Environ. Sci. Technol. **2004**, *38,* 904−911

Solution Chemistry Effects on Orthophosphate Adsorption by Cationized Solid Wood Residues

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Adsorption of orthophosphate anions in aqueous solution by cationized milled solid wood residues was characterized as a function of sorbate-to-sorbent ratio (≈0.001−2.58 mmol of P/g substrate), pH (3−9), ionic strength, *I* (no *I* control; 0.001 and 0.01 M NaCl), reaction time (4 min to 24 h), and in the presence of other competing anions (0.08−50 mM SO_4^{2-}; 0.08−250 mM NO_3^-). Sorption isotherms revealed the presence of two kinds of adsorption sites corresponding to high and low binding affinities for orthophosphate anions. Consequently, a two-site Langmuir equation was needed to adequately describe the data over a range of solution conditions. In addition to higher sorption capacity, cationized bark possessed a higher binding energy for orthophosphate anions compared to cationized wood. The sorption capacity and binding energy for bark were 0.47 mmol of P g^{-1} and 295.7 L $mmol^{-1}$, respectively, and for wood, the corresponding values were 0.27 mmol g^{-1} and 61.4 L $mmol^{-1}$. Both the sorption capacity and binding energy decreased with increasing *I*, due to competition from Cl^- ions for the available anion-exchange sites. The surface charge characteristics of cationized bark (pH_{zpc} = 7.9) acted in concert with orthophosphate speciation to create a pH-dependent sorption behavior. Orthophosphate uptake was quite rapid and attained equilibrium levels after 3 h. Both SO_4^{2-} and NO_3^- influenced percent removal but required high relative competing anion to $H_2PO_4^-$ molar ratios, i.e., 2.5−3 for SO_4^{2-} and 25 for NO_3^-, to cause appreciable reduction. These results support our hypothesis that adsorption of orthophosphate anions on cationized bark involves ion exchange and other specific Lewis acid−base interactions.

Introduction

There is growing interest in the use of renewable biomaterials as sorbents for treatment of water and wastewater containing low levels of contaminants from nonpoint sources of pollution. In the past, the focus has been on using traditional sorbents, such as activated carbon or ion-exchange resins, for treatment of contaminated water originating from point sources of pollution. In addition to high initial capital investment and operating costs in large-scale applications, resin sorbents are derived from nonrenewable resources and activated carbon often poses disposal problems after use (*1*, *2*). The goal of our research is to develop water treatment sorbents from low-cost renewable biomaterials such as solid wood residues or forest residues. Solid wood residues such as bark, sawdust, and shavings are available in large quantities at sawmills and related wood processing industries. Forest residues, such as slash, are often left unused on the forest floor after harvesting operations, and it has been suggested by fire ecologists that accumulation of these residues contributes to propagation of catastrophic wildfires.

A number of studies have examined the use of solid wood residues as sorbents for heavy metals, pesticides, and dyes (*3*−*8*). However, no studies have been reported that examined application of these sorbents for removal of nutrient anions, such as, orthophosphate from water. Elevation of phosphorus (P) concentrations above natural critical levels in sensitive water bodies, including lakes, ponds, and streams, accelerates eutrophication, which greatly diminishes the quality of surface water by restricting its use for fisheries, recreation, industry, and drinking (*9*−*12*). Thus, new and sustainable technologies are required for developing novel sorption media for removal and prevention of excess P from entering sensitive water bodies.

Phosphorus losses in surface runoff occur in two major forms: dissolved or sediment bound. Dissolved P exists in water as one of several orthophosphate anions (depending on pH as PO_4^{3-}, HPO_4^{2-}, or $H_2PO_4^-$), inorganic polyphosphates, and some organic P compounds dissolved in the water phase. Particulate P comprises pure crystalline P minerals, amorphous precipitates, and P sorbed onto soil particles and eroded organic matter (*13*). Dissolved P is available for immediate uptake by algae, whereas sediment-bound P provides a variable but long-term source in water bodies. Thus, removal of dissolved P is essential for inhibiting undesirable algal growth in sensitive surface waters.

The potential of a synthetic cross-linked polymeric hydrogel to remove phosphate from aquaculture wastewater effluents to low enough levels [<0.01 mg/L] so as to facilitate direct discharge to natural surface waters was highlighted by Kioussis et al. (*14*) and Kofinas and Kioussis (*15*). This sorbent was synthesized by cross-linking poly(allylamine hydrochloride) (PAA·HCl) with epichlorohydrin in aqueous solution to form a water-insoluble polymer network with fixed ammonium sites for anion exchange with phosphate anions in solution. In a previous study, we reported on the preparation and preliminary characterization of the sorption capacity of cationized milled bark for orthophosphate anions (*16*). The principal objective of the present study is to determine the mechanism of adsorption of orthophosphate anions and the effect of solution chemistry (sorbate-to-sorbent ratio; pH; ionic strength *I*; presence of competing anions) and reaction time on the sorption capacity of cationized bark.

Materials and Methods

Sorbent Preparation. Milled wood or bark of loblolly pine (*Pinus taeda L.*), 60/80 mesh size, was extracted with a 10% aqueous solution of *N*-methyl pyrrolidone in a Soxhlet apparatus to remove extractives. After drying in an oven at

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10.1021/es034819z CCC: $27.50
Published on Web 12/30/2003

105 °C for 6 h, samples were cationized with a 1% aqueous solution of PAA·HCl. Detailed description of the cationization procedure is provided in Tshabalala et al. (*16*).

Batch Sorption Experiments. Batch experiments were conducted in duplicates by adding 0.1 g of cationized milled bark or wood to a 60 mL polypropylene (PP) bottle. Varying amounts of stock solution containing 1000 mg of P/L (from NaH_2PO_4) were added to the PP bottle to give a series of solutions with initial orthophosphate (C_o) concentrations ranging from 0.00323 to 6.45 mmol of P L^{-1}. Sorbate-to-sorbent ratios range from 0.0013 to 2.58 mmol of P/g substrate. The total weight of the substrate and solution in each bottle was adjusted to be equal to 40 g using DI water to provide a solid-to-liquid ratio of 1:400. The substrates were allowed to react with orthophosphate solutions for 20 h at 25 ± 1 °C on a mechanical end-over-end shaker at 7 rpm. Cationized residue (no orthophosphate) blanks were identically prepared. After equilibration, the suspensions were allowed to settle for 1 h and then filtered through a 0.45 μm PP syringe filter. The pH value of the filtrate was measured using an Accumet AR-50 pH/conductivity meter before analyzing it for dissolved reactive phosphorus (DRP) using a Lachat autoanalyzer (Zellweger Analytics, Milwaukee, WI) by following the standard molybdate-based colorimetric methods at a wavelength of 880 nm (*17*). The difference between initial and final DRP concentrations was used to calculate percentage removal. The filtrate was also digested in a block digester using acid persulfate to determine total dissolved phosphorus.

Initial sorption experiments were conducted in the absence of a background electrolyte (i.e., no *I* control) to avoid competitive effects from the presence of other anions. With an increase in C_o from 0 to 6.45 mmol of P L^{-1}, the activity coefficient of $H_2PO_4^-$ (dominant P species under our solution conditions) varies from 1 to 0.89. Without pH control the equilibrium pH values after 24 h of reaction were 4.46 ± 0.21 and 3.68 ± 0.063 for cationized bark and wood systems, respectively.

Since cationized bark showed higher P sorption capacity than cationized wood, subsequent experiments to elucidate solution chemistry effects were conducted only on cationized bark samples. To determine the effect of solution chemistry, batch experimental protocol detailed above was followed with appropriate modifications. For example, two different concentrations of NaCl (0.01 and 0.001 M) were used as background electrolyte to create different *I* conditions. pH-effect experiments were conducted at a constant C_o of 1.612 mmol of P L^{-1}, and 0.01 M HCl or NaOH was used to obtain pH values ranging from 3 to 9 with a background comprising DI water (i.e., no *I* control) or 0.01 M NaCl. To determine the effect of competing anions, solutions containing a fixed C_o of 0.4 mM (from NaH_2PO_4) were reacted simultaneously with 0.1 g of cationized bark in the presence of different amounts of sulfate (SO_4^{2-}, 0.08−50 mM from K_2SO_4) or nitrate (NO_3^-, 0.08−250 mM NO_3^- from $NaNO_3$). The R_i (initial SO_4^{2-} or NO_3^- to orthophosphate molar ratio) values ranged from 0 to 125 (equilibrium pH 4.4 ± 0.28) and 0 to 625 (equilibrium pH 4.21 ± 0.26) for systems with SO_4^{2-} and NO_3^-, respectively. The suspensions were mixed for 20 h, after which the filtrate was analyzed for pH and DRP. Sulfate and NO_3^- concentrations were determined using a Dionex DX 500 ion chromatography at the Soil and Plant Analysis Laboratory, University of Wisconsin, Madison (eluent 1.0 mM $NaHCO_3$, 3.5 mM Na_2CO_3). Time dependence of orthophosphate sorption onto cationized bark was determined by reacting 0.4 mmol of P L^{-1} with cationized bark (0.01 M NaCl) for different time periods ranging from 4 min to 24 h.

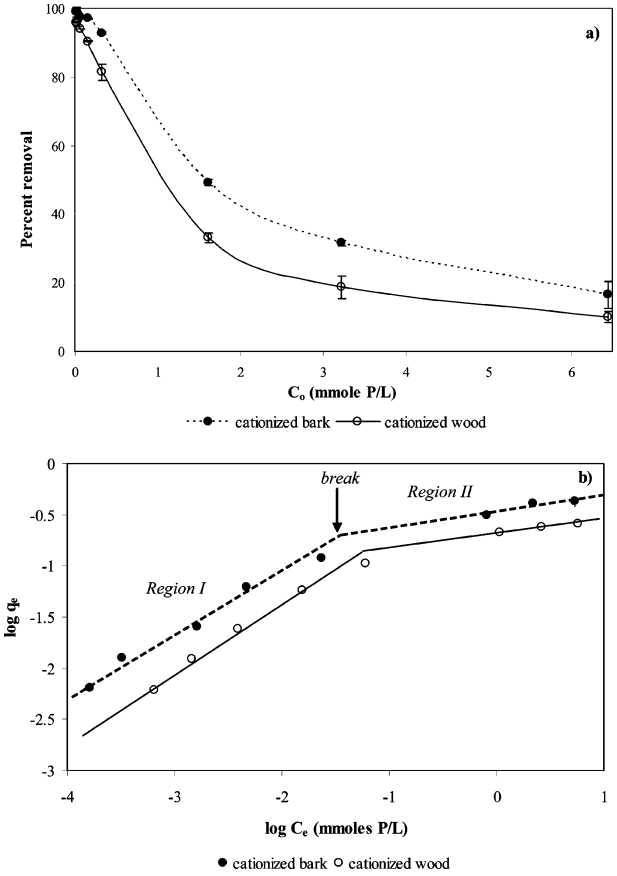

FIGURE 1. (a) Effect of initial concentration (C_o) of orthophosphate on its percent removal by cationized bark and cationized wood at equilibrium pH of 4.46 ± 0.21 and 3.68 ± 0.063, respectively. (b) Freundlich isotherms for orthophosphate sorption onto cationized bark and wood at equilibrium pH of 4.46 ± 0.21 and 3.68 ± 0.063, respectively. Experiments were conducted in a DI water medium with no ionic strength (*I*) control for both the sorbents. C_e is the equilibrium orthophosphate concentration, and q_e is the orthophosphate sorption capacity. Error bars (±1 standard deviation) if not shown are within the symbols.

Results and Discussion

Changes in surface chemistry and morphology of milled bark after cationization with PAA·HCl have been characterized using elemental composition analysis, scanning electron microscopy, energy-dispersive X-ray spectroscopy, inverse gas chromatography, and zeta potential measurements. Detailed information on surface characteristics of cationized milled bark along with the proposed reaction pathway is provided in Tshabalala et al. (*16*).

Sorbate-to-Sorbent Ratio. Orthophosphate anion interacts strongly with both cationized milled bark and wood but appears to show a stronger affinity for bark compared to wood. Sorption levels on a percent removal basis varied with C_o, reaching a level greater than 80% at C_o < 0.3 mM before decreasing with increasing C_o (Figure 1a). Both the noncationized milled bark and wood adsorbed negligible (<5%) amounts of orthophosphate from solution. The effect of sorbate-to-sorbent ratio, i.e., P-to-substrate, on the interaction of orthophosphate with cationized lignocellulose materials is illustrated using sorption isotherms shown in Figure 1b, where equilibrium orthophosphate concentration (C_e; mmol of P L^{-1}) is plotted as a function of sorption capacity (q_e; mol of P sorbed g^{-1}). When data is available over a wide range of C_e, sorption isotherms plotted on a double-logarithmic format typically have an initial region with unit slope at low C_e (called "linear" since a unit slope in log−log

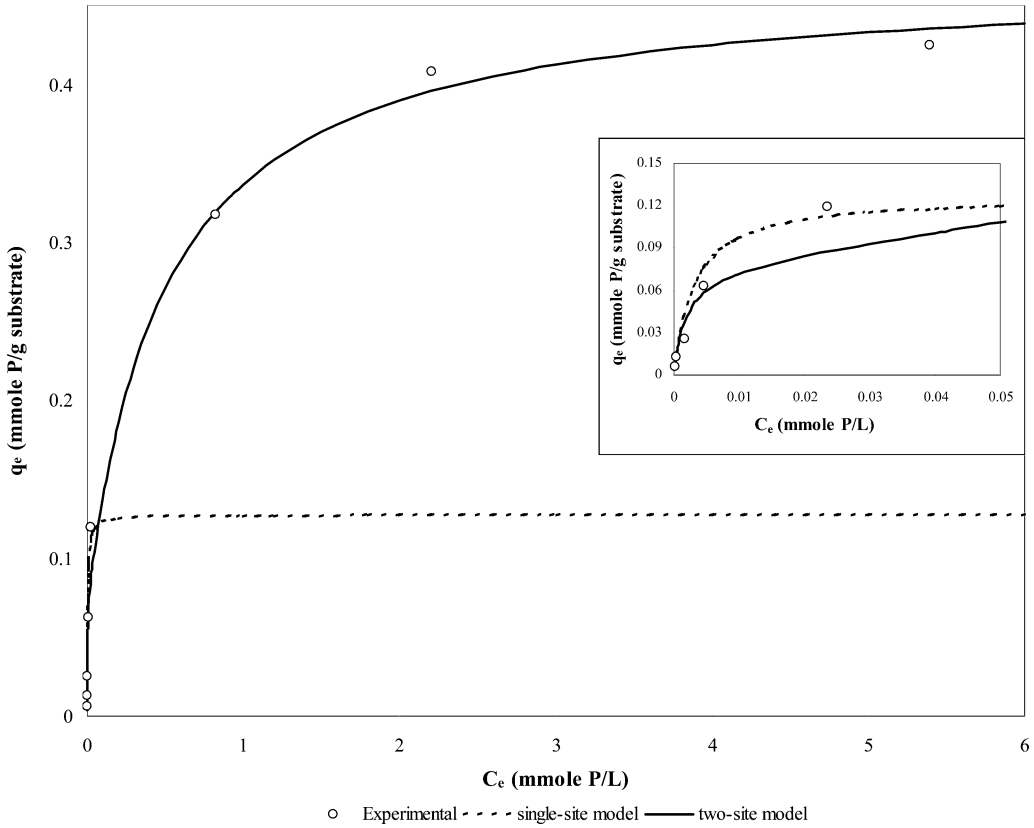

FIGURE 2. Description of experimental data on orthophosphate sorption by cationized bark (pH = 4.46 ± 0.21; no *I* control) using the single-site and two-site Langmuir models. Inset shows the model fits at low C_e values. Error bars if not shown are within the symbols.

format results in a linear arithmetic plot), a nonlinear region with less than 1:1 slope, and a saturation region corresponding to full occupancy of sorbent reactive sites (*18*, *19*). The isotherms for both cationized bark and wood do not reveal the linear region at low C_e levels. However, a decrease in the slope values (from 0.63 to 0.16 for cationized bark and from 0.66 to 0.2 for cationized wood) with increasing C_e is quite evident and suggests the presence of more than one kind of adsorption sites with different affinities (region I, higher binding strength; region II, lower binding strength) for orthophosphate anions. It is remarkable that the C_e (0.036 mmol of P L^{-1}) at which this slope change or "break" occurs is almost the same for both cationized bark and wood.

Two well-known adsorption isotherm models, namely, the Freundlich and Langmuir equations, were initially applied to describe the batch experimental data. The linearized Freundlich equation is given by (*20*)

$$\log q_e = \log K + \frac{1}{n}\log C_e \qquad (1)$$

where K (mmol of P g^{-1}) and n (L g^{-1}) are constants. The adsorption constant (K) is related primarily to the capacity of cationized lignocellulose materials for orthophosphate anions, and n is related to the strength of adsorption (*20*). Figure 1b illustrates the application of the Freundlich equation to describe phosphate sorption to cationized bark and wood. Although a single straight line can produce a reasonable fit (fit not shown in Figure 1b, but relevant parameters are $K = 0.319$ mmol of P g^{-1}, $n = 2.55$ L g^{-1}, and $r^2 = 0.954$ for cationized bark; $K = 0.19$ mmol of P g^{-1}, $n = 2.53$ L g^{-1}, and $r^2 = 0.934$ for cationized wood), it is apparent that two sorption regions with significantly different slopes exist as a function of C_e. These regions contain sites with different binding energies for orthophosphate anions. The hypothesis is that at low surface coverage sorption takes place at the higher affinity sites (region I) and, once these sites are saturated, further sorption occurs at lower affinity sites (region II). Similar observations have been reported for adsorption of P to soils (*21*, *22*).

The linearized Langmuir equation has the following form (*20*)

$$\frac{1}{q_e} = \frac{1}{K_1 K_2 C_e} + \frac{1}{K_2} \qquad (2)$$

where C_e is the equilibrium P concentration, mmol of P L^{-1}; q_e is the amount of P sorbed, mmol of P g^{-1}; K_2 is the maximum P sorption capacity, q_{max}, mmol g^{-1}; K_1 is a constant, related to the strength of adsorption, L $mmol^{-1}$. A fit of the experimental data using Langmuir isotherm yielded the following parameters: K_1 values for cationized bark and wood are 328.12 and 77.32 L $mmol^{-1}$ and K_2 equal to 0.127 and 0.128 mmol g^{-1}, respectively. Although the Langmuir model provided a good "overall" fit of the experimental data, significant deviation from linearity was observed at higher C_e levels (fit not shown). The inadequacy of a single-site Langmuir equation to describe the experimental data at high sorption capacities is clearly highlighted in Figures 2 and 3 (comparison between experimental and single-site model) for cationized bark and wood, respectively. Therefore, we used a multisite equation to describe the sorption data. The multisite (two sites) Langmuir equation can be expressed as (*21*)

$$q_e = \frac{K_1^{I} K_2^{I} C_e}{1 + K_1^{I} C_e} + \frac{K_1^{II} K_2^{II} C_e}{1 + K_2^{II} C_e} \qquad (3)$$

where the superscripts I and II correspond to regions (or mechanisms) containing sorption sites with different affinities (i.e., high and low, respectively) and K_1 and K_2 are related to

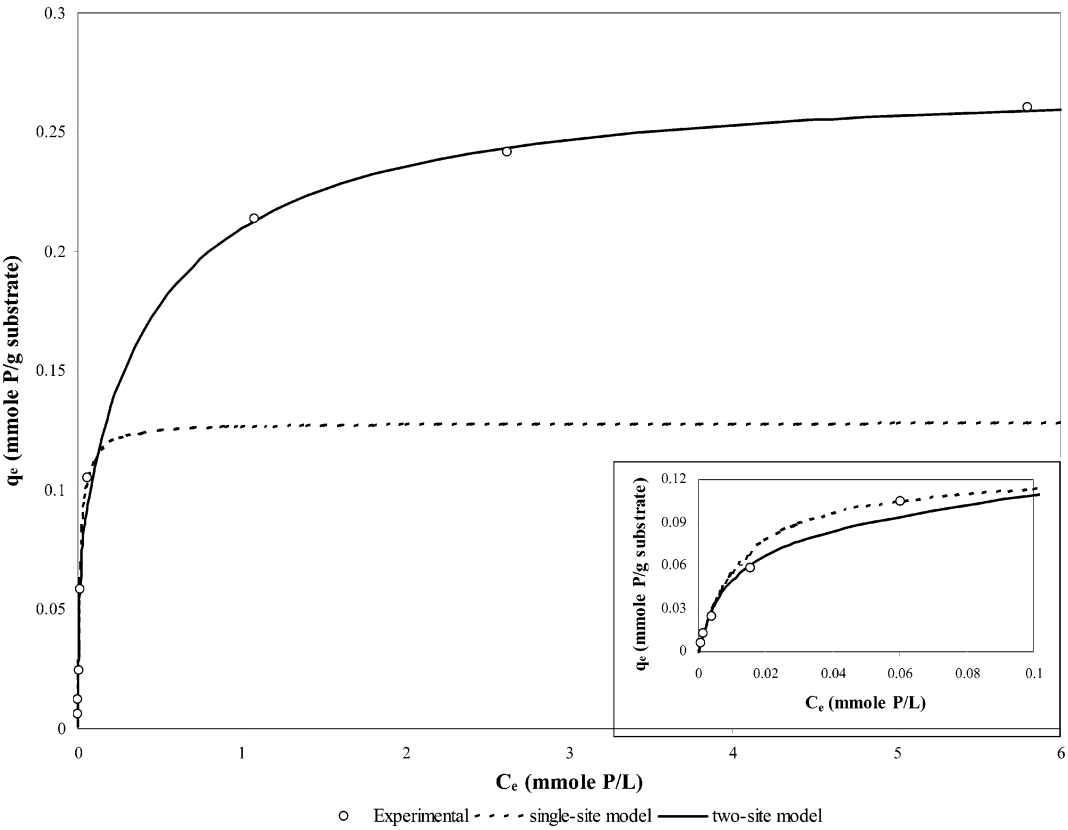

FIGURE 3. Description of experimental data on orthophosphate sorption by cationized wood (pH = 3.68 ± 0.063; no *I* control) using the single-site and two-site Langmuir models. Inset shows the model fits at low C_e values. Error bars if not shown are within the symbols.

TABLE 1. Two-Site Langmuir Model Parameters for Different Sorbent and Solution Conditions[a]

	region I		region II[b]		overall	
sorbent and background conditions	K_1^I	K_2^I	K_1^{II}	K_2^{II}	binding energy	sorption capacity
cationized bark (no *I* control)	586	0.075	1.98	0.395	587.98	0.470
cationized wood (no *I* control)	121	0.084	1.97	0.19	122.97	0.274
cationized bark (0.001 M NaCl)	44.25	0.145	1.68	0.16	45.93	0.305
cationized bark (0.01 M NaCl)	39.58	0.05	1.40	0.233	40.98	0.283

[a] Units: K_1 in L mmol^{-1} P; K_2 in mmol of P g^{-1} substrate. [b] The value of K_2^I was subtracted from each q_e value for data in region II, and the adjusted q_e was used in linearized Langmuir equation to obtain parameter values for region II sites.

binding energy (strength) and maximum sorption capacity, respectively. The adsorption maximum (K_2^{total}) for a sorbent is the sum of K_2^I (higher energy region I sites) and K_2^{II} (lower energy region II sites). The above model satisfactorily described orthophosphate sorption to cationized bark (Figure 2 and the inset) and wood (Figure 3 and the inset) over the entire range of C_e, and the corresponding model parameters are provided in Table 1. To accurately describe orthophosphate sorption to three soils for C_e up to 0.45 mmol of P L^{-1}, Syers et al. (*21*) used two types of sites with widely different (33−91 times) binding strengths. They found that the ratio of sites in region I to total sorption capacity (K_2^I/K_2^{total}) varied from 0.4 to 0.52. Using initial orthophosphate levels up to 1 mM on 41 soils from southern England and eastern Australia, Holford et al. (*22*) found that 23% of the total orthophosphate sorption occurred on high-energy sites, and the ratio of binding energies of the two site types (K_1^I/K_1^{II}) was 100. Our data indicates that region I sites in cationized bark have a significantly higher affinity for orthophosphate than the region II sites (K_1^I/K_1^{II} in Table 1) and accounted for ≈16% of total sorption. In contrast, a greater fraction (31.1%) of orthophosphate was sorbed to high-energy sites in cationized wood with binding energy 61 times greater than those of region II sites. Although cationized wood has a slightly higher capacity of high energy sites (K_2^I) than cationized bark, the binding energy constant for orthophosphate was much higher for cationized bark (K_1^I of 586 vs 121). The binding energy constants for region II are similar for both the cationized lignocellulose materials; however, cationized bark has twice as much sorption capacity in this region than cationized wood. Cationized bark not only has a higher overall adsorption capacity (0.47 mmol of P g^{-1} substrate) than cationized wood (0.274 mmol of P g^{-1}), but also contains sites with higher binding energies for orthophosphate.

Figure 4 shows the proposed scheme for sorption of orthophosphate anions on cationized bark by (A) Lewis acid−base interactions with an amine group (note, similar interactions are also possible with hydroxy groups), (B) combination of Lewis acid−base and ionic interactions with an amine and a quaternary ammonium group, and (C) ionic interactions with ammonium groups. Although orthophosphate anions have more than one mode of interaction with cationized bark, it is very likely that mode B could be the underlying mechanism for orthophosphate sorption in region I (higher binding strength), whereas modes A and C are likelyto be responsible for lower affinity sorption in region

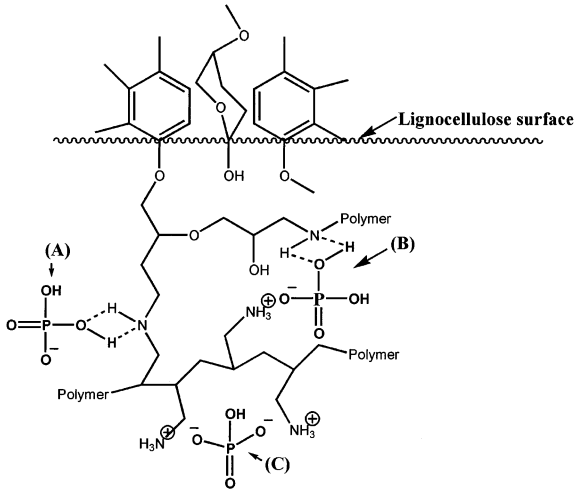

FIGURE 4. Proposed scheme for adsorption of orthophosphate anions on cationized bark by Lewis acid−base interactions (A), by a combination of Lewis acid−base and ionic interactions (B), and by ionic interactions (C).

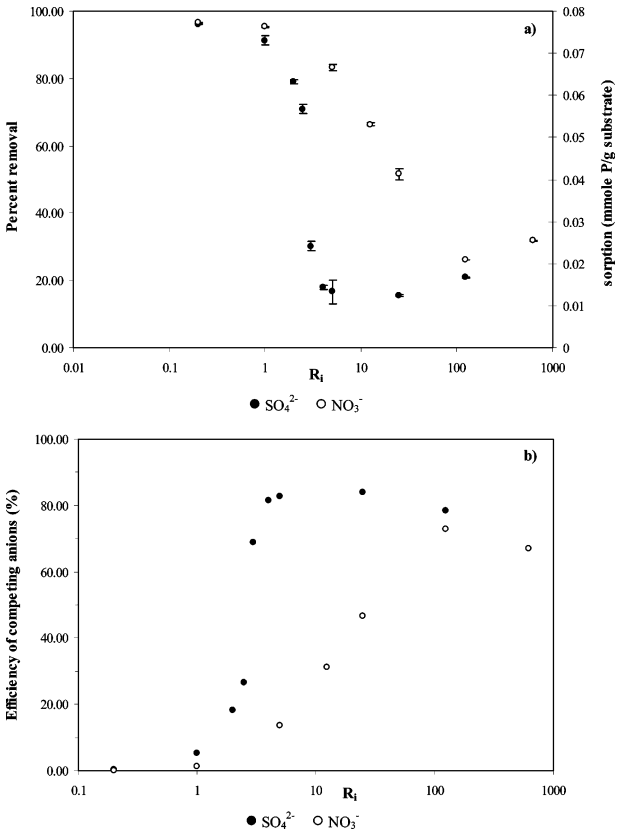

FIGURE 5. (a) Reduction of orthophosphate sorption by cationized bark due to presence of competing anions (SO_4^{2-} or NO_3^-) (pH = 4.4 ± 0.28 for the SO_4^{2-} system, no *I* control; pH = 4.21 ± 0.24 for the NO_3^- system and no *I* control). Error bars if not shown are within the symbols. (b) Efficiency of SO_4^{2-} or NO_3^- in reducing orthophosphate sorption by cationized bark.

II. The relative distribution of amine, ammonium, and hydroxy groups in cationized bark is pH dependent. The pH-dependent changes in surface charge characteristics of cationized bark (shown in Figure 7b) provide a rough estimate of the relative surface distribution of the amine, ammonium, and hydroxy groups and also some clues as to which mode of orthophosphate interaction is likely to predominate under different solution conditions. Cationized bark is positive between pH 3 and 7.9 ($pH_{ZPC} = 7.9$) and turns negative at pH > 8. Ammonium sites would predominate under acidic conditions (experimental data available up to pH 3) with their concentration decreasing with increasing pH values, and the converse is true for the amine sites. The isotherms were generated at pH ≅ 4.5. At these pH values, $H_2PO_4^-$ is the dominant orthophosphate species and all three modes of interactions are possible. However, interaction mode A may not be very important at low pH values because it is very likely that there may be an ammonium group close by that would react the same way as mode B.

A comparison of the P sorption characteristics of cationized milled bark against other well-known sorbents was performed using data obtained in our laboratory and by other researchers. Celi et al. (*23*) reported a sorption maximum of 0.091 mmol of P g^{-1} for goethite in the presence of 0.01 M KCl. Using poorly crystalline gibbsite with no *I* control, we obtained a sorption maximum of 0.086 mmol of P g^{-1}. The maximum phosphate-sorption capacity and the corresponding pH for different clay minerals (10 mM K^+ background) were determined by Oh et al. (*24*): hematite (0.07 mmol of P g^{-1} at pH 5.4), goethite (0.53 at pH 5.4), and alumina (0.552 at pH 5.4). McLaughlin et al. (*25*) also provide the following sorption capacities of several Al- and Fe-containing compounds for orthophosphate: allophane (2.8 mmol g^{-1}), Al gel fresh (2.33), Fe gel (1.93), Al gel aged (1.03), Fe gel dried (0.412), Fe-coated kaolinite (0.185), hematite (0.125), goethite (0.103), gibbsite (0.032), and kaolinite (0.037). Except for allophane and freshly prepared Al and Fe gels, cationized milled bark compares favorably to these materials.

Presence of Competing Anions. Since cationized milled bark showed a relatively higher sorption capacity for orthophosphate anions than wood, the rest of the discussion of solution chemistry effects (i.e., competitive sorption, dependence on *I*, pH, and reaction kinetics) will focus only on cationized bark. Figure 5a shows orthophosphate sorption as affected by the presence of SO_4^{2-} and NO_3^- at different R_i (molar ratio of competing anions to orthophosphate; 0−125 and 0−625 for SO_4^{2-} and NO_3^-, respectively) values. Percent sorption was calculated based on the activity of diprotic orthophosphate {$H_2PO_4^-$} with activity coefficients determined using the extended Debye−Hückel equation (at $I < 0.1$ M) and the Davies equation at higher *I*. Both of these anions reduce orthophosphate sorption at relative molar ratios exceeding 1, with SO_4^{2-} competing more effectively for exchange sites than NO_3^-. At $R_i = 1$, the divalent SO_4^{2-} is able to displace only 4.8% (≈0.004 mmol of P g^{-1}) of the sorbed diprotic $H_2PO_4^-$. The sorption plots have a sigmoidal profile with the one for SO_4^{2-} being sharper and an inflection point between R_i of 1 and 2, and the corresponding plot for NO_3^- is at R_i close to 5. These inflection points correspond to molar ratios of competing anions above which an appreciable decrease in orthophosphate sorption occurs. Sigmoidal competition curves, especially for SO_4^{2-}, indicate strong competition once a specific activity is reached. This type of competitive behavior has been observed during cation exchange (Mg^{2+} replacing Ca^{2+}) on vermiculite (*26*).

The ability of these anions to compete with orthophosphate can also be illustrated by plotting efficiency of SO_4^{2-} or NO_3^- (Figure 5b) calculated using the following expression given by Deb and Datta (*27*)

$$\text{Efficiency of competing anions (\%)} = \left(1 - \frac{\text{orthophosphate sorbed in the presence of } SO_4^{2-} \text{ or } NO_3^-}{\text{ortho-}PO_4 \text{ sorbed when added alone}}\right) \times 100 \quad (4)$$

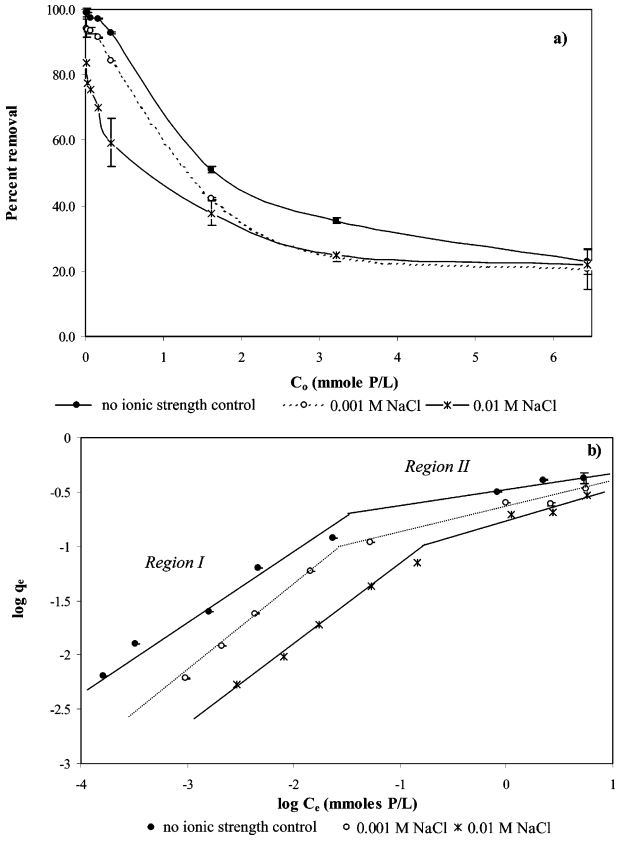

FIGURE 6. (a) Effect of ionic strength on sorption of orthophosphate by cationized bark (equilibrium pH for no *I* control, 0.001 M NaCl, and 0.01 M NaCl is 4.46 ± 0.21, 4.57 ± 0.09, and 4.86 ± 0.08, respectively). (b) Freundlich isotherms for orthophosphate sorption as a function of *I*. C_o and C_e are the initial and equilibrium orthophosphate concentrations, and q_e is the orthophosphate sorption capacity. Error bars if not shown are within the symbols.

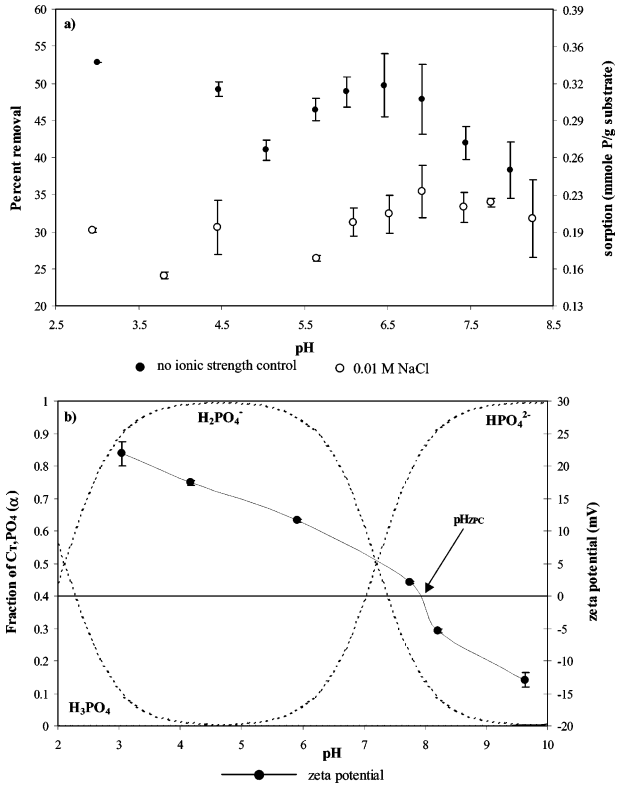

FIGURE 7. (a) Effect of pH on orthophosphate sorption by cationized bark (C_o = 1.612 mmol of P L^{-1}). (b) The charge characteristics of cationized bark (zeta potential) and pH-dependent aqueous speciation of orthophosphate. Error bars if not shown are within the symbols.

SO_4^{2-} has a much higher efficiency in lowering orthophosphate sorption to cationized bark than NO_3^-. For example, to achieve a 50% reduction in sorption, R_i has to be between 2.5 and 3 for SO_4^{2-} and slightly greater than 25 for NO_3^-. Both of these aprotic anions did not completely displace the diprotic $H_2PO_4^-$. The maximum displacement efficiency was only 83.7% and 72.7% for SO_4^{2-} and NO_3^-, respectively. Despite its higher negative charge, excess divalent SO_4^{2-} is required to displace diprotic $H_2PO_4^-$. This observation is supported by our hypothesis, stated earlier, that sites with different binding energies (regions I and II) exist in cationized bark and initial orthophosphate sorption occurs on the high-energy region I sites. Since the aprotic NO_3^- or SO_4^{2-} is unable to effectively compete and completely displace orthophosphate, it is likely that a portion of orthophosphate is bound to cationized bark via a specific sorption mechanism. Note that at a C_o of 0.4 mM used for competitive sorption experiments, 100% sorption corresponds to a surface excess of 0.08 mmol of P g^{-1}. The capacity of region I sites (Table 1) under no *I* control and at 0.01 M is 0.075 and 0.05 mmol of P g^{-1}, respectively. Interaction modes A and B (Figure 4) are specific for orthophosphate. Since SO_4^{2-} and NO_3^- are not protonated, they cannot enter into Lewis acid−base interactions in the same manner as monoprotic or diprotic orthophosphate anions. It is also conceivable that the orientation and spacing between adjacent ammonium groups, or between ammonium and amine groups, or between ammonium and hydroxy groups, or between amine and hydroxy groups are just perfect for relatively stronger interactions with orthophosphate compared to SO_4^{2-} or NO_3^- anions. At higher R_i values, however, these anions can exert an influence on mode B interaction of orthophosphate by competing for the cationic ammonium sites.

Ionic Strength. Two different *I* values, 0.001 and 0.01 M NaCl were used, and the results were compared with those obtained for cationized bark with no *I* control (DI background) described earlier. The effect of *I* on phosphate sorption is illustrated in Figure 6a and b. An increase in *I* (from no *I* control to 0.01 M) lowered the extent of sorption up to a C_o of 3.223 mmol of P L^{-1} (Figure 6a) and shifted the sorption isotherms toward higher C_e levels (Figure 6b). The C_e value at which slope change or "break" occurs between region I and region II is 0.0316, 0.0281, and 0.2 mmol of P L^{-1} for no *I* control, 0.001 M NaCl, and 0.01 M NaCl, respectively.

While our percent removal plots and isotherms (Figure 6a and b) present an overall picture showing moderate *I* dependence, region-specific (region I vs II) effects can be evaluated using the results obtained from modeling the data with the two-site Langmuir equation (Table 1). With increasing *I*, there is a decrease in the binding energy constants (K_1) for both regions I and II as well as the overall sorption capacity (K_2^{total}). The overall binding energy constant (K_1^{total}) decreased by more than an order of magnitude. K_2^{total} decreased by 34% and 40.4% as *I* increased to 0.001 and 0.01 M, respectively. While comparing K_1 and K_2 values for regions I and II it is important to note that the R_i (Cl^{-1} to orthophosphate molar ratio) values significantly differ for these regions. R_i decreases with increasing C_o and, hence, with increasing C_e. Consequently, the data points lying in region I have been obtained at much higher R_i values than those in region II. For example, at 0.01 M NaCl, the R_i values for region I range from 710 to 36, whereas they are between 7 and 1.8 for region II. Despite these differences in R_i values, there is a greater reduction in the sorption capacity for region II sites (K_2^{II}) and, thereby

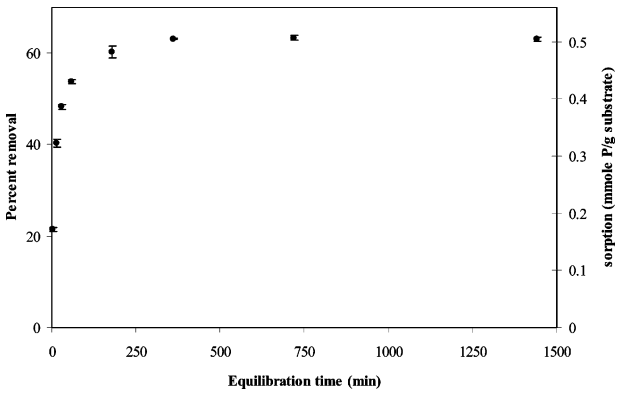

FIGURE 8. Effect of reaction time on orthophosphate sorption by cationized bark (equilibrium pH 4.59 ± 0.01; C_o = 0.4 mmol of P L^{-1}; 0.01 M NaCl background). Error bars if not shown are within the symbols.

overall capacity (K_2^{total}), with increasing *I* than the corresponding effect on region I. There are two possible ways by which increasing *I* can influence orthophosphate sorption by cationized bark: (i) reduced solution-phase activity of $\{H_2PO_4^-\}$, dominant species between pH 3 and 7.2, and (ii) increased competition from Cl^- for exchange at ammonium sites. Percent removal values in Figure 6a were calculated using $\{H_2PO_4^-\}$, and therefore, the activity coefficient effect is accounted for. As explained above for the influence of SO_4^{2-} or NO_3^-, competitive effects from Cl^- are likely to mainly affect nonspecific ionic interactions (mode C) and mode B to some degree (at high R_i values). Consequently, increasing *I* can affect orthophosphate sorption in both regions I and II. However, it is likely to be more significant in region II, as supported by the multisite modeling results.

pH Effect. At the higher *I* of 0.01 M, only a slight pH-dependent behavior was observed with maximum removal occurring around pH 7.5 (Figure 7a). In the system with no *I* control, orthophosphate removal exhibited a moderate pH dependence, resembling the sorption envelope typically observed during anion interaction with oxides and clay minerals. The extent of orthophosphate removal by cationized bark decreased between pH 3 and 4.8, increased up to pH 6.5, and then decreased at increasing pH values (Figure 7a). The sorption trend can be attributed to a combination of the pH-dependent speciation of orthophosphate and surface charge characteristics (pH_{ZPC} = 7.9) of the cationized bark as shown in Figure 7b. The concentration of $H_2PO_4^-$ increases up to pH ≈ 5, above which it decreases. The concentration of HPO_4^{2-} is increasing throughout the range used for the pH-effect experiments. Although the monoprotic HPO_4^{2-} would be more strongly attracted electrostatically toward cationized bark than diprotic $H_2PO_4^-$, the decrease in surface charge acts in concert with orthophosphate speciation to influence the extent of removal. Other researchers have observed a monotonic decrease in phosphate sorption by hematite, goethite, and alumina between pH 5 and 7 (*24*, *28*). The effectiveness of cationized bark in the circum-neutral pH range is desirable for its use to treat water and wastewater from nonpoint sources of pollution.

Reaction Kinetics. Time-dependent (4 min to 24 h) sorption of orthophosphate to cationized bark is shown in Figure 8. To evaluate reaction kinetics under conditions where competitive anionic interactions exist, this experiment was conducted in a background containing 0.01 M NaCl. Initial rapid removal of orthophosphate from solution was observed up to 1 h, after which the rate decreased and an apparent equilibrium was reached at 3 h. Faster uptake after short reaction times, 63.8% and 85.1% of maximum sorption occurred within 15 min and 1 h, respectively, makes it viable to use milled bark cationized with PAA·HCl for real-world applications.

Our results indicate that cationization of lignocellulosic materials by reaction with PAA·HCl imparts surface charge characteristics that could be exploited for removal of orthophosphate anions from surface water runoff. The adsorption site capacities for orthophosphate on cationized bark or wood compare quite favorably with other well-known P sorbents. Cationized bark is also highly effective in the circum-neutral pH range, which represents a significant advantage over other anionic sorbents, such as Al and Fe oxides where maximum orthophosphate sorption occurs between pH 4 and 5 (*23*, *29*). The ability of cationized bark to bind significant amounts within short contact times (<15 min), in the presence of commonly encountered competing anions (SO_4^{2-}, NO_3^-), combined with its effectiveness over a wide pH range should enhance its applicability for treatment of high volumes of water and wastewater containing low but undesirable levels of dissolved reactive P.

Acknowledgments

Financial support provided for this project by the USDA Forest Service Forest Products Laboratory, Madison, WI, the Massachusetts Department of Food and Agriculture, the Cranberry Institute, and the Wisconsin Cranberry Board is gratefully acknowledged.

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Received for review July 24, 2003. Revised manuscript received October 31, 2003. Accepted November 12, 2003.

ES034819Z