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STORMWATER FILTRATION OF TOXIC HEAVY METAL IONS USING LIGNOCELLULOSIC MATERIALS SELECTION PROCESS, FIBERIZATION, CHEMICAL MODIFICATION, AND MAT FORMATION

James S. Han
U.S. Department of Agriculture, Forest Service. Forest Products Laboratory, Madison, Wisconsin U.S.A

Lignocellulosic materials were evaluated for their effectiveness in filtering toxic heavy metals from stormwater. Kenaf, alfalfa, juniper, and aspen fibers were used as models to evaluate the effectiveness and limitations of chemical modification and the extent of fiber degradation. Individual and mixed aqueous solutions of nickel, copper, zinc, and cadmium in various concentrations were exposed to the lignocellulosic fibers to estimate ion-exchange capacity and competition between ionic species. The potential of lignocellulosic fibers to act as filters is related to their sugar, extractives, and lignin contents and physical properties. Fiberization and formation of fibers into mats and the cost and availability of the filtration process are also discussed.

1 INTRODUCTION

Agro-based fibers such as kenaf, roselle, and tobacco have been shown to be effective in sorption of heavy metal ions from stormwater filtration systems. In

contrast, most wood-based fibers have a relatively low capacity for filtering heavy metals [1-3]. Although researchers have tried to increase the sorption capacity of lignocellulosic fibers through chemical modification, more success has been achieved with bark and marine fibers [4–10]. Chemical modification has either been too expensive or it has caused other problems, such as bleeding of excessive quantities of colored organic compounds, odor, or further pollution through the use of toxic chemicals.

It is important to understand that lignocellulosic materials are not pure polymers. Their main constituents are cellulose, lignin, hemicellulose, and extractives. Except for cellulose, the chemical structure of these components can differ widely. Consequently, removal of heavy metals can be governed by any of four basic mechanisms: absorption, adsorption, ion exchange, and chelation. The most probable mechanism may be ion exchange.

The goal of the work reported here was to examine agro- and wood-based fibers that can be formed into a mat so that massive stormwater can be filtered at reasonable residence time and low cost. Maximum capacity, competition between ionic species, and interference caused by calcium are covered in this report.

To compare one type of fiber to another, it was necessary to pulverize the different substrates to an equal particle size and to expose them to high metal concentrations to estimate maximum sorption rates.

2 PROCEDURE

2.1 Fiber selection and preparation

Kenaf, alfalfa, pinyon juniper, and aspen fibers were used as model fibers for filtration. Digested alfalfa fiber represents a major potential source of fiber supply. About 23 millions tons of digested fiber could be recovered from the 45 million tons of alfalfa produced annually in the United States. Pinyon juniper is

prolific on national lands in the southwest and adjacent states (2.8 million hectares) as well as in Mexico (>10 million hectares). Pinyon juniper, which has high extractives content and bark, has shown a fairly high sorption rate. Aspen fibers were used because of their high hemicellulose content.

Most lignocellulosic raw materials need to be reduced in size before they can be used for filtration. One method is pulverization through chipping followed by Wiley, ball- or hammer-milling, or by sawing. Pulverization ignores the integrity of anatomical structure. The Wiley mill used for screening had two stationary blades and a rotor with four cutting edges that revolve at a high speed; the resultant shearing action minimized moisture loss.

The other method, fiberization through refining or mechanical pulping, preserves fiber integrity and the final product is a collection of fibers. Like wood fibers, agro-based or nonwood fibers need to be reduced before they can be used for filtration. The usual process used in our laboratory is refining, which allows the fiber to be made into a web or mat and also washes the substrates. Refining can be tailored by varying steam pressure, duration, and types of plates.

2.2 Chemical Modification

Sulfonation was conducted by dissolving 168 g sodium sulfite and 19 g sodium bicarbonate in 1 L water (stock solution); 10 mL of this mixture was added to 100 g fiber, stirred, and heated to 70°C for 2 h.

Sulfonation in combination with refining was performed by mixing the sample with equivalent volume of stock solution and enough water to soak the sample. Refining was conducted after 1 week.

2.3 Reagents and Analysis

Standard AAS reference was purchased or 1000-mg/L standard stock solutions were prepared from nickel (II) nitrate hexahydrate, zinc nitrate hexahydrate, copper metal, anhydrous cadmium chloride, and calcium carbonate dissolved in

equivalent of 2% nitric acid. Sodium sulfite and bicarbonate were reagent grade.

Samples were analyzed by atomic absorption spectrophotometry (AAS).

3 FILTRATION CAPACITY OF UNMODIFIED FIBERS

3.1 Kenaf

Kenaf bast fibers were ground to pass 0.18-mm (30-mesh)screen; any fines less than 0.18 mm (80 mesh) were removed. Fibers were oven dried for 24 h at 40°C. Standard stock solutions were used to make solutions of individual metals (4, 20, and 40 mg/L) and mixed metals (1, 5, and 10 mg/L; 4, 20, and 40 mg/L total metal ion concentration, respectively). One gram of sample was weighed into a 25-mL Erlenmeyer flask and 25 mL standard solution was pipetted into the flask. Samples were covered with Parafilm and oscillated for residence time of 1, 3, and 6 days. Samples were then vacuum filtered and analyzed by AAS-flame methods.

Figs. 1 and 2 show removal rates of individual metal ions by kenaf after 1 day residence time. Kenaf was most effective at removing cadmium. Kenaf was more effective at removing ions from solutions of mixed metals than from solutions of individual metals. For mixed solutions as for individual metal solutions, kenaf was most effective at removing cadmium (fig. 3).

3.2 Alfalfa

Fiber and sample preparation and sample analysis were the same as that for kenaf. Only mixed ion solutions were prepared at concentrations of 1, 10, 50, and 100 mg/L (4, 40, 200, and 400 mg/L total metal ion concentration, respectively). Residence times were 1 h, 1 day, 3 days, and 6 days (1, 24, 72, and 144 h, respectively).

Alfalfa provided a much better filtration substrate than did kenaf (fig. 4). Residence time had the greatest effect on the rate of copper removal. For the 50-

mg/L (fig. 5) and 100-mg/L (fig. 6) concentrations, rate of removal increased with length of residence time. These results suggest that at higher ion concentrations, removal rate increases with an increase in residence time.

Alfalfa influenced the order in which metals were removed. Active sites were taken by more active Cu, Cd, and Zn ions. As individual ions, all four ions had about the same ion-exchange capacity at 40 mg/L and 6 days of residence time.

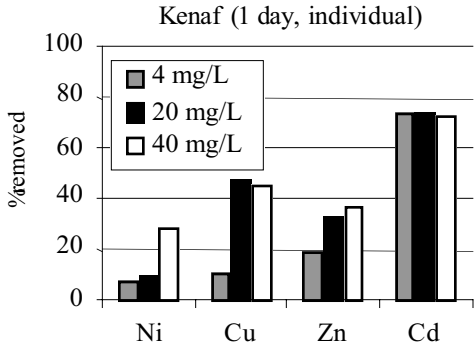

Fig. 1 Percentage of individual ions removed.

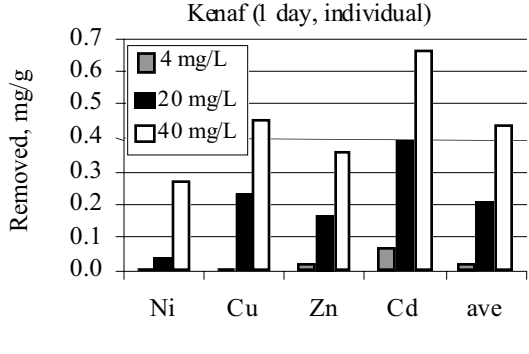

Fig. 2 Amount of individual ions removed.

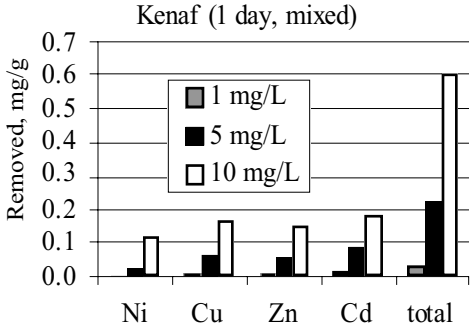

Fig. 3 Amount of mixed ions removed.

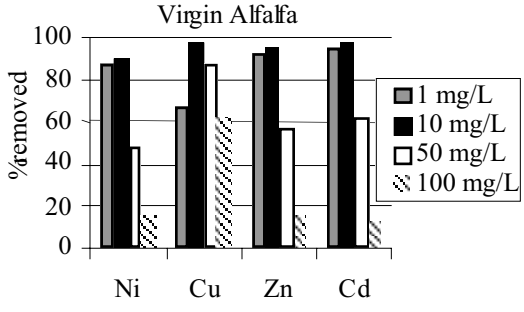

Fig. 4 Percentage of mixed ions removed

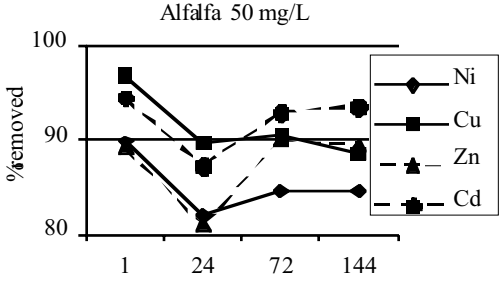

Fig. 5 Percentage alfalfa removed at 50 mg/L.

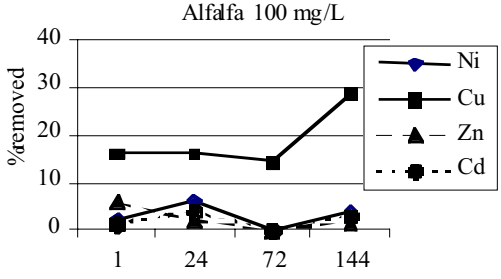

Fig. 6 Percentage alfalfa removed at 100 mg/L

5 FILTRATION CAPACITY OF MODIFIED FIBERS

5.1 Juniper

The pinyon juniper sample was mixture of wood and bark. Since the sample contained some bark, it was expected to have high filtration capacity. Chips were soaked in a mixture of sodium sulfite and sodium bicarbonate at ambient temperature for a week and then refined so that modification and refining could be conducted simultaneously.

Fiber was prepared by Wiley milling (W) or refining (R). A 0.18-mm screen was used for Wiley milling. For refining, chips (5 kg) were steamed at 413 kPa for 3 min; feed rate was 6.5 and plate gap was 0.015.

Only mixed ion solutions were prepared; concentrations were 1, 10, 50, and 100 mg/L (4, 40, 200, and 400 mg/L total metal ion concentration, respectively). Calcium was added to duplicate solutions to determine its effect on filtration capacity of hard water. Residence time was 1 day.

The best overall results were obtained with a combination of milling and sulfonation (fig. 7). Calcium exerted a greater effect on filtration capacity of milled fibers compared to refined fibers (fig. 8).

5.2 Aspen

Only wood chips were used in this experiment. Like juniper, aspen wood chips were sulfonated. Addition of calcium to the solution reduced sorption capacity (fig. 9). In sulfonated aspen, sorption capacity was increased for zinc and cadmium at higher concentrations (fig. 10).

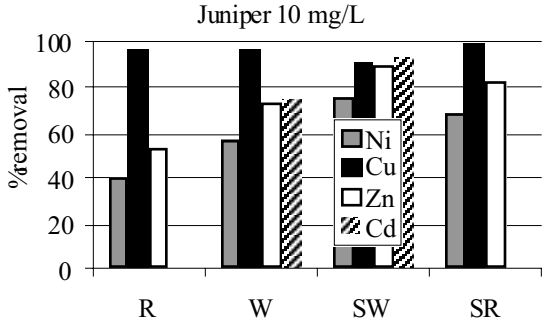

Fig. 7 Percentage juniper removed at 10 mg/L. R is refining; W, Wiley mill; SW sulfonation + Wiley mill; SR, sulfonation + refining.

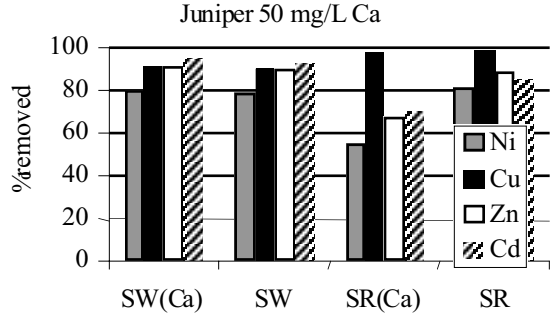

Fig. 8 Percentage juniper removed at 50 mg/L plus calcium.

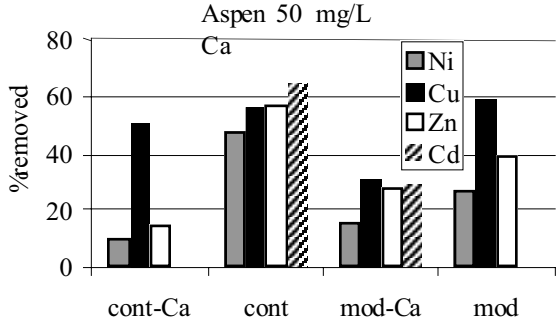

Fig. 9 Effect of sulfonation (mod) and calcium (mod-Ca) on filtration capacity of aspen compared to control (cont).

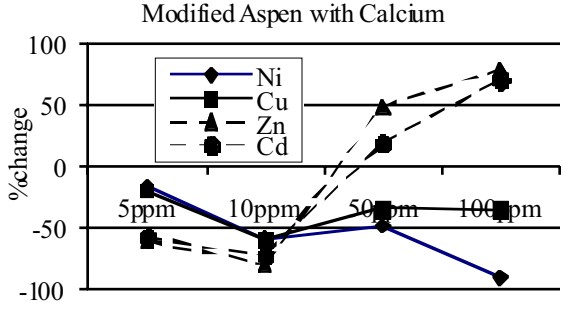

Fig. 10 Percentage of change caused by addition of calcium.

5 BIODEGRADABILITY OF LIGNOCELLULOSIC MATERIALS

One benefit of using lignocellulosic materials for filtration is their biodegradability after the filtration is disposed of. Most lignocellulosic materials, especially agricultural fibers, will degrade in contact with moisture or water; some lignocellulosic materials, such as flax and straw, will degrade within days or weeks. Others, such as coconut fiber and sphagnum moss, will withstand degradation. The extent of biodegradability can be predicted based on chemical composition, physical properties, and preservative activities. High lignin content is the most desirable factor for biodegradation. To test biodegradation, coconut, flax, and sphagnum moss fibers were exposed to adverse conditions. Fibers were placed in fish culture tanks at about 27°C for 6 to 92 days. Lignin content remained stable and glucan and xylan contents were decreased with increase in residence time (table 1). After only 10 days, flax lost 43% weight (28.70 g compared to 48.57 g control weight). When in contact with fresh water, marine fibers such as kelp, which have a high natural sorption rate, degrade much faster than does flax.

Fiber and residence time	K. lignin	Arabinan	Galactan	Rhamnan	Glucan	Xylan	Mannan
Coconut, 0 day	34.50	1.04	0.42	0.10	33.99	16.85	0.22
Coconut, 92 day	34.40	0.82	0.66	0.39	8.38	4.26	0.50
Flax, 0 day	22.90	0.37	3.53	0.30	69.09	18.87	4.22
Flax, 6 days	22.90	0.75	1.75	0.70	27.52	5.22	2.18
Sphagnum moss, 0 day	18.40	0.82	5.52	1.51	24.12	4.12	3.62
Sphagnum moss, 9 days	17.77	0.50	4.32	1.23	17.29	2.81	2.97

Table 1 Decomposition of fibers (%).

Common name	Botanical name	Classification	Lignin (%)	Capacity
Sugar cane, bagasse	Saccharum officinarum	Straw fiber	19.9	0.3
Oak	Quercus spp.	Hardwood fiber	23.2	0.5
Gum	Liquidambar styraciflua	Hardwood fiber	24.3	0.5
Aspen	Populus grandidentata	Hardwood fiber	21.8	0.9
Redcedar, Eastern	Juniperus virginiana	Softwood fiber	40.0	1.2
Loblolly pine, cone	Pinus taeda	Softwood fiber	36.4	1.5
Lecheguilla	Agave lecheguilla	Bast fiber	15.2	2.0
Coconut, shell	Cocos nucifera	Shell	35.5	2.6
Jute	Corchorus capsularis	Bast fiber	13.5	3.8
Sisal	Agave sisalana	Leaf fiber	12.5	4.9
Kudzu, fiber	Pueraria lobata	Bast fiber	15.5	5.2
Abacca	Musa textilis	Leaf fiber	12.5	5.5
Roselle	Hibiscus sabdariffa	Bast fiber	9.5	5.3
Flax	Linum usitatissimum	Bast fiber	2.9	5.5
Kudzu, bark	Pueraria lobata	Bast fiber	19.3	8.2
Kenaf, fiber	Hibiscus cannabinus	Bast fiber	9.9	8.5
Hemp	Cannabis sativa	Bast fiber	3.0	9.5
Salicornia	Salicornia bigelovii	Bast fiber	13.5	10.1
Tobacco, fiber	Nicotina tabacum	Bast fiber	16.5	10.5
Sunn hemp	Crotalaria juncea	Bast fiber	11.1	11.8
Tobacco, bark	Nicotina tabacum	Bast fiber	9.5	14.3

Table 2 Removal capacity of copper (mg/g substrate) at pH 5.5.

6 FACTORS THAT AFFECT SORPTION CAPACITY

6.1 Fiber chemistry

The possible explanation for why lignocellulosic materials have some degree of heavy metal ion sorption capacity can be explained in terms of cellulose, lignin, hemicellulose, and extractives.

Cellulose, a homopolysaccharide of glucose units, is the most abundant lignocellulosic material and a stable compound. Cotton with high cellulose content shows very low sorption capacity.

The generally high sorption capacity of nonwoods can be attributed to syringyl lignin. Guaiacyl lignin is found in softwoods and a mixture of syringyl and guaiacyl lignin in hardwoods. The general order of sorption capacity for nonwoods, hardwood, and softwood is nonwood (3%–10%) > hardwood (20%–25%) > softwoods (26%–32%). Two assumptions can be made about the relationship of lignin to sorption capacity: (1) the lower the lignin contents, the higher the sorption capacity or (2) low lignin content represents low density and easy accessibility of ions to active sites. Table 2 compares various lignocellulosic materials in increasing order of copper sorption capacity

Hemicellulose is a group of heterogeneous polysaccharides. In softwoods, hemicellulose takes the form of galactoglucomannan, arabinoglucuronoxylan, and arabinogalactan). In hardwoods, hemicelluloses are glucuronoxylan and glucomannan. Mannose, with an axial hydroxyl group on C-2, and galactose, with an axial hydroxyl group on C-4, can provide active sites for ion exchange. Hemicellulose is chemically less stable than cellulose. Some hardwoods, such as aspen, with high hemicellulose content show high sorption capacity.

Extractives can be regarded as nonstructural wood or plant constituents and can be identified as fats, phenolics, resin, etc. Some barks contain tannins and the extractives can vary. A good example is juniper. Extractives of juniper wood are thujaplicins (α, β, γ). Generally called tropolones, thujaplicins are unsaturated 7-membered carbon ring nootkatin, dolabrin, thujaplicinols (α, β),

and pygmaein [12]. These extractives provide carbonyl and hydroxyl groups to contribute in ion exchange. Monomeric flavonoids, which can be derived from juniper bark, are known to have metal complexation properties .There are three possible metal complexing sites within a flavonol, which contain hydroxyls at C-3,5, 3', and 4 [13].

We conclude that cellulose and lignin make minimum contributions to ion exchange and hemicellulose and extractives are the major players. Chelation is another possible chemical reaction in the presence of flavonoids.

The sorption capacity of lignocellulosics for metal ions is generally described as adsorption. The cations are attracted to negatively charged active sites throughout the lignocellulosic materials. The exact location of the active sites has yet to be determined, but it is believed that hydroxyl and carbonyl groups are the main suppliers of active sites. These groups are abundant in lignocellulosics, yet they are tightly bonded to each other in cellulose and lignin and thus are not available unless hydrogen bonding is broken through chemical modification.

6.2 Chemical modification

Various groups have studied chemical modification of lignocellulosics [5-11]. Simkovic [6] introduced hydroxypropyl groups using epichlorohydrin. However, Using 13C-NMR, he was not able to verify their linkage to polysaccharide.

Sulfonation is a pulping procedure that acts on lignin. Sulfonated lignin becomes soluble in water and delignification occurs at 170°C. Our sulfonation procedure was a mild process. Our intention was not to remove all the lignin but to sulfonate some lignin to increase ion exchange capacity.

6.3 Shape of filtration medium

Substrates used as filtration media need to be formed into a shape that maximizes surface area. One possibility is pellets. We recommend formation of the material into nonwoven mats or webs. Mats or webs can be formed by either

the Rando Webber or Dan Webber methods. Both methods work in a similar manner; Rando Webber is based on a needle-laying process and Dan Webber on an air-laying process. Substrate fibers need to be at least 1 mm long for such mats. Binding chemicals are usually added. Such chemicals reduce filtration capability and warrant careful examination before use.

7 CONCLUSION

Various kinds of agro- and wood-based fibers can be used to filter toxic heavy metals from stormwater. To test the techniques described in this paper, we are installing a stormwater filtration system in the Madison area and hope to expand it to other areas with high pollution levels. The most effective fibers for filtration are available at very low or no cost. Moreover, many fibers yield co-products such as tobacco stalks, corn ears, and rice hulls. Research is needed on the most effective fibers for stormwater filtration.

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