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Phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride

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Abstract

Biomass-based filtration media are of interest as an economical means to remove pollutants and nutrients found in stormwater runoff. Refined aspen wood fiber samples treated with iron salt solutions demonstrated limited capacities to remove (ortho)phosphate from test solutions. To provide additional sites for iron complex formation, and thereby impart a greater capacity for phosphate removal, a fiber pretreatment with an aqueous solution of a non-toxic anionic polymer, carboxymethyl cellulose (CMC), was evaluated. 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 at a 4% concentration in water. Soxhlet extractions of chipped aspen wood and refined aspen wood fiber samples showed a higher extractives content for the refined material. Analysis of these extracts by FTIR spectroscopy suggested that the higher extractives content for the refined material resulted from the fragmentation of cell wall polymers (e.g., lignin, hemicelluloses) normally insoluble in their native states. Spectroscopic analysis of CMC and ferrous chloride treated fibers showed that the complex formed was sufficiently stable to resist removal during subsequent water washes. Equilibrium sorption data, which fit better with a Freundlich isotherm model than a Langmuir isotherm model, showed that phosphate removal could be enhanced by the CMC pretreatment. Results suggest that the process outlined may provide a facile means to improve the phosphate removal capacity of biomass-based stormwater filtration media.
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1. Introduction

Most natural surface waters (e.g., lakes, ponds) are either nitrogen or phosphorous limited (Kioussis et al., 1999; Unnithan et al., 2002). Stormwater runoff containing elevated levels of phosphorous can disrupt the balance of nutrients and lead to the proliferation of algae and aquatic weeds; such unrestrained growth often results in lower dissolved oxygen contents that cause fish kills (Kofinas and Kioussis, 2003; Zhao and Sengupta, 1998). Accordingly, a need exists for cost effective measures to remove phosphates from stormwater runoff. This is especially true in urban and suburban environments where widespread fertilizer use, and the accumulation of yard debris, often occur near impervious surfaces that channel nutrients to surrounding aquatic ecosystems.

Biomass, either in its native state, or chemically modified, has been suggested as an option to capture water pollutants and nutrients. Wood processing residues (e.g., sawdust, bark) and agricultural residues (e.g., corncobs) have been targeted because of their availability and assumed low value (Shukla et al., 2002; Tshabalala et al., 2004; Vaughan et al., 2001). In the case of heavy metals, sorption can occur through the inherent chemistry of the biomass. Improvements in sorption performance can be

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achieved by the application of treatments to either make available or retain functional groups contributing to heavy metal sorption. For example, base treatments can cleave esters thereby providing more carboxylate functionality for complex formation (Min et al., 2004). Condensed tannins, a group of phenolic extractives, complex with metal ions through their ortho hydroxyl functionality (Laks, 1989); cross-linking reactions have been used to retain these extractives in the biomass (Vazquez et al., 1994; Palma et al., 2003).

The types of phosphates found in natural waters include organically bound phosphates, soluble orthophosphates, and polyphosphates (Ayoub et al., 2001; Kioussis et al., 1999). The lack of significant inherent phosphate sorption capacity for selected forms of biomass appears to necessitate chemical modification. Unfortunately, most improvements in the soluble phosphate sorption capacities of biomass resources involve treatments with toxic chemicals or multi-step reaction schemes that increase costs and produce waste streams. Our strategy has been to target environmentally benign treatments that increase phosphate retention capacity, yet do not interfere with a key attribute of the biomass, that being its biodegradability. Studies have shown that iron adsorbed on synthetic filtration media (Unnithan et al., 2002) or biomass (Han et al., 2003) can impart a capacity to remove phosphates from water. To provide additional sites for iron complex formation, we pretreated our substrate with an aqueous solution of a non-toxic anionic polymer, carboxymethyl cellulose (CMC). 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.

2. Methods

Refined aspen wood fiber was obtained from a hardboard plant (Georgia Pacific, Philips, WI); aspen wood chips, sold as animal bedding (AlphaPet, Inc., St. Louis, MO), were purchased from a local retailer. The CMC sodium salt (Aldrich) used was labeled as having an ultra low viscosity (10–55 mPa · s for a 4% aqueous solution at 25 °C) and the ferrous chloride (J.T. Baker) was the tetrahydrate.

2.1. Fiber analyses

Refined wood fiber was sequentially extracted (20 h per solvent) in a Soxhlet apparatus with hexane, 95% ethanol, and then water. Another wood fiber sample was subjected to Soxhlet extraction with only water. Wood chips were ground in a Wiley mill equipped with a No. 5 mesh screen before sequential extraction as above. Hexane and ethanol extracts were dried in vacuo at room temperature; water extracts were freeze-dried. FTIR spectra were collected using a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Smart Golden Gate MKII Single Reflection ATR accessory. Fiber samples were placed on the diamond crystal and pressure applied with the anvil affixed to the accessory clamping mechanism. Extracts were also analyzed directly by applying a small amount of dry extract on the diamond crystal with a spatula.

2.2. Fiber treatment

Refined wood fiber to be treated was transferred to aqueous treatment solutions of 1%, 2%, 3%, or 4% (w/w) CMC; deionized water was used as a control. One part dry fiber was added to 20 parts treatment solution by weight. Wetted fibers were allowed to stand (1 h) before the application of a vacuum (15 min) to facilitate saturation. The fibers were then allowed to stand (4 h) before filtering in a Büchner funnel. CMC treated fibers were air-dried and then dried further in an oven (60 °C) before treating with solution of 2%, 4%, 8%, or 12% (w/w) ferrous chloride as above (1 h soak, 15 min vacuum, 4 h soak). Treated fibers were filtered in a Büchner funnel 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 (Whatman, No. 4) to improve dewatering. Filtered fiber samples were air-dried and then oven-dried (65 °C) before characterization by FTIR spectroscopy and iron content analysis (EPA Method 6010B, Galbraith Laboratories, Inc., Knoxville, TN). After screening the efficacy of different ratios of CMC and ferrous chloride, large batches (1 kg) of treated fiber were prepared with aqueous treatment solutions of 4% (w/w) CMC and then 12% (w/w) ferrous chloride tetrahydrate (CMC/Fe treated fiber), or 12% ferrous chloride tetrahydrate alone (Fe treated fiber), for determining sorption isotherms.

2.3. Sorption analyses

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 of a solution (100 mg/L) of potassium dihydrogenphosphate (98 + %, Aldrich). Aliquots of treated fiber (0.1 g) and phosphate solution (50 mL) were added to small bottles that were then capped and shaken (150 rpm, 24 h) under ambient conditions. The final average pH values for 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). Analy-

ses were carried out in triplicate. For the Langmuir isotherm, 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:

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

The Freundlich isotherm is empirical where K (L/g) and $1/n$ are constants that characterize the adsorption capacity of the adsorption system:

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

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).

3. Results and discussion

Refined aspen wood fiber was selected as our substrate since it could readily be formed into filtration mats and the extractives content of the wood is low compared to other forms of biomass. Bark is an example of a form of biomass containing high concentrations of extractives such as methanogenic toxic tannins; leaching of these compounds during industrial debarking operations ultimately reduces the efficacy of water treatment operations (Field et al., 1988). Since the tannins appear to improve metal cation retention, cross-linking reactions are used to keep these extractives from leaching out (Vazquez et al., 1994; Palma et al., 2003). Alternatively, for the modification of bark for phosphate sorption, an extraction step was used to remove high amounts of leachable extractives prior to chemical modification (Tshabalala et al., 2004).

3.1. Quantification of extractives

To assess the extractives content of our substrate, aspen wood chips and refined aspen wood fiber samples were subjected to sequential extractions in a Soxhlet apparatus with solvents of increasing polarity (Table 1). Extraction of the wood chips with hexane and ethanol gave a combined 2.8% yield of extractives based on the dry weight of the starting material. This value was consistent with that reported in the literature for aspen wood (Fengel and Wegener, 1984). Higher levels of extractives were obtained with the refined wood fiber. This undoubtedly resulted from the more finely divided nature of the refined material. In addition to the sequential extractions (hexane, ethanol, water), a sample of the refined wood fiber was also extracted with only hot water to determine the amount of material that could potentially be leached by water alone. The high amount of material removed (9.75%) showed that the majority of the extractives in the ethanol extract were sufficiently polar to be removed by hot water; under circumstances where extractives may be a concern, the results suggest that extracting with only water may provide a sufficient alternative to sequential extractions with organic solvents. However, any extraction step could potentially be avoided if the chemistries of any extractable materials are deemed to be as harmless as the cell wall material itself. To address this possibility, the extracts were characterized by FTIR spectroscopy.

Table 1
Extractive yields for aspen wood chips and refined aspen wood fiber

	Extractive yield (%)[a]	
	Wood chips	Refined wood fiber
Sequential extraction		
Hexane	0.27	0.47
Ethanol	2.54	9.14
Water	1.10	3.19
Total	3.91	12.80
Water alone	nd[b]	9.75

[a] Percentage of oven dry material.
[b] nd = not determined.

3.2. Characterization of extractives

Extracts from the refined aspen wood fiber were subsequently characterized by FTIR spectroscopy. As to be expected, the FTIR spectrum (Fig. 1) of the small amounts of hexane soluble materials we obtained gave signals consistent with the aliphatic C–H (2921, 2851, 1463 cm^{-1}) and carbonyl (1733 cm^{-1}) functionalities of plant waxes. The FTIR spectra for the ethanol and water extracts were analogous to those spectra reported for lignins and celluloses (Fengel and Wegener, 1984). Although the spectra are similar between these extracts, the spectrum for the ethanol extract shows definite signals near 1600 (C=C stretch), 1500 and 1450 cm^{-1} (both C–C vibration) consistent with aromatic structures. Interestingly, the majority of

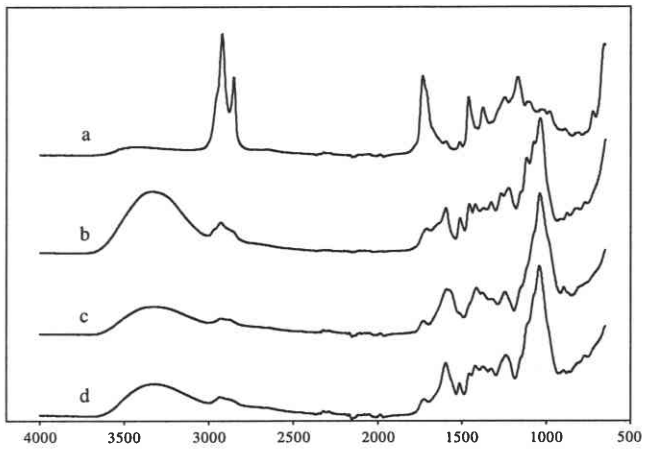

Fig. 1. FTIR spectra of extracts from refined aspen wood fiber: sequential extractions with (a) hexane, (b) 95% ethanol, and (c) water; single extraction with (d) water alone.

the ethanol soluble materials were also extracted when only water was used as the extraction solvent. Consistent with this observation, the FTIR spectrum for the extract obtained by water extraction alone was intermediate the spectra for the ethanol and water extracts we obtained by sequential extraction. For the wood chips, the aromatic signals in FTIR spectrum recorded for the ethanol extract were more pronounced (spectrum not shown); these signals were more readily attributable to true phenolic extractives (e.g., lignans) known to be present in this wood species (Hathway, 1962). At this juncture, it should be realized that the refining process makes available fragments of cell wall polymers (hemicelluloses, lignin) that would not normally fall under the term of wood extractives. For example, studies on loblolly pine fibers showed increased release of hemicelluloses with increased refiner pressures (Groom et al., 2000). Accordingly, it is likely that any hemicellulose and lignin fragments possibly released from our refined wood fiber could be reduced through changes in refiner operations. Losses in hemicelluloses with carboxylic acid functionality could result in a lower inherent capacity to retain iron, however, such losses would be negligible relative to the level of carboxylate functionality imparted though the CMC pretreatments.

3.3. Development of filtration media

Preliminary experiments in our laboratories demonstrated that by treating the refined aspen wood fibers with iron salts (e.g., ferric and ferrous chlorides), we could impart a capacity to remove phosphates from test solutions; untreated fiber samples showed no detectable phosphate removal capacity. These results were in agreement with other studies demonstrating that retained iron imparted a capacity to remove phosphate from test solutions (Han et al., 2003; Unnithan et al., 2002). To provide additional sites to complex iron cations, and thereby impart greater phosphate removal capacity, the refined wood fibers were treated 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% (w/w) concentration in water. Analysis of the CMC treated fiber samples by FTIR spectroscopy showed an increase in signals at about 1600 cm^{-1} indicative of increasing amounts of available carboxylate functionality (spectra not shown). A nearly identical series of spectra was obtained for our samples treated with CMC and then ferrous chloride (Fig. 2). Accordingly, the CMC and ferrous chloride treatment provided a complex that was sufficiently stable to resist removal during subsequent washing steps. Screening experiments with selected concentrations of CMC and ferrous chloride showed that solutions containing 4% (w/w) CMC and 12% (w/w) ferrous chloride (CMC/Fe treated fiber) provided the highest capacities for phosphate retention. A sample prepared under these conditions had an iron content (2.09%) that was sevenfold higher than the control (0.28%) treated with ferrous chloride alone (Fe treated fiber). Given the above evidence for CMC retention and increased iron content, the media prepared under these conditions were used for generating sorption isotherms.

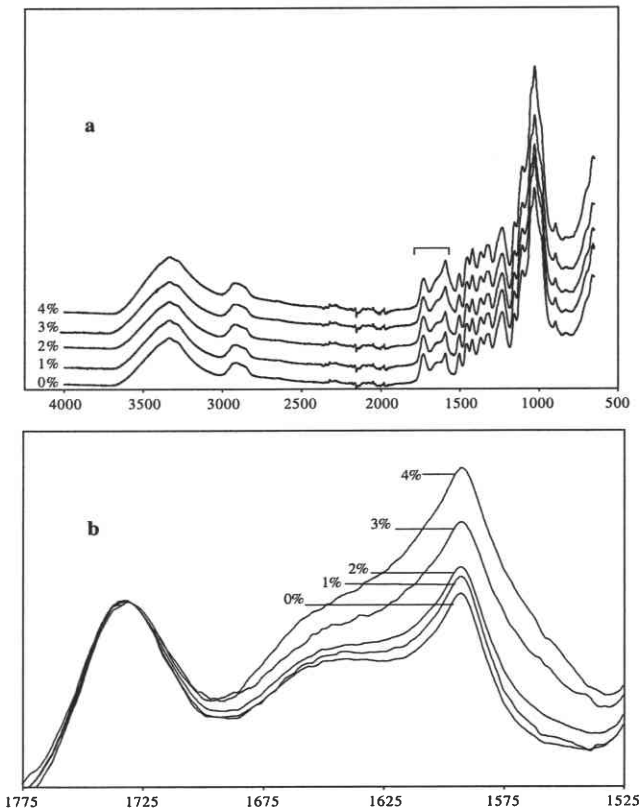

Fig. 2. FTIR spectra of refined aspen wood fiber treated with 0–4% (w/w) CMC and 12% (w/w) ferrous chloride solutions; CMC concentrations are as labeled on (a) full spectra and (b) expanded spectra.

3.4. Sorption isotherms

The observed points of phosphate uptake capacity (q_e) for the CMC/Fe and Fe treated fiber samples in various effluent phosphate concentrations (C_e) are shown in Fig. 3. Equations for Freundlich and Langmuir isotherms are given in Table 2. For both the CMC/Fe and Fe treated fibers, the Freundlich isotherm model gave a better fit than the Langmuir isotherm model as shown by the higher R^2 values. It should be noted that the Freundlich isotherm, which was originally empirical, can be derived on the basis of two factors, namely the lateral interaction between the adsorbed molecules and the energetic surface heterogeneity, both of which are generally observed with precipitation processes (Yang, 1998); the Langmuir isotherm is theoretically derived and corresponds to monolayer coverage of the adsorbent surface without the lateral interaction. With our filtration medium, it appears that the iron cations retained are available to convert the soluble phosphates to an insoluble form; the refined wood fibers provide a

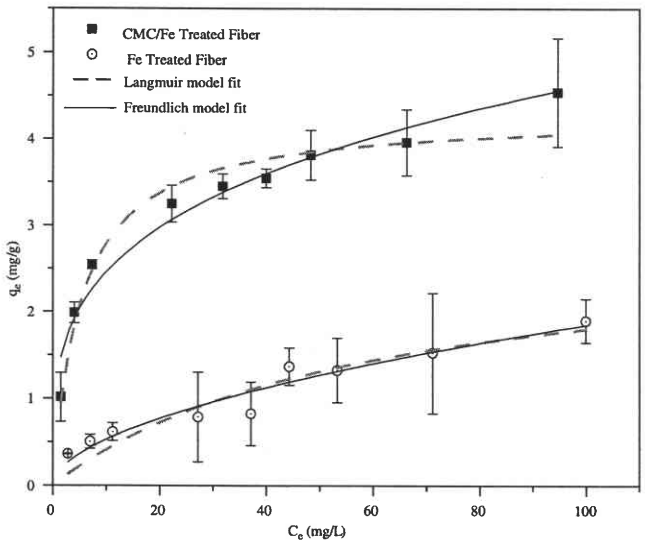

Fig. 3. Phosphate adsorption isotherms for CMC/Fe treated, and Fe treated, refined aspen wood fiber.

Table 2
Freundlich and Langmuir isotherm equations for CMC/Fe treated and Fe treated aspen wood fibers

Sample	Freundlich isotherm		Langmuir isotherm	
	Equation	R^2	Equation	R^2
CMC/Fe treated	$q_e = 1.3C_e^{0.27}$	0.962	$q_e = 0.82C_e/(1 + 0.19C_e)$	0.957
Fe treated	$q_e = 0.15C_e^{0.54}$	0.940	$q_e = 0.06C_e/(1 + 0.02C_e)$	0.889

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 uptake capacity of the CMC/Fe treated fiber (4.3 mg/g) is higher thereby suggesting that it could be used as an alternative to inorganic filter media.

4. Conclusions

Pretreating refined aspen wood fiber with an aqueous solution of CMC provides additional sites to complex iron cations and thereby imparts greater phosphate removal capacity; the complex formed was sufficiently stable to resist removal during water washings. Sorption of phosphate on treated and control fiber samples showed a better fit with a Freundlich isotherm model and may be attributed to phosphate precipitation within the filtration medium. Results suggest that the process outlined may provide a facile means to improve phosphate removal by biomass-based stormwater filtration media.

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