CHARACTERIZATION AND TREATMENT OF WOOD FIBER FOR PHOSPHATE REMOVAL FROM WATER

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ABSTRACT: Treatment of refined aspen wood fiber with aqueous iron salt solutions imparted limited capacities to remove phosphate from test solutions. Alternatively, fiber samples were pretreated with an aqueous solution of a non-toxic anionic polymer, carboxymethyl cellulose (CMC), to provide additional sites to complex iron cations and thereby impart greater phosphate retention. Equilibrium sorption data showed that an increase in phosphate removal capacity could be achieved for a two-stage treatment (4% CMC, 12% ferrous chloride) over the corresponding single-stage iron salt treatment. Analysis of the CMC treated fiber by FTIR spectroscopy demonstrated the presence of the polymer by signals indicative of the carboxylate anion functionality. Sorption of phosphate on treated fiber samples showed a better fit with a Freundlich isotherm model than a Langmuir isotherm model. Results indicate that our biomass-based filtration medium may provide a cost-effective means to remove phosphate from stormwater runoff.

INTRODUCTION

The sound stewardship of aquatic ecosystems involves the implementation of strategies to manage the balance of nutrients controlling surface water quality. Most natural surface waters are either nitrogen or phosphorous limited (Kioussis et al., 1999). Stormwater containing elevated levels of phosphorous can contribute to the proliferation of algae and aquatic weeds that are both aesthetically unpleasing and promote lower water oxygen contents that lead to fish kills. The control of discharges from point sources can often be achieved through established treatment processes and regulations. A need remains for cost effective stormwater control measures, especially in urban and suburban environments where widespread fertilizer use and the accumulation of yard wastes occur near impervious surfaces that channel contaminants to natural surface waters.

Recent reports in the literature suggest that chemically modified biomass can be used to capture water pollutants (e.g., heavy metals) and nutrients such as soluble phosphates (Shukla et al., 2002, Unnithan et al., 2002). Wood processing residues (e.g., sawdust, bark) and agricultural residues (e.g., corncobs) have been targeted because of their availability and assumed low value (Tshabalala et al., 2004, Vaughan et al., 2001). Sorption of heavy metals can occur through the inherent chemistry of the biomass. Improvements in heavy metal sorption can be achieved by the application of base treatments to take full advantage of the ion exchange capacity of cell wall matrix (Min et al., 2004); alternatively, cross-linking reactions have been used to retain the heavy metal binding capacity of extractives such as tannins (Vazquez et al., 1994, Palma et al., 2003). In the case

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of phosphates, the use of biomass appears to require some sort of treatment. Unfortunately, many of these retention capacity improvements rely on toxic chemicals or multi-step reaction schemes that increase costs and produce waste streams. Here we report our findings from the evaluation of a filtration medium comprised of refined aspen wood fibers impregnated with solutions of CMC and ferrous chloride, both of which can be recycled thereby minimizing processing concerns.

MATERIALS AND METHODS

Preparation of Filtration Media. Refined aspen wood fiber was obtained from a hardboard plant in Wisconsin. The CMC sodium salt (Aldrich) used was labeled as having an ultra low viscosity (10-55 cps for a 4% aq. soln. at 25 °C) and the ferrous chloride (J.T. Baker) was the 4-hydrate. Fiber to be treated was transferred to either aqueous treatment solutions of 1, 2, 3, or 4% (w/w) CMC or deionized water; 1 part-dry fiber was added to 20 parts treatment solution by weight. The wetted fibers were allowed to stand (1 hr.) before the application of a vacuum (15 min.) to facilitate saturation. The fibers were then allowed to stand (4 hrs.) before filtering over a couple sheets of filter paper in a Büchner funnel. Air-dried CMC treated fibers were dried further in an oven (60 °C) before treating with solution of 2, 4, 8, or 12% (w/w) ferrous chloride as above (1 hr. soak, 15 min. vacuum, 4 hr. soak). CMC and ferrous chloride treated fibers were filtered through a Büchner funnel alone (no filter paper) and washed with 2 volumes of deionized water. Fiber samples were then washed again as above except the Büchner funnel contained a few sheets of filter paper to improve dewatering. Filtered fiber samples were air-dried and oven-dried as above before testing. After screening the efficacy of different ratios of CMC and ferrous chloride, large batches (1 kg) of treated fiber were prepared with 4% CMC and 12% ferrous chloride (CMC/Fe), or 12% ferrous chloride alone (Fe), for determining sorption isotherms and kinetics.

Sorption Isotherm Model. CMC/Fe and Fe treated fibers were ground in a Wiley mill to pass a 40 mesh sieve to ensure a homogeneous sample for isotherm testing. Phosphate test solutions at selected concentrations were prepared by serial dilution from a solution (100 mg/L) of potassium dihydrogenphosphate, (98 + %, Aldrich). Aliquots of treated fiber (0.1 g) and phosphate solution (0 to 100 mg/L, 50 mL) were added to small bottles (50 mL) that were then capped and shaken (150 rpm, 24 hrs.) under ambient conditions. The final pH of the phosphate solutions containing CMC/Fe and Fe treated fibers were 4.8 ± 0.2 and 5.3 ± 0.3, respectively. Suspensions were filtered through a syringe filter (0.45-μm pore size) and phosphate concentrations determined by inductively coupled plasma optical emission spectrometry (Jobin Yvon, Inc., Ultima ICP–OES, Edison, NJ). The values for initial phosphate concentration (C_0) and final phosphate concentration (C_e) were used to calculate the uptake capacity (q_e) as the amount of phosphate sorbed at equilibrium per amount of powdered fiber sample (mg/g). Results are based on the average of analyses carried out in triplicate.

A characteristic of the Langmuir isotherm is that the loading of sorbate onto the sorbent approaches a maximum value, Q_{max} (mg/g), as the concentration increases. This corresponds to monolayer coverage of the adsorbent surface by a Langmuir constant, b (L/mg), related to the free energy of adsorption:

$$q_e = \frac{bQ_{\max}C_e}{1+bC_e} \qquad (1)$$

The Freundlich isotherm is empirical and is used for heterogeneous surface energies where K (L/g), a measure of sorption capacity, and $1/n$, a measure of sorption intensity, are Freundlich constants:

$$q_e = KC_e^{1/n} \qquad (2)$$

To obtain the best estimate of all constants for the Langmuir (1) and Freundlich (2) isotherms, data were fitted with nonlinear regressions using a least squares fitting program (Origin 7.0, OriginLab Corp., Northampton, MA).

RESULTS AND DISCUSSION

Development of Filtration Media. Refined aspen wood fibers were selected as a filtration medium since they could readily be formed into filtration mats and the extractives content of the wood is relatively low. While some extractives such as tannins may improve metal cation retention, cross-linking reactions seem to be necessary to keep said extractives from leaching out (Vazquez et al., 1994, Palma et al., 2003). Alternatively, modification of bark has been preceded by an extraction step to remove high amounts of leachable extractives (Tshabalala et al., 2004).

Initial experiments demonstrated that by treating the refined aspen wood fibers with iron salts, we could impart limited capacities to remove phosphates from test solutions; untreated fiber samples showed no detectable phosphate retention. To provide additional sites to complex iron cations, and thereby impart greater phosphate retention, the fibers were pretreated with CMC solutions before treating with ferrous chloride solutions. Problems with excessive viscosities during the screening of commercially available CMC products led to the selection of an ultra low viscosity CMC product that was still usable up to a 4% concentration in water. Analysis of fiber samples treated with 0-4% CMC by FTIR spectroscopy showed an increase in signals at about 1600 cm^{-1} indicative of increasing amounts available carboxylate anion functionality (Figure 1). Screening experiments with selected concentrations of CMC and ferrous chloride showed that solutions containing 4% CMC and 12% ferrous chloride could be used to produce a filtration medium with significantly higher capacities for phosphate retention.

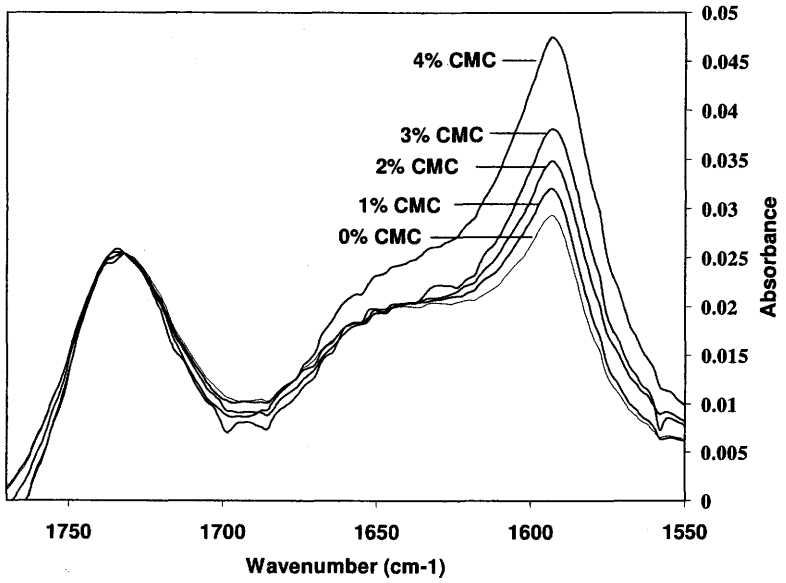

FIGURE 1. FTIR Spectra of Refined Aspen Fiber Treated with CMC Solutions.

Sorption Isotherms. The sorption equilibrium is one of the most important physicochemical aspects of the sorption process as a unit operation. Figure 2 shows the observed points of phosphate sorbed capacity (q_e) of CMC/Fe and Fe treated fiber in various effluent phosphate concentrations (C_e) in relation to the curves calculated from the constants in Table 1. The R^2 values in Table 1 show that the Freundlich isotherm model yielded a slightly better fit than did the Langmuir isotherm model in the sorption of phosphate onto both of CMC/Fe and Fe treated fibers. As mentioned earlier, the Freundlich isotherm is empirical whereas the Langmuir isotherm is theoretically derived and corresponds to monolayer coverage of the adsorbent surface. With our filtration medium, it would appear that the iron cations retained are available to convert the soluble phosphates to an insoluble form; the refined aspen fibers provide a matrix to support the CMC/Fe complex. Accordingly, the lower degree of fit for the Langmuir isotherm may be explained by a phenomenon of phosphate precipitation rather than adsorption of a phosphate monolayer on a discrete surface.

Phosphate sorption capacities for various inorganic filter media based on iron or aluminum containing minerals (kaolinite, goethite), as well as iron and aluminum oxide coated silicates (sand, olivine), were calculated and ranged from 0.4 to 2 mg/g (Ayoub et al., 2001, Baker et al., 1998, Brady and Weil, 1999). The sorption capacity of the CMC/Fe treated fiber (4.3 mg/L) is higher thereby suggesting that it could be used as an alternative to inorganic filter media.

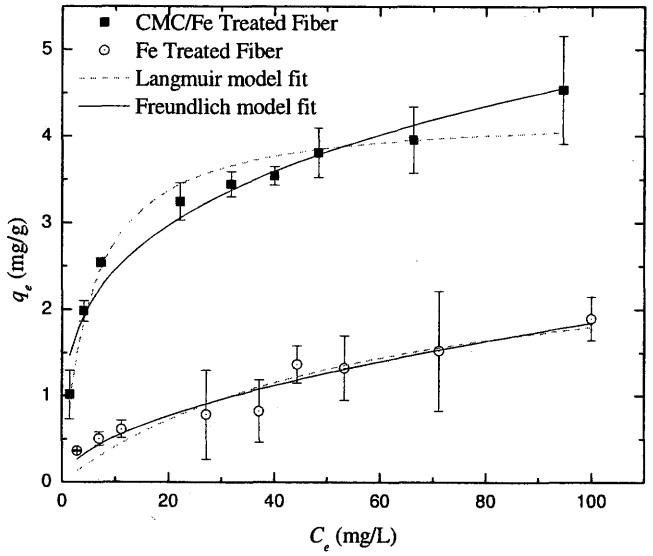

FIGURE 2. Isotherms of Phosphate Adsorption for CMC/Fe and Fe Treated Fiber.

TABLE 1. Isotherm Constants for Phosphate Adsorbed onto CMC/Fe and Fe Treated Fibers

	Freundlich Isotherm			Langmuir Isotherm		
Sorbent	***1/n***	***K* (L/g)**	R^2	Q_{max} **(mg/g)**	***b* (L/mg)**	R^2
CMC/Fe-Treated	0.27 ± 0.02	1.3 ± 0.12	0.962	4.3 ± 0.15	0.19 ± 0.03	0.957
Fe-Treated	0.54 ± 0.06	0.15 ± 0.04	0.940	2.9 ± 0.70	0.02 ± 0.01	0.889

CONCLUSIONS

Pretreating refined aspen wood fiber with an aqueous solution of CMC provides additional sites to complex iron cations and thereby imparts greater phosphate retention. Sorption of phosphate on CMC/Fe and Fe treated fiber samples showed a better fit with a Freundlich isotherm model than a Langmuir isotherm model. Results suggest that our biomass-based filtration medium may provide a cost-effective means to remove phosphate from stormwater runoff.

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