maintained at 0.01 M using $NaNO_3$. The samples. were sealed and placed in a shaker at room temperature. After 48 h of shaking, the suspension was filtered immediately with a 0.45-µm filter. Phosphorus concentration of the filtered solutions was analyzed by ICP-AES.

Adsorption kinetic experiments were performed in 1,000-mL solutions with 2.0 g of sample powders. The initial phosphorus concentration of the solution was 10 ppm, and the pH of the solution was maintained at 6.4 using HNO_3 and NaOH solutions. The suspension was stirred by a magnetic bar, and the samples were taken at various times during the 5-h experiment. Phosphorus concentrations of these samples were also measured by ICP-AES.

2.3 Column Test

Juniper mats charged with iron species at the Wayne National Forest were removed from the filtration boxes, washed with water, dried, and taken to actual sites at two dairy farms in the New York City watershed (Han 2002, 2003). The actual phosphate removal capacity was not clearly determined. The mats were cut into 4.5-cm diameter plugs combined with a Gilson Minipuls 3 pump at a flow rate of 4 mL/min. The pH of the phosphorus solution was adjusted to 7. Five plugs were weighed, packed into a 4.5-cm glass column, and eluted with 30 ppm phosphorus solution. A Gilson Fraction Collector 204 was used to collect 20-mL fractions at a flow rate of 4mL/min. The weight of the plugs, phosphorus concentration, total volume of standard solution to be eluted, and flow rate were determined based on practical experience; total elution time was limited to about 15 h so that a experimental set could be finished overnight.

2.4. Field Test

The filtration system was installed at two dairy farms selected from about 350 small farms scattered throughout the Catskill/Delaware watershed. There is no regulation limiting total maximum daily load (TMDL) of phosphates for individual farms, and small dairy farms discharge a considerable amount of phosphorus to the watershed. Cows are milked twice per day. After millung, the milking system is washed through three cycles with pure water, detergent, and acid cleaner. The wastewater from the milking system contains phosphorus from the detergent, and milk trapped in the milking system is drained directly to the land. The farms use manure as a nutrient source for cropland. There are some regulations that limit how much manure can be spread, but enforcement is apparently hard to regulate. The filtration system with the WNF02 mats was connected to the milk-house drain pipe to reduce the amount of phosphorus in the wastewater.

The filtration box was designed at the Forest Products Laboratory and made of fiberglass by a commercial builder. The filter frames are fitted into 13 slots in the box and 10 filter mats are placed inside the box (Fig. 1). The mathematical treatment of flow is described by Hur et al. [2003].

Water samples were collected twice/day for 3 days. Samples were taken at the inlet and outlet of the filtration box. The samples were analyzed at the Forest Products Laboratory by ICP-AES. Amount of total dissolved phosphorus was measured.

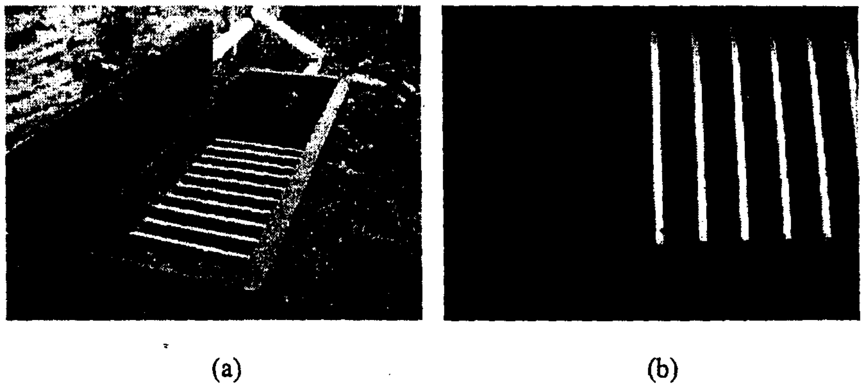

Figure I. Lignocellulosic filtration system: (a) filtration box; (b) filter frames inside filtration box.

3. RESULTS AND DISCUSSION

3.1. Elemental Analysis

Table 1 shows the contents of inorganic components in the solid samples. Juniper and base-treated juniper contained 4.670 and 6.533 mg/g iron, respectively. After these mats were used in the Wayne National Forest, the amount of iron in the WNF01 and WNF02 mats increased to 129.5 and 134.9 mg/g, respectively, while amounts of the other components were similar before and after treatment. After the treatment in the Wayne National Forest, iron components were mainly attached on the filter mats. Those filter mats contained about 13 wt % iron species.

Table 1 Elemental analysis of inorganic components in samples

Sample	Contents (mg/g)				
	Al	Fe	Pb	S	Zn
Juniper	0.112	4.670	0.177	4.592	0.100
Base-treated Juniper	0.116	6.533	0.184	4.763	0.103
WNF01	0.103	129.5	0.169	8.466	0.102
WNF02	0.076	134.9	0.254	7.027	0.068

The iron species originated from the water at the filtration sites. Many AMD sites are situated in the Wayne National Forest. The AMD sites drain strongly acidic water, and many metal elements are mobilized under strongly acidic conditions. The type of metal elements depends on the AMD site. The water at the AMD site where the filter mats are installed contains abundant iron species, compared with other metal components.

Several mechanisms involve the deposition of iron species on filter mats [Tiemann et al. 1999, Reddad et al. 2002]. Iron species are deposited on the filter surface through chemical interactions such as replacement with calcium ions and adsorption on active sites (e.g., phenolic or carboxylate sites). The mats physically block the solid, so that the solid is suspended on the mats.

3.2. Adsorption Behavior

Figure 2 shows the kinetic behavior of each sample. As expected, the sorption capacity of juniper and base-treated juniper is almost zero since phosphorus uptake remains around zero. Without any modification, lignocellulosic materials barely show any sorption capacity for phosphorus. In contrast, the kinetic data of WNF01 and WNF02, the filter media modified with iron species, sorption capacity for phosphorus. At first, the uptake of phosphorus increased; after 100 min, the sorption of phosphorus reached an equilibrium state.

The data points were fitted to several kinetic equations [Tiemann et al. 1999, Reddad et al. 2002, Romero-Gonzalez et al. 2001] and the results are represented in Table 2. Based on the determination coefficients for each model, the pseudo second order model and the parabolic diffusion model match well with the kinetic data. Since the parabolic diffusion equation is induced from diffusion-controlled adsorption, matching the results with parabolic diffusion equation supports that the kinetics of phosphorus sorption on WNF01 and WNF02 is diffusion-controlled. In addition, the pseudo second order model fitted the kinetic data well, showing kinetic constants (k) of 0.0526 and 0.0809 g/mg/min for WNF01 and WNF02, respectively, which indicates that adsorption on the filter surface is closer to chemisorption [Ho and McKay 2000].

Table 2. Determination coefficients for each model equation

Sample	Pseudo 1st	Pseudo 2nd		r^2		
	r^2	r^2	k (g/mg/min)	Power function	Simple elovich	Parabolic diffusion
WNF01	0.906	0.998	0.0526	0.923	0.911	0.930
WNF02	0.914	0.983	0.0809	0.769	0.769	0.942

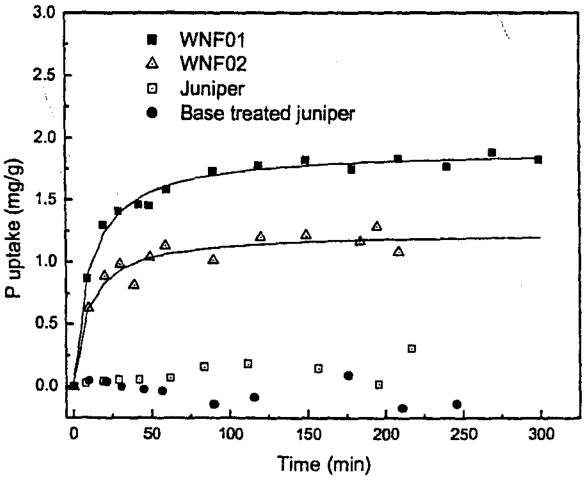

Figure 2. Kinetics of phosphorus adsorption for each sample.

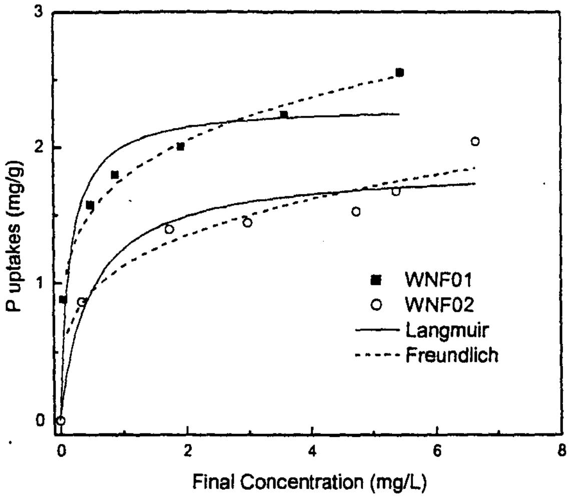

Figure 3. Isotherms of phosphorus adsorption for each sample and fitted lines.

Isotherms for phosphorus adsorption and their fitted results are shown in Figure 3 and Table 3. With determination coefficients, it is not apparent which isotherm model is dominant in the isotherm data. The Q_{max} (maximum adsorbate loading onto adsorbent) values of WNF01 and WNF02 were 2.31 mg/g and 1.85 mg/g, respectively, which indicates that washing slightly reduced the phosphorus sorption capacity of the filter medium The same phenomenon was observed in the kinetic results. However, since those figures are similar to the capacities of natural inorganic products that have been used for phosphorus removal, the modified lignocellulosic filter media are comparable with other inorganic filter media. Table 4 lists phosphorus sorption capacities of diverse filters reported in the literature [Ayoub et al. 2001, Brady 1999, Baker 1998].

Table 3. Parameters from fit of isotherms to Freundlich and Langmuir models

Sample	Freundlich*			Langmuir*		
	k	1/n	r^2	Q_{max} (mg/g)	b	r^2
WNF01	1.76	0.211	0.986	2.31	6.41	0.947
WNF02	1.12	0.260	0.891	1.85	2.06	0.942

Langmuir ($q_{eq} = \dfrac{bQ_{max}C_{eq}}{1+bC_{eq}}$) and *Freundlich* ($q_{eq} = KC_{eq}^{1/n}$).

Table 4. Phosphorus sorption capacities of diverse filter media

Sorbent	Type	Q_{max}(mg/g)	Preferred pH	Reference
Kandiustalf	Kaolinite, Fe oxides	0.394	—	Brady et al. (1990)
Rhodustaf	Kaolinite, Fe oxides	0.465	—	Brady et al. (1990)
Tropohumults	Fe, Al oxides, kaolinite	2.060	—	Brady et a.l (1990)
Iron and aluminum oxide coated sand	Fe, Al oxides	0.011-0.033	6.9–7.7	Ayoub et al (2001)
Iron and aluminum oxide coated olivine	Fe, Al oxides	0.015-0.035	8–9	Ayoub et al (2001)
Goethite[a]	Fe oxides	1.3[a]	8–9	Baker et al (1998)
AA300G[a]	γAl oxides	2.0[a]	8–9	Baker et al (1998)
C-70[a]	α Al oxides	1.0[a]	8–9	Baker et al (1998)
Iron(III) –loaded carboxylated Polyacrylamide-grafted sawdust[a]	Fe	9.38	2.5	Unnithan et al (2002)

3.3 Column Test

An adsorption test was necessary to evaluate the behavior of the filter media in varied concentration or weight. However, it was necessary to evaluate behavior in an ideal condition (see section 2.3) to find out what this medium is capable of The same experiment was conducted six times; the calculated maximum phosphorus adsorption capacity was 3 to 4 mg/g. As long as there were iron species in the medium, phosphorus was adsorbed by the medium. P is the actual concentration of 30 ppm phosphorus solution after passing through the filter medium. Pnet is how much P was adsorbed by the medium (30 - P). Lower concentrations of Fe decreased adsorption of P (Fig. 3). The unwanted Fe was adsorbed by the addition of cation-exchanging juniper media. The adsorption capacity of a cation exchanger (another type of chemically modified juniper) is about 10 times that of an anion-exchanger. The undesired Fe concentration was dramatically decreased by the addition of cation-exchanger after the anion-exchanger (Fig.4). Of course, total adsorption capacity was decreased in this operation.

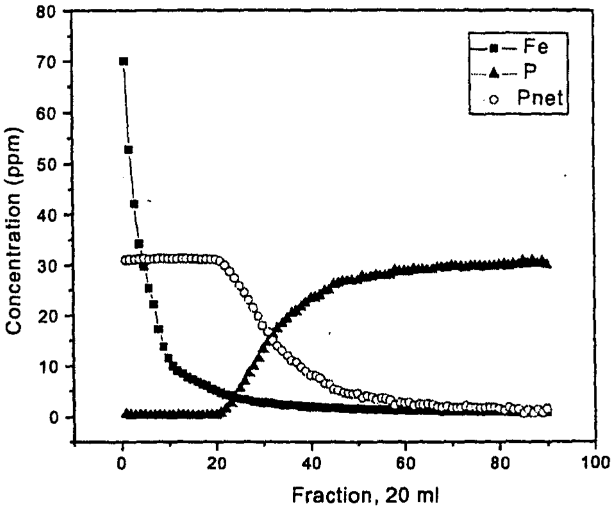

Figure 3. Elution of standard 30 ppm P solution as a function of fraction.

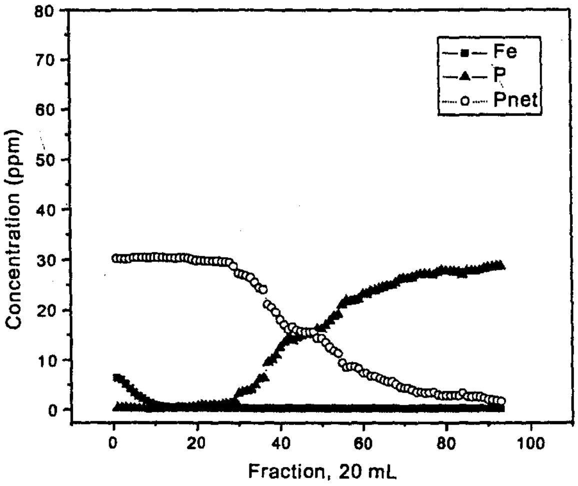

Figure 4. Elution of standard 30 ppm P solution as a function of fraction. Cation-exchanger was added at the end ofcolumn to control Fe.

3.4. Field Test

In the laboratory tests, only inorganic phosphorus was used as an adsorbate. However, phosphorus in wastewater exists in several forms—particular phosphorus, organic phosphorus, inorganic phosphorus, total phosphorus, and so on. In the field test, the phosphorus concentration refers to the amount of total dissolved phosphorus; every water sample was filtered with a 0.45-µm microfilter before analysis. In addition, in the laboratory test, the removal of phosphorus with the filter was accomplished through physicochemical processes, but the removal mechanism in the field condition is complicated. Except for adsorption, another possible process for phosphorus removal in the field is biological removal by microorganisms on the lignocellulosic filter mats. According to Chiou et al. [2001] and Morgenroth and Wilderer [1998], the biofilm forms on a support material; in this case, the lignocellulosic filter medium removes phosphorus from water.

Table 5 shows the results of the performance of filter media that were installed on the farms. Removal efficiency varied in daily sampling; the average removal efficiency of WNF02 was 41.51% at 59.19 ppm of inlet phosphorus concentration. This result implies that the filtration system containing the lignocellulosic-based filters decreased the amount of phosphorus loaded to the watershed from the farm by about 40%.

Table 5. Phosphorus analysis of water samples taken at inlet and outlet of filter box

Sampling		Concentration of total dissolved phosphorus			Removal efficiency (%)
		Inlet (ppm)	Outlet (ppm)	Delta	
Day 1	a.m.	57.55	34.89	22.65	39.36
	p.m.	57.57	19.87	37.70	65.48
Day 2	a.m.	56.41	31.41	24.99	44.30
	p.m.	59.76	44.02	15.73	33.60
Day 3	a.m.	64.68	42.94	21.73	33.60
Average value		59.19	34.62	24.57	41.51

4. CONCLUSION

When modified with Fe species, the lignocellulosic filter materials showed sorption capacities for removing phosphorus from water. In the isotherm test, Q_{max} was 1.85 mg/g, which is comparable with that of other natural filter media. In the column test, the maximum capacity was about 3.5 mg/g. However, some iron was released when this reaction took place. The overall adsorption rate was about 40% reduction at the 60 ppm range of phosphorus using one filtration unit. The cost of this filtration system is relatively inexpensive, and there is room for improving this system.

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