ELSEVIER

Biosorbents prepared from wood particles treated with anionic polymer and iron salt: Effect of particle size on phosphate adsorption

Thomas L. Eberhardt [a,*], Soo-Hong Min [b]

[a] *USDA Forest Service, Southern Research Station, 2500 Shreveport Highway, Pineville, LA 71360, USA*
[b] *Samsung Corporation, Technology Division, 270-1, Seohyun-Dong, Bundang-Gu, Sungnam-Si, Gyonggi-Do 463-824, Republic of Korea*

Abstract

Biomass-based adsorbents have been widely studied as a cost-effective and environmentally-benign means to remove pollutants and nutrients from water. A two-stage treatment of aspen wood particles with solutions of carboxymethyl cellulose (CMC) and ferrous chloride afforded a biosorbent that was effective in removing phosphate from test solutions. FTIR spectroscopy of the biosorbent samples showed a decrease in the intensity of the carboxylate signal coinciding with a decrease in particle size. Elemental analysis results showed the iron content of both the biosorbent samples, and wood particles treated with ferrous chloride alone, to also decrease with particle size. The relationship between iron content and particle size for the biosorbent samples appeared to be a function of both the amount of CMC–Fe complex and the efficiency of removing free iron ions after treating. Sorption testing results showed a strong linear correlation between the phosphorous uptake capacities and the iron contents of the samples adjusted for losses of iron during testing. As anticipated, pretreating with the anionic polymer provided additional sites to complex iron and thereby imparted a greater phosphorous uptake capacity. Although the larger wood particles provided a greater amount of iron for phosphate removal, smaller wood particles may be preferred since they afforded the lowest release of iron relative to the amount of phosphate removed.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: Adsorption; Biomass; Biosorbent; Carboxymethyl cellulose; Phosphate

1. Introduction

Adsorbents based on biomass, often called biosorbents, have been widely studied as a cost-effective and environmentally-benign means to remove pollutants (heavy metals, hydrocarbons) and nutrients (nitrates, phosphates) from water. Most of the emphasis has been placed on byproducts of agriculture or wood processing that are readily available and have limited utility, thereby making them lower in cost. Primary threats to water quality have shifted towards non-point sources such as agricultural runoff and urban stormwater. Generally, in these instances, the financial resources dedicated to containment are scarce thus necessitating low-cost options that are relatively simple to implement.

Numerous reports in the literature describe the use of biosorbents to remove pollutants, such as heavy metals, from water. Many of these studies rely on the inherent capacity of biomass to adsorb heavy metals through the extractives and cell wall chemistries (Randall et al., 1974; Randall, 1977; Yu et al., 2003; Acemioglu and Alma, 2004). To augment adsorption capacities, chemical modifications have been applied (Vazquez et al., 1994; Shibi and Anirudhan, 2005; Shin and Rowell, 2005; Shukla and Pai, 2005). Whereas some treatments appear to add little to the biosorbent cost, others are obviously cost prohibitive because of the use of expensive reagents, significant energy demands during processing, and the generation of toxic waste streams.

The use of biosorbents for plant nutrients is less straightforward and therefore has received considerably less attention. Specifically, whereas the adsorption of metal ions can occur through chemistries already present in biomass, sig-

---

* Corresponding author. Tel.: +1 318 473 7274; fax: +1 318 473 7246.
E-mail address: teberhardt@fs.fed.us (T.L. Eberhardt).

nificant adsorption of soluble nitrates and phosphates necessitates some sort of chemical modification (Orlando et al., 2002; Unnithan et al., 2002; Tshabalala et al., 2004). In several cases, chemical modifications involve strategies to increase the adsorption of iron which then imparts a capacity to retain phosphate. Such treatments range from simple base treatments (Han et al., 2005) to the grafting of carboxylate groups (Unnithan et al., 2002).

A novel approach currently under investigation for increasing the loading of iron in biomass involves a pre-treatment with carboxymethyl cellulose (CMC), a non-toxic anionic polymer; this provides additional sites to bind iron ions which impart a capacity to remove phosphate from water. Initial results with refined aspen wood fiber treated with CMC and ferrous chloride showed higher iron contents and phosphorous uptake capacities compared to wood fiber treated with ferrous chloride alone. Batch isotherm testing showed that the Freundlich isotherm gave the best fit with the sorption data (Eberhardt et al., 2006). As an alternative to the refined aspen wood fiber, it was of interest to determine if aspen wood particles would serve as a better substrate. Refining is carried out in the presence of water and requires heat energy both during refining and subsequent fiber drying operations. Refining also results in much higher extractives contents via the degradation of some of the cell wall polymers. Alternatively, wood particles can be prepared by simply grinding wood in a relatively dry condition, thereby requiring significantly less energy for processing and yielding the lowest possible extractives contents. Wood particles may also be preferred for their greater hydraulic conductivity. Here we report our results from the characterization and testing of biosorbents prepared with aspen wood particles of different size classes.

2. Methods

2.1. Materials and general methods

Refined aspen wood fiber was obtained from a hardboard plant (Georgia Pacific, Philips, WI) and used as received. Wood particles were prepared by grinding aspen wood chips (AlphaPet, Inc., St. Louis, MO) in a Wiley mill equipped with a 5-mesh screen and then sieving on a sieve shaker (W.S. Tyler, Ro-Tap, Model RX-29) equipped with 20-, 35-, and 80-mesh sieves. The CMC sodium salt (Aldrich) used for the treatments was labeled as having an ultra low viscosity (10–55 mPa 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 Thermo Nicolet (Madison, WI) Nexus 670 spectrometer equipped with a Thermo Nicolet Smart Golden Gate MKII single reflection ATR accessory. Samples were placed on the diamond crystal and pressure applied with the anvil affixed to the accessory clamping mechanism. Iron contents by elemental analysis (EPA Method 6010B) were conducted by Galbraith Laboratories, Inc. (Knoxville, TN). Phosphorous concentrations of the solutions from sorption testing were determined using a Jobin Yvon, Inc. (Edison, NJ) Ultima ICP-OES instrument.

2.2. Biosorbent preparation

Wood fiber and particle samples to be treated were each 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 h) before the application of a vacuum (15 min) to facilitate saturation. Samples were allowed to stand for a second period of time (4 h) before filtering in a Büchner funnel with filter paper (Whatman, No. 1). Treated samples were each dried under ambient conditions and then in an oven (60 °C). CMC-pretreated and untreated samples were transferred to a 12% (w/v) solution of ferrous chloride in deionized water, using a sample to treatment solution ratio of 1:20, and processed as above (1 h soak, 15 min vacuum, 4 h soak). After filtering through 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.

2.3. Sorption analyses

Biosorbents, and samples of wood fiber and particles treated with ferrous chloride alone, 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 test solution (50 mL) were added to small plastic bottles that were then capped and shaken (150 rpm, 24 h) under ambient conditions. Suspensions were filtered through a syringe filter (0.45-μm pore size) before analysis by ICP-OES. The values for initial and final phosphorous concentrations were used to calculate the phosphorous uptake capacity (mg/g) as the amount of phosphorous sorbed at equilibrium per amount of sample. Results are based on two separate analyses, each carried out in triplicate.

2.4. Linear correlation plots

Sorption data were pooled and linear correlations determined using Microsoft Excel (2002) SP-1. Average values for the amount of iron released during sorption testing were used for comparison to single determinations of iron content by elemental analysis. Likewise, average values for phosphorous uptake capacity were used for comparison to the adjusted iron contents which were based on the iron content less the average amount of iron released during sorption testing.

3. Results and discussion

3.1. CMC penetration

FTIR spectra of refined aspen wood fiber samples treated with a series of CMC and ferrous chloride solutions exhibited the ability to detect different loadings of CMC within the fiber matrix by the intensity of the carboxylate signal at about $1600 \, cm^{-1}$ (Eberhardt et al., 2006). An analogous result was obtained from a comparison of the FTIR spectra from the biosorbent samples and untreated wood fiber and particles (Fig. 1). Interestingly, for the biosorbent samples, the FTIR spectra showed a decrease in the intensity of the carboxylate signal coinciding with a decrease in particle size; the spectra for the biosorbent samples prepared from the wood fiber and the 35–80 mesh wood particles were fairly similar. Control samples of untreated wood particles also showed a slight decrease in the carboxylate signal with a decrease in particle size. Normalization with the peak at $1730 \, cm^{-1}$, instead of the peak at $1240 \, cm^{-1}$, showed a greater degree of signal overlap among the untreated samples (spectra not shown). The slight decrease in signal intensity for the untreated controls is therefore likely an artifact of the analysis of

Fig. 1. FTIR spectra of biosorbent samples and control (untreated) wood fiber and particle samples (numbers indicate particle size range).

different particle sizes by FTIR spectroscopy and the signal selected for normalizing the spectra. For the biosorbent samples, the more pronounced decrease in carboxylate functionality may therefore be attributed to a decrease in the amount of the CMC–Fe complex. It is likely that the higher surface area for the smaller wood particles resulted in a greater proportion of the CMC–Fe complex being removed during the washing steps following sample treatment.

Observations of refined aspen wood fiber by confocal microscopy following a treatment with CMC and a polymeric fluorescent dye (tetramethylrhodamine isothiocyanate-dextran) showed that the CMC loaded into the wood fiber partially filled the fiber lumens. Application of this technique to the wood particles did not produce suitable images because of the high intensity stray fluorescence and the inability of the laser to penetrate the fiber bundles. Given that the CMC had been shown to penetrate into accessible fiber lumens of the refined wood fiber, penetration of the polymer likely occurred in similarly accessible fiber lumens in the wood particles.

3.2. Iron contents

Aliquots of the biosorbent samples, and samples of the wood fiber and particles treated with ferrous chloride alone, were subjected to elemental analysis to determine iron contents. As expected, all samples pretreated with CMC had significantly higher iron contents (Table 1). For example, the iron content of a sample of wood fiber receiving the CMC pretreatment was 7-fold higher than that for wood fiber without this pretreatment. This suggested that the CMC pretreatment provided additional sites to complex iron ions from the ferrous chloride treatment solution. For the CMC-pretreated wood particles, iron contents decreased along with particle size. This result was anticipated given that the FTIR spectra appeared to show that the amount of CMC–Fe complex decreased with particle size (Fig. 1). For wood particles treated with ferrous chloride alone, the iron content also decreased along with particle size. This was attributed to the greater surface area for the smaller wood particles that resulted in a higher efficiency in removing free iron ions during the rinsing step
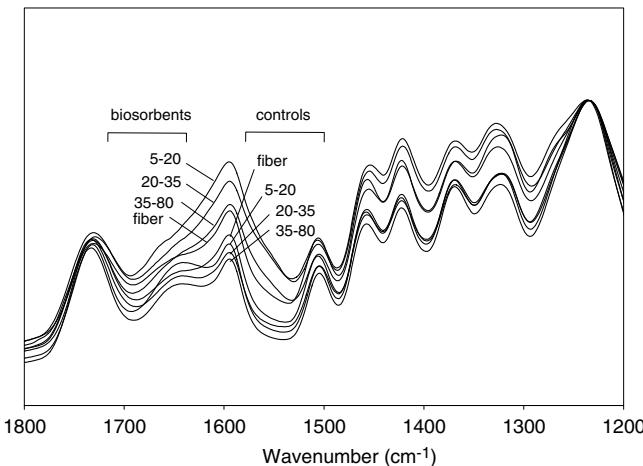
Table 1
Iron contents and sorption testing results for biosorbent samples and wood fiber and particle samples treated with ferrous chloride alone

Treatment	Substrate	Iron content (mg/g)	Iron released (mg/g)	Adjusted iron content (mg/g)	Proportion of iron retained (%)	Phosphorous uptake capacity (mg/g)	Phosphorous:iron ratio[a]
Ferrous chloride alone	Refined fibers	2.8	0.14 ± 0.02	2.7	94.9	0.67 ± 0.16	4.7
	5–20 mesh particles	9.9	1.65 ± 0.13	8.2	83.3	2.78 ± 0.17	1.7
	20–35 mesh particles	5.1	0.64 ± 0.04	4.5	87.5	1.57 ± 0.10	2.5
	35–80 mesh particles	2.9	0.15 ± 0.02	2.7	94.7	0.65 ± 0.34	4.3
CMC and ferrous chloride	Refined fibers	20.9	1.65 ± 0.33	19.2	92.1	5.67 ± 0.51	3.4
	5–20 mesh particles	15.1	1.35 ± 0.21	13.8	91.1	4.14 ± 0.69	3.1
	20–35 mesh particles	10.3	0.55 ± 0.07	7.8	94.7	3.00 ± 0.19	5.5
	35–80 mesh particles	9.8	0.22 ± 0.03	9.6	97.8	2.32 ± 0.13	10.6

[a] Ratio of phosphorous uptake capacity values to values for iron released.

following the ferrous chloride treatment. Accordingly, the relationship between iron content and particle size for the biosorbent samples appears to be a function of both the amount of CMC–Fe complex present and the efficiency in removing free iron ions during rinsing.

3.3. Iron released during sorption testing

During sorption testing, the concentration of iron in the test solution was monitored in addition to the change in test solution phosphorous concentration. Plotting the values for iron content against the average values for iron released gave good linear correlations (biosorbent, $R^2 = 0.90$; Fe-alone treated, $R^2 = 0.99$) when the data were grouped according to the applied treatment (Fig. 2). Thus, for either treatment, the amount of iron released was proportional to the iron content. Similar particle sizes gave similar amounts of iron released when comparing the two treatments. This suggested similar amounts of free iron (i.e., not bound to anionic groups in wood or CMC) between the two treatments for any given particle size. In the case of the wood fiber, both the iron content and iron released values were much higher with the CMC-pretreated samples suggesting that the CMC–Fe complex may also provide a matrix in which free iron can be entrained.

Values for the adjusted iron content were calculated as the iron content minus the average amount of iron released. The proportion of iron retained was then calculated from the values for the iron content (before sorption testing) and the adjusted iron contents (after sorption testing). At this juncture, it is interesting to note that as the particle size decreases, the proportion of iron retained increases (Table 1). It would therefore appear that at the smaller particle sizes, a greater proportion of the iron is complexed with the CMC or the cell wall; with the larger particle sizes, a greater amount of free iron would appear to be entrained, not being removed during the washing steps in the sample treatment process.

3.4. Phosphorous uptake capacity

The values for iron released into the test solutions were plotted against the values for phosphorous uptake capacity for both the biosorbent (Fig. 3) and Fe-alone treated (Fig. 4) samples. In both cases, the amount of iron released was linearly correlated with the phosphorous uptake capacity (biosorbent, $R^2 = 0.92$; Fe-alone treated, $R^2 = 0.95$). This result was anticipated given that the amounts of iron released were linearly correlated with the iron contents. More appropriately, plotting the values for adjusted iron content against the average values for phosphorous uptake capacity (Fig. 5) showed a strong linear correlation ($R^2 = 0.98$). This suggested that irrespective of the applied treatment, the amount of iron retained by these woody substrates imparted the capacity to remove phosphate from water.

The ratios of the phosphorous uptake capacity values to the values for iron released were calculated and are also shown in Table 1. For the Fe-alone treated samples, the ratio calculated for the wood fiber was similar to the 35–80

Fig. 3. Linear correlation of values for iron released during sorption testing with phosphorous uptake capacities for biosorbent samples.
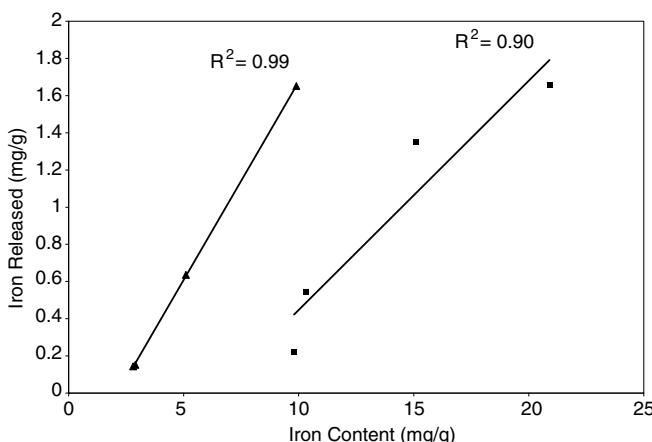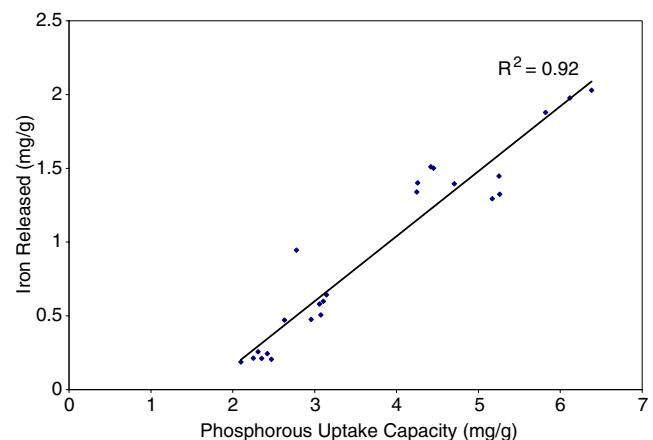

Fig. 2. Linear correlation of values for iron content with values for iron released during sorption testing (■, biosorbent samples; ▲, Fe-alone treated samples).
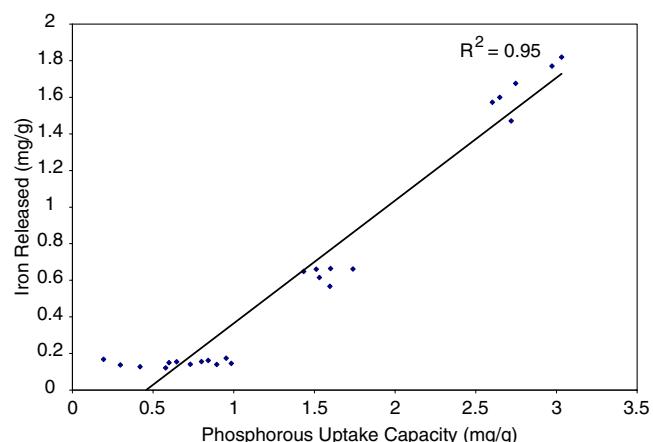

Fig. 4. Linear correlation of values for iron released during sorption testing with phosphorous uptake capacities for Fe-alone treated wood fiber and particle samples.
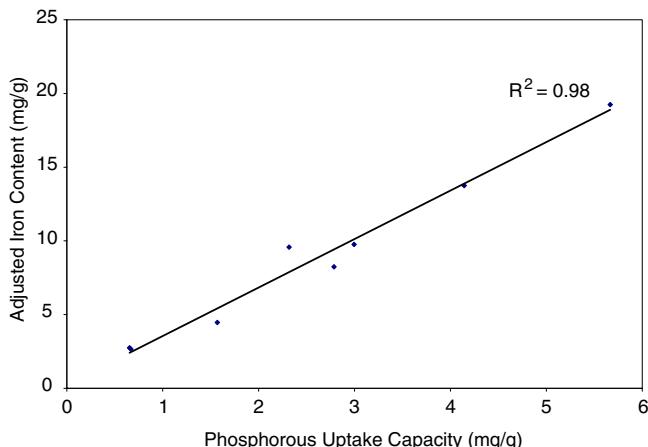
Fig. 5. Linear correlation of adjusted iron contents with phosphorous uptake capacities for biosorbent samples and Fe-alone treated wood fiber and particle samples.

mesh wood particles. In contrast, a much higher ratio was obtained for the CMC-pretreated wood particles in this size class compared to the wood fiber treated in the same manner. Together the results suggest that the CMC pretreatment of the 35–80 mesh wood particles results in the most efficient use of the applied iron in terms of both retention and availability for phosphate removal from water.

Finally, in the case of the wood particles, it should be noted that the phosphorous uptake capacity decreased with the decrease in particle size. This is unlike results reported for heavy metal ion adsorption in sawdust where there was decrease in adsorption with increasing particle size because of factors such as diffusional path length or mass transfer resistance, contact time, and blockage of some diffusional paths (Shukla et al., 2002). Since the entire woody matrix in sawdust has the capacity to adsorb metal ions, the above-mentioned factors can be rationalized. For the CMC-pretreated wood particles, the phosphorous uptake capacity is a function of both the iron content that is bound in the woody matrix and the CMC–Fe complex. Since the amount of CMC–Fe complex increases with increasing particle size, the CMC pretreatment results in the larger wood particles providing a greater amount of iron 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.

4. Conclusions

Irrespective of whether or not the CMC pretreatment was used, the amounts of iron retained in the woody substrates determine the phosphorous uptake capacities. Pretreating with the anionic polymer provides additional sites to complex iron ions and thereby imparts a greater phosphorous uptake capacity. Calculating the ratio of phosphorous uptake capacity to the amount of iron retained, it appears that the smallest wood particles (35–80 mesh) pretreated with CMC provide the most efficient use of the applied iron in terms of both retention and availability for phosphate removal from water.

Acknowledgments

References

Acemioglu, B., Alma, M.H., 2004. Sorption of copper (II) ions by pine sawdust. Holz Roh Werkst. 62, 268–272.

Eberhardt, T.L., Min, S.-H., Han, J.S., 2006. Phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride. Biores. Technol. 97, 2371–2376.

Han, J.S., Min, S.-H., Kim, Y.-K., 2005. Removal of phosphorous using AMD-treated lignocellulosic material. Forest Prod. J. 55, 48–53.

Orlando, U.S., Baes, A.U., Nishijima, W., Okada, M., 2002. Preparation of agricultural residue anion exchanger and its nitrate maximum adsorption capacity. Chemosphere 48, 1041–1046.

Randall, J.M., 1977. Variations in effectiveness of barks as scavengers for heavy metal ions. For. Prod. J. 27, 51–56.

Randall, J.M., Bermann, R.L., Garrett, V., Waiss Jr., A.C., 1974. Use of bark to remove heavy metal ions from waste solutions. For. Prod. J. 24, 80–84.

Shibi, I.G., Anirudhan, T.S., 2005. Adsorption of Co(II) by a carboxylate-functionalized polyacrylamide grafted lignocellulosics. Chemosphere 58, 1117–1126.

Shin, E.W., Rowell, R.M., 2005. Cadmium ion sorption onto lignocellulosic biosorbent modified by sulfonation: the origin of sorption capacity improvement. Chemosphere 60, 1054–1061.

Shukla, S.R., Pai, R.S., 2005. Adsorption of Cu(II), Ni(II) and Zn(II) on modified jute fibres. Biores. Technol. 96, 1430–1438.

Shukla, A., Zhang, Y.-H., Dubey, P., Margrave, J.L., Shukla, S.S., 2002. The role of sawdust in the removal of unwanted materials from water. J. Hazard. Mater. B95, 137–152.

Tshabalala, M.A., Karthikeyan, K.G., Wang, D., 2004. Cationized milled pine bark as an adsorbent for orthophosphate anions. J. Appl. Polym. Sci. 93, 1577–1583.

Unnithan, M.R., Vinod, V.P., Anirudhan, T.S., 2002. Ability of iron (III)-loaded carboxylated polyacrylamide-grafted sawdust to remove phosphate ions from aqueous solution and fertilizer industry wastewater: adsorption kinetics and isotherm studies. J. Appl. Polym. Sci. 84, 2541–2553.

Vazquez, G., Antorrena, G., Gonzalez, J., Doval, M.D., 1994. Adsorption of heavy metal ions by chemically modified *Pinus pinaster* bark. Biores. Technol. 48, 251–255.

Yu, L.J., Shukla, S.S., Dorris, K.L., Shukla, A., Margrave, J.L., 2003. Adsorption of chromium from aqueous solutions by maple sawdust. J. Hazard. Mater. B100, 53–63.