POLYMER-TREATED WOODY BIOMASS: A FILTRATION MEDIUM FOR REMOVING PHOSPHATE FROM WATER

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ABSTRACT: A two-stage treatment of refined aspen wood fiber with solutions of carboxymethyl cellulose (CMC) and ferrous chloride afforded a filtration medium that was effective in removing phosphate from test solutions. To assess the stability of the filtration medium, samples exposed to the test solutions were analyzed by FTIR spectroscopy. The resultant spectra indicated that a significant amount of the carboxylate functionality, imparted by the CMC, remained with the fiber. Determinations of iron and phosphorous levels in these samples by elemental analysis confirmed that the CMC provided additional sites to complex iron ions, and that phosphate removed from the test solutions was retained within the filtration medium. To better understand the distribution of the CMC in the fiber matrix, treatments were also carried out with CMC containing a polymeric fluorescent dye. Observations by confocal laser scanning microscopy showed partial filling of the fiber lumens. To address concerns related to the hydraulic conductivity of the fibers, aspen wood particles of different sizes were also treated. Results showed that the phosphorous uptake capacity decreased with decreasing particle size. Measurement of iron released into the test solutions suggested that the smaller wood particles may be preferred since they showed the lowest release of iron relative to the amount of phosphate removed.

INTRODUCTION

Since most natural surface waters are either nitrogen or phosphorous limited (Kioussis et al., 1999), stormwater containing elevated phosphorous levels is often the culprit for the proliferation of algae and aquatic weeds. Cost effective stormwater control measures are needed in environments where widespread fertilizer use and other forms of agricultural runoff have been linked to the eutrophication of nearby natural surface waters. Numerous reports in the literature suggest that chemically-modified biomass can be used to capture heavy metals (Shibi and Anirudhan, 2005; Shin and Rowell, 2005; Shukla and Pai, 2005). Far fewer reports involve the use of biomass for the sorption of hydrocarbons (Boving and Zhang, 2004) and nutrients, such as soluble nitrates (Orlando et al., 2002) and phosphates (Tshabalala et al., 2004, Unnithan et al., 2002). The adsorption of metal ions can occur through chemistries already present in the biomass, but for the adsorption of phosphate, the use of biomass has typically relied on some sort of chemical modification. For example, carboxylated polyacrylamide-grafted sawdust provided an increased retention of iron ions thereby providing adsorption sites for phosphate (Unnithan et al., 2002). Alternatively, a simple base treatment applied to juniper fiber provided a biomass-based ion exchanger that adsorbed sufficient amounts of iron to significantly increase the phosphorous removal efficiency (Han et al., 2005). An option under investigation in our laboratory is the use of a non-toxic anionic polymer, carboxymethyl cellulose, to increase the loading of iron ions in refined aspen wood fibers thereby imparting an improved capacity to remove phosphate from stormwater (Eberhardt et al., 2006). Here we report our latest findings on our characterization of this filtration medium as well as adaptations to simplify the process and improve functionality.

MATERIALS AND METHODS

Materials and General Methods. Refined aspen wood fiber, obtained from a hardboard plant (Georgia Pacific, Philips, WI), was used as received. Wood particles were obtained by grinding aspen wood chips (AlphaPet, Inc., St. Louis, MO) in a Wiley mill equipped with a 5 mesh screen and then classifying with a sieve shaker (W.S. Tyler, Ro-Tap, Model RX-29) equipped with 20, 35, and 80 mesh sieves. The moisture contents (wet weight basis) of the wood fiber (6.0%) and the wood chips (8.9%) were determined by drying aliquots in an oven at 103 ± 2 °C. The CMC sodium salt (Aldrich) used for the

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treatments was labeled as having an ultra low viscosity (10-55 mP·s for a 4% aq. soln. at 25 °C, MW = 100,000-150,000) and the ferrous chloride (J.T. Baker) was the 4-hydrate. FTIR spectra were collected using a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Smart Golden Gate MKII single refection ATR accessory. Samples were placed on the diamond crystal and pressure applied with the anvil affixed to the accessory clamping mechanism. Elemental analyses were conducted by Galbraith Laboratories, Inc. (Knoxville, TN).

Preparation of Filtration Media. Wood fiber and wood particles to be treated were transferred to a treatment solution of 4% (w/v) CMC in deionized water using a sample to treatment solution ratio of 1:20. After wetting, samples were allowed to stand (1 hr.) before the application of a vacuum (15 min.) to facilitate saturation. Samples were allowed to stand for a second period of time (4 hrs.) before vacuum filtration over filter paper in a Büchner funnel. Treated samples were dried under ambient conditions and then in an oven (60 °C). CMC-treated and untreated samples were transferred to a 12% (w/v) solution of ferrous chloride in deionized water, using the same sample to treatment solution ratio, and processed as above (1 hr. soak, 15 min. vacuum, 4 hr. soak). After vacuum filtration with a Büchner funnel alone (no filter paper), the samples were washed with 2 volumes of deionized water. Samples were then washed into a Büchner funnel containing 2 sheets of filter paper which facilitated dewatering. Samples were dried as above before testing.

Sorption Testing. The CMC/Fe- and Fe-treated samples, from both the wood fiber and wood particles, were ground in a Wiley mill equipped with a 40 mesh screen to ensure a homogeneous sample for sorption testing. The phosphate test solution (100 mg/L) was prepared by dissolving potassium dihydrogenphosphate (98 + %, Aldrich) in deionized water. Aliquots of each sample (0.2 g) and the test solution (50 mL) were added to small plastic bottles that were then capped and shaken (150 rpm, 24 hrs.) under ambient conditions. Suspensions were filtered through a syringe filter (0.45-μm pore size) and phosphorous concentrations determined by ICP-OES (Jobin Yvon, Inc., Ultima ICP–OES, Edison, NJ). The values for initial and final phosphorous concentrations were used to calculate the uptake capacity (mg/g) as the amount of phosphorous sorbed at equilibrium per amount of sample. Results are based on averages from analyses carried out in triplicate.

Confocal Laser Scanning and Scanning Electron Microscopies. Wood fiber (50 mg) was treated with a solution (1 mL) containing CMC (3%, w/v) and tetramethylrhodamine isothiocyanate-dextran (1%, w/v, Sigma, MW = 155,000) using the above-described treatment process. Dried fibers were fixed on glass microscope slides with Permount (Fisher Scientific) mounting medium and observed using a Bio-Rad MRC-1024ES confocal laser scanning microscope. Dried fibers, both untreated and CMC/Fe-treated, were mounted on aluminum stubs with a conductive double-sided tape and imaged with a LEO EVO40 scanning electron microscope under ultra high vacuum conditions with a 2 keV accelerating potential.

RESULTS AND DISCUSSION

Initial experiments demonstrated that by treating refined aspen wood fiber with iron salts, one could impart limited capacities to remove phosphate from test solutions; untreated fiber samples showed no detectable phosphate removal. To provide additional sites to complex iron ions, and thereby impart greater phosphorous uptake capacities, fiber samples were pretreated with CMC solutions before treating with the ferrous chloride solutions. Batch isotherm testing showed that the sorption of the phosphate gave a better fit with the Freundlich isotherm model than the Langmuir isotherm model (Eberhardt et al., 2006). This suggested a mechanism of phosphate precipitation within the filtration medium rather than the adsorption of a phosphate monolayer on a discrete surface.

At this juncture, it remained to be verified that the phosphate removed from solution was indeed retained by the filtration medium; it was plausible that if iron ions were released from the filtration medium, the mechanism of phosphate removal from solution could have involved the precipitation of the phosphate apart from said filtration medium. To address this issue, CMC/Fe- and Fe-treated fibers were recovered

and dried for analysis by FTIR spectroscopy and elemental analysis. FTIR spectroscopy of samples not subjected to sorption testing showed the CMC/Fe-treated fiber to have greater signal intensity at about 1600 cm^{-1} than that for the Fe-treated fiber (Figure 1); this is indicative of the added carboxylate functionality from the CMC. Analysis of CMC/Fe-treated fiber after sorption testing also showed a greater signal intensity in this region albeit somewhat reduced from that observed before sorption testing. This finding suggests that some of the CMC-Fe complex on the surface of the fibers may have been sloughed off during sorption testing.

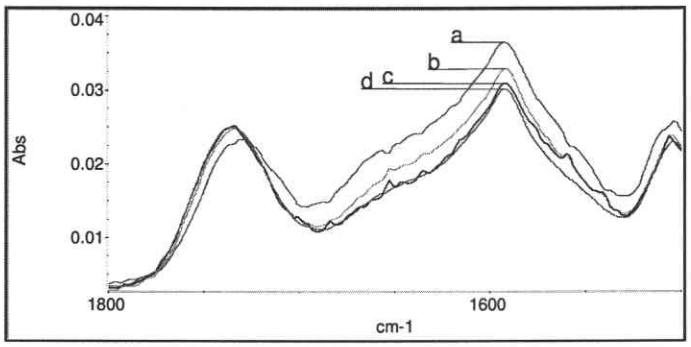

FIGURE 1. FTIR Spectra of Refined Aspen Wood Fiber before and after Sorption Testing: CMC/Fe-Treated (a = before, b = after) and Fe-Treated (c = before, d = after).

Results from the elemental analyses are shown in Table 1. These data demonstrate the significantly higher iron content for the CMC/Fe-treated fibers over that for the Fe-treated fibers. This resulted in the much greater capacity of the CMC/Fe-treated fibers to remove phosphate from the test solutions. The elemental analysis results provide evidence that the phosphate removed from the phosphate test solutions was retained by the filtration media. Moreover, the findings indicate that the CMC-Fe complex is sufficiently stable so as to provide a viable option for increasing the phosphorous uptake capacity for biomass-based filtration media.

TABLE 1. Iron and Phosphorous Contents of CMC/Fe-Treated and Fe-Treated Refined Aspen Wood Fibers before and after Sorption Testing

Filtration Medium Preparation	Sorption Testing	Iron Content (mg/g)	Phosphorous Content (mg/g)
Fe-Treated	Before	2.8	0.11
Fe-Treated	After	2.5	0.97
CMC/Fe-Treated	Before	20.9	0.054
CMC/Fe-Treated	After	16.3	4.58

Our investigation of the CMC/Fe-treated fiber then focused on developing a better understanding of the location of the CMC-Fe complex in the fiber matrix. Confocal laser scanning microscopy was used since it provided the ability to obtain images at the surface of a fiber through to the lumen. As expected, addition of a fluorescent dye (rhodamine B) to a solution of 4% (w/v) CMC in deionized water simply resulted in fiber staining. To circumvent this problem, we explored the use a polymeric version of the dye, tetramethylrhodamine isothiocyanate-dextran, which would not stain the fibers but be carried along

with the CMC during the treatment process. The lack of fluorescence with low additions of the polymeric dye resulted in the use of a concentration of 1% (w/v). To adjust for the increased solution viscosity from the polymeric dye, the concentration of the CMC in the treatment solution was adjusted from 4% to 3% (w/v). Images obtained by confocal laser scanning microscopy are shown in Figure 2. Bright fluorescence in the lumens of the fibers shows that under the treatment conditions employed, the CMC partially filled the lumens of the refined aspen wood fibers. Accordingly, a significant amount of the CMC-Fe complex is sufficiently encapsulated to prevent losses by abrasion. Observations by scanning electron microscopy were consistent with this result since similar images were obtained for fiber samples before and after the CMC/Fe treatment (Figure 3). Thus the CMC-Fe complex may have coated the fibers, but did not appear to remain as large deposits, except for those within the fiber lumens.

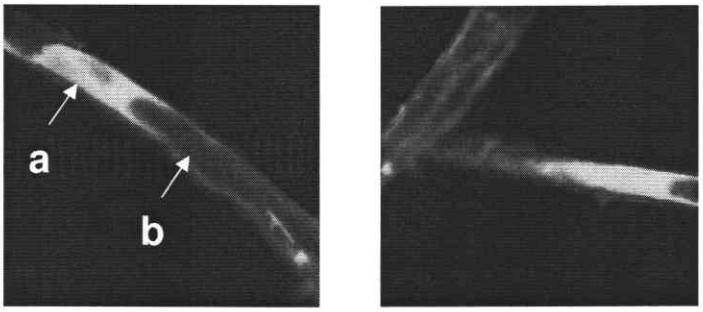

FIGURE 2. Confocal Laser Scanning Microscopy Images of Refined Aspen Wood Fibers after Treatment with CMC and Polymeric Dye (a = lumen with CMC and polymeric dye, b = empty lumen).

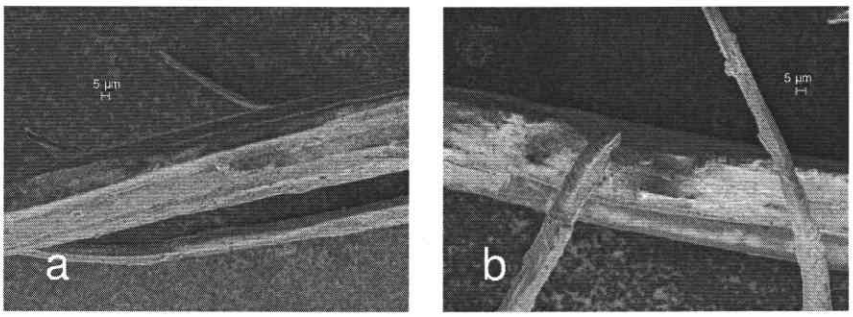

FIGURE 3. Secondary Electron Images of Refined Aspen Wood Fibers before (a) and after (b) CMC/Fe-Treatment.

As an alternative to the refined aspen wood fibers, it was of interest to determine if aspen wood particles might serve as a suitable substrate for the CMC-Fe complex. Whereas the refining process is carried out with steam/water, wood particles could be prepared by simply grinding wood in a relatively dry condition. Wood particles were also considered as an option to address concerns related to the hydraulic conductivity of the fibers. Wood particles in size classes of 5-20, 20-35, and 35-80 mesh were treated as before and subjected to sorption testing to determine the values for phosphorous uptake capacity and the release of iron into the test solution. Samples based on the wood fibers were prepared in parallel with the wood particles for direct comparison. Preliminary results in Figure 4 show that the phosphorous uptake capacities were higher for the original batch of CMC/Fe-treated fibers as compared to the most recent batch. In the case of the wood particles, the phosphorous uptake capacity decreased with decreasing particle size. This result was not anticipated since metal ion adsorption in sawdust was

suggested to decrease with increasing particle size due to factors such as diffusional path length, mass transfer resistance, contact time, and blockage of some diffusional paths (Shukla et al., 2002). Given the apparent correlation between the values for phosphorous uptake capacity and the iron released, it appears that the larger particles provide a greater amount of iron ions for phosphate removal from solution. However, smaller wood particles may be preferred since they showed the lowest release of iron relative to the phosphorous uptake capacity.

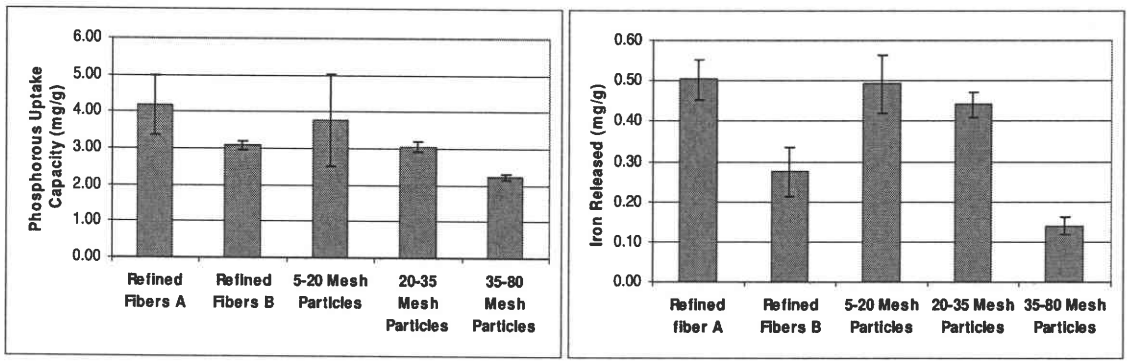

FIGURE 4. Phosphorous Uptake Capacity and Iron Released into Phosphate Test Solution for CMC/Fe-Treated Fibers and Particles from Aspen Wood (labels A and B identify original and subsequently prepared batches of CMC/Fe-treated fiber, respectively).

CONCLUSIONS

Pretreating refined aspen wood fiber with an aqueous solution of CMC provides additional sites to complex iron ions and thereby imparts a greater phosphorous uptake capacity. Results suggest that our biomass-based filtration medium may provide a simple means to remove phosphate from stormwater runoff.

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