Cationized Milled Pine Bark as an Adsorbent for Orthophosphate Anions

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ABSTRACT: More efficient adsorption media are needed for removing dissolved phosphorus in surface water runoff. We studied the use of cationized pine bark as a sorbent for dissolved phosphorus in water. Cationized pine bark was prepared by treating extracted milled pine bark with polyallylamine hydrochloride (PAA HCl) and epichlorohydrin (ECH) in aqueous medium. Attachment of PAA HCl to the bark was monitored by percentage of weight gain and nitrogen content. Changes in bark surface chemistry were characterized by zeta potential and inverse gas chromatography measurements. Energy dispersive x-ray analysis and scanning electron microscopy were used to determine changes in chemical composition and morphology of the cationized bark. The cationized bark showed a decrease in the dispersive component of the surface energy and a barely measurable change in the surface acid–base properties. In the pH range 2.5 to 7.9, the cationized bark showed a positive zeta potential, which changed to negative at pH 7.9 or higher. By comparison, the zeta potential of control extracted bark remained negative throughout the pH range of 2.5 to 9. We propose that the reaction of bark with PAA HCl results in a surface network of fixed cationic sites of quaternary ammonium that have mobile chloride ions as counter anions. Preliminary results from batch adsorption experiments indicate that cationized milled bark has an estimated maximum adsorption capacity of approximately 12.65 mg phosphate/g, which compares favorably with that of other well-known phosphorus sorbents. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1577–1583, 2004

Key words: adsorption; morphology; polyelectrolytes; renewable resources; surfaces

INTRODUCTION

Agricultural and urban runoff has been identified as a major source of phosphorus entering sensitive water bodies such as lakes, ponds, or streams.[1] Elevation of phosphorus levels in these water bodies above natural critical levels accelerates eutrophication, the natural aging of lakes or streams. Eutrophication has been identified as the main cause of poor surface water quality.[2] Eutrophication restricts water use for fisheries, recreation, industry, and drinking because it results in the increased growth of undesirable algae and aquatic weeds and in the depletion of dissolved oxygen in bottom waters.[3] Phosphorus in surface runoff occurs in two major forms: dissolved or sediment bound. Dissolved phosphorus exists in water as one of several orthophosphate anions (PO_4^{3-}, HPO_4^{2-}, or $H_2PO_4^{-}$) depending upon pH. Dissolved phosphorus is available for immediate uptake by algae, and sediment-bound phosphorus provides a variable but long-term source of phosphorus to algae.

Various strategies for decreasing phosphorus levels in surface runoff have been proposed. These strategies can be divided into two major categories: source management and transport management.[4] Source management focuses on matching application rates of phosphorus fertilizers to uptake by plants and crops and on matching livestock dietary phosphorus input to animal requirements. It has been argued that source management would decrease the amount of surplus phosphorus in soils or excreted manure that might be entrained in surface runoff. This contention has yet to be proven in practice.

Transport management focuses on using intervention strategies such as vegetated riparian zones or buffer strips, detention ponds, constructed wetlands, infiltration systems (porous pavements, infiltration trenches, and basins), and filtering systems (surface, underground sand, perimeter, and bioretention filters; submerged gravel wetlands).[5] One advantage of filter-

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ing systems is that they are versatile and can be implemented in a variety of areas, including those where space is at a premium. However, commonly used filtration media, such as sand or gravel, are inadequate for removing dissolved phosphorus. Thus, more efficient adsorption media are required for use in filtering systems for removing dissolved phosphorus in surface water runoff.

Interest is growing in the use of wastes from forest products industries as adsorption media for removing a wide range of contaminants from wastewater. A number of studies have explored the use of bark for removing heavy metal ions,[6–8] reactive dyes,[9] and pesticides[10] from water. A recent study investigated the use of cationized wood sawdust for removing anionic residual dyes from water.[11]

Chemical precipitation and biofiltration are the two most commonly used methods for removing dissolved phosphorus from wastewater.[12,13] Although effective in that regard, these processes have some shortcomings. Chemical precipitation produces sludge, which poses dredging and disposal problems. Biofiltration is sensitive to fluctuations in phosphorus load and temperature.

Anion exchange resins, activated alumina, and zirconium oxides have also been explored for removing dissolved phosphorus in water.[14–19] Zhao and Sengupta[20] highlighted the use of polymeric ligand exchangers for removing phosphate from wastewater, and Kioussis et al.[21] described the use of polymeric hydrogels for binding phosphate in aquaculture wastewater. Although these materials are effective, they are largely derived from nonrenewable resources. Bearing this fact in mind, we decided to study the use of cationized pine bark as a sorbent for dissolved phosphorus in water.

Pine bark constitutes a significant fraction of underutilized low-value forest residue. Approximately 18% of the weight of logs from conifers, such as southern pine, is bark.[22] The majority of bark is used as low-grade thermal fuel. Apparently, this practice is for the sole purpose of avoiding a large solid waste management problem. In general, bark has a complex chemical structure that consists of nonextractable and extractable components.[23–25] It is the nonextractable components—polysaccharides (cellulose, hemicellulose, and pectic substances), phenolic polymers (lignin and high-molecular-weight tannins), and cross-linked polyesters (suberin and cutin)—that can be exploited for attaching cationic groups to bark tissue.

Various methods of attaching cationic groups to cellulose or lignocellulose materials have been reported in the literature.[11,26,27] Gruber et al.[28] examined new approaches for attaching quaternary ammonium groups to cellulose and demonstrated that the use of oligoionomers results in very high cationic densities on the fiber surfaces.

The objectives of the present research are to explore the use of cationized lignocellulosic materials as adsorbents for dissolved phosphorus and to develop methods for attaching cationic sites on lignocellulosic substrates. The present study describes cationization of milled pine bark with polyallylamine hydrochloride (PAA HCl) using epichlorohydrin (ECH) as a spacer and cross-linking agent.

EXPERIMENTAL

Materials

Bark chips consisting mainly of loblolly pine (*Pinus taeda* L.) were obtained from a pulp mill in Mississippi. Chips were delivered to the Forest Products Laboratory in a sealed container within 1 week after sampling from a debarker. Chips were allowed to air dry for 8 h at ambient temperature before being placed in a drum dryer to dry overnight at 105°C. Oven dried chips were milled and sieved into fractions of different mesh sizes ($>$ 60, 60/80, 80/100, 100/200 mesh, and 230/270 mesh, U.S. Standard Sieves). One fraction (60/80 mesh) was selected for use in the current experiments. The other fractions were stored to be used in other experiments. PAA HCl (average M_w ca 15,000), ECH, *N*-methyl pyrrolidinone (NMP), and all other reagents were purchased from Aldrich (Milwaukee, WI) and were used as received.

Methods

Preparation of bark–PAA HCl

Using the 60/80-mesh fraction, bark–PAA HCl was prepared in two steps. First, a sample of the 60/80-mesh fraction was extracted for 24 h with 10% aqueous solution of NMP in a Soxhlet apparatus to remove leachable components of the bark, including polyphenols, carbohydrates, and resin compounds.[29] The extracted sample was allowed to air dry overnight at ambient temperature and then placed in an oven at 105°C to dry for 6 h. Second, a weighed sample of the oven-dried milled bark was suspended in 1% aqueous solution of PAA HCl. The solid to liquid ratio in the suspension was 1:10. For every 100 g bark, 2.5 g sodium hydroxide pellets were added and the suspension was thoroughly mixed until the sodium hydroxide pellets had dissolved. Thereafter, 20 mL ECH was added for every 100 g bark in the suspension. The suspension was mixed thoroughly at room temperature for 1 h and then poured into a tray to dry for 72 h at ambient temperature. The air-dried product was rinsed several times with deionized water, filtered, and dried at 65°C to a constant weight.

Characterization of bark–PAA HCl

The extent to which PAA HCl reacted with the bark substrate was determined by percentage of weight

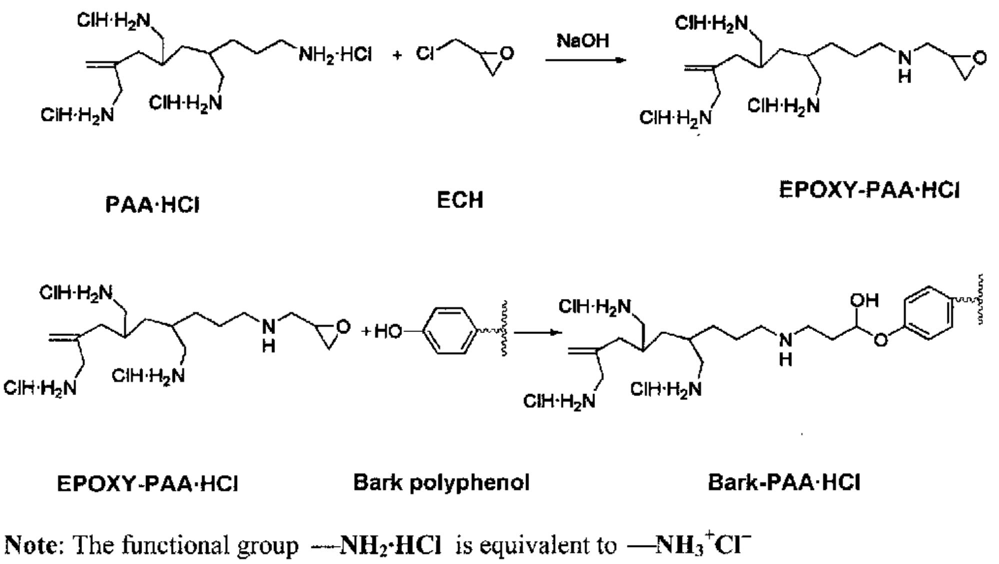

Figure 1 Proposed reaction pathway for attachment of polyallylamine hydrochloride (PAA HCl) to bark substrate.

gain and nitrogen content after exhaustive rinsing of bark–PAA HCl with deionized water. Nitrogen content was determined by Galbraith Laboratories, Inc. (Knoxville, TN).

Zeta potential measurements were used to characterize changes in the surface charge of bark–PAA HCl and control extracted bark. For that purpose, 50 mg each of bark–PAA HCl and control extracted bark samples (270 mesh) were suspended in 100 mL deionized water. The suspension pH was adjusted to the appropriate pH value in the range of 2 to 10 by addition of 0.01*M* NaOH or HCl. The zeta potential was measured by means of a Zeta Sizer 3000H (Malvern Instruments, Inc., Southborough, MA).

Inverse gas chromatography (IGC) was used to measure changes in the surface energy and acid–base characteristics of bark–PAA HCl. The IGC measurements were performed according to published procedures,[30] except that the correction factors were not applied for gas compressibility and water vapor pressure of the bubble flow meter soap solution.

Energy dispersive x-ray analysis (EDXA) was used to characterize changes in the elemental composition of bark–PAA HCl. EDXA was carried out on a Tracor-Noran TN-5500™ energy dispersive x-ray analyzer (ThermoNoran, Middleton, WI).

Surface morphology of bark–PAA HCl was characterized by scanning electron microscopy (SEM). The SEM images were obtained on a Jeol JSM-840 scanning electron microscope (Jeol USA, Inc., Peabody, MA).

Adsorption measurements

The adsorption experiments were conducted in deionized water solutions of sodium dihydrogen phosphate, without any additional background electrolyte or pH adjustments. A given mass (0.1 g) of cationized bark was mixed in duplicate with a constant volume (40 mL) of sodium dihydrogen phosphate solutions of different initial concentrations (0.1, 0.5, 1, 2, 5, 10, 50, 100, 200, and 500 mg/L) in a 60-mL polypropylene bottle. The mixtures were allowed to equilibrate for 24 h at 25 ± 1°C on a mechanical end-over-end shaker at 7 rpm. After equilibration, the mixtures were filtered through a 0.2-μm polytetrafluoroethylene (PTFE) filter. The pH of the filtrate was recorded, and the phosphate concentration in the filtrate was determined by the standard molybdate-based colorimetric method using a Lachat autoanalyzer (Lachat Instruments, Milwaukee, WI).[31] The amount of phosphate adsorbed by the cationized bark was determined from the difference between the concentrations of the phosphate solutions before and after equilibration.

RESULTS AND DISCUSSION

Characterization of bark–PAA HCl

The proposed reaction pathway for attachment of PAA HCl to the bark substrate is illustrated in Figure 1. PAA HCl reacts with ECH in the presence of NaOH to form an epoxy derivative of PAA HCl. The byproducts of this reaction are NaCl and H_2O (not shown in Fig. 1). The epoxy derivative most likely attaches to the bark substrate via the nonextractable phenolic polymers of bark, such as lignin or proanthocyanidins. Nonextractable proanthocyanidins are extremely reactive polyphenols that may constitute up to 97% of the total proanthocyanidins in bark.[32]

The extent to which PAA HCl reacted with the bark substrate was determined by percentage of weight

TABLE I
Weight Percent Gain and Nitrogen Content of Bark–PAA HCl

Sample	Nitrogen (%)	Weight gain (%) Measured	Weight gain (%) Expected
Bark–PAA HCl	1.7 ± 0.42 (N = 5)	13.2	16.0[a]
Epoxy–PAA HCl	10.6	100	100
Control extracted bark	< 0.5[b]	0	0

[a] Calculated by comparing the nitrogen content of bark–PAA HCl and that of an equivalent amount of the reaction product of epichlorohydrin and PAA HCl

[b] Below limit of quantitation.

gain of the oven-dried bark–PAA HCl after exhaustive rinsing with deionized water to remove NaCl formed as a byproduct of the reaction of ECH with PAA HCl. If we assume that the nitrogen content of bark–PAA HCl is solely due to PAA HCl reacted with the bark substrate, then we can calculate the expected weight percent gain of the bark from the nitrogen content of an equivalent amount of the reaction product of epichlorohydrin and PAA HCl deposited on a glass substrate. The results are summarized in Table I. The actual weight percent gain was lower than expected due to slight dissolution of the bark substrate under the reaction conditions used in this study. Figure 2 shows representative EDXA spectra of (a) control extracted bark and (b) bark–PAA HCl before exhaustive rinsing with deionized water. The presence of a strong chloride peak in bark–PAA HCl could be attributed to bound PAA HCl, unreacted residual PAA HCl and ECH, or the reaction byproduct, NaCl. To ensure that the observed chloride peak did not arise from NaCl, unreacted residual PAA HCl, or unreacted ECH, bark–PAA HCl was exhaustively rinsed with deionized water until the pH and conductivity of the rinse water were practically constant at an approximate pH value of 3.59 and specific conductivity ≅ 164 μS/cm, respectively. At this point, it was assumed that any unreacted residual PAA HCl or ECH and the reaction byproduct NaCl were completely washed off by this exhaustive rinsing procedure. Figure 2(c) shows the spectrum of bark–PAA HCl after exhaustive rinsing with deionized water. The amount of NaCl recovered in the rinse water was determined by inductively coupled plasma spectrometry. Since the measured molar ratio (1.80) of Cl/Na was greater than its theoretical value (1.62) in NaCl, it is reasonable to conclude that, in addition to NaCl, the rinse water contained other chlorides, including some HCl that was leached from PAA HCl bonded to the bark substrate. In addition, it is reasonable to ascribe the strong chloride peak observed in the EDXA spectrum of bark–PAA HCl to PAA HCl attached to the bark substrate.

Comparison of representative SEM images of bark–PAA HCl and control extracted bark did not reveal any discernible differences between bark–PAA HCl and control extracted bark (Fig. 3). Images of bark–PAA HCl [Fig. 3(a)] and control extracted bark [Fig. 3(b)] showed details of the coarse architecture of the bark surface, which consisted of expanded parenchymatous cells, scattered throughout with collapsed sieve tubes. Thus, the surface morphology of the bark was not compromised by treatment with PAA HCl. This is important because a desirable property of bark as an adsorbent is its coarse and porous surface structure. Such a structure is expected to be conducive to entrapping colloidal sediment with minimal effect on the low resistance to water flow of a filtration bed packed with bark particles. Changes in IGC surface energy and acid–base characteristics of bark after treatment with PAA HCl were estimated from the specific retention volume, V_g, of IGC neutral and acid–base probes at different column temperatures on matched deactivated glass columns packed with equal weights of bark–PAA HCl and control extracted bark particles. The physicochemical properties of IGC probes used in this study are summarized in Table II.[33,34]

The specific retention volume V_g of an IGC probe is calculated from eq. (1):

$$V_g = (273.15/T_c)(t_r - t_{Ar})F/W \qquad (1)$$

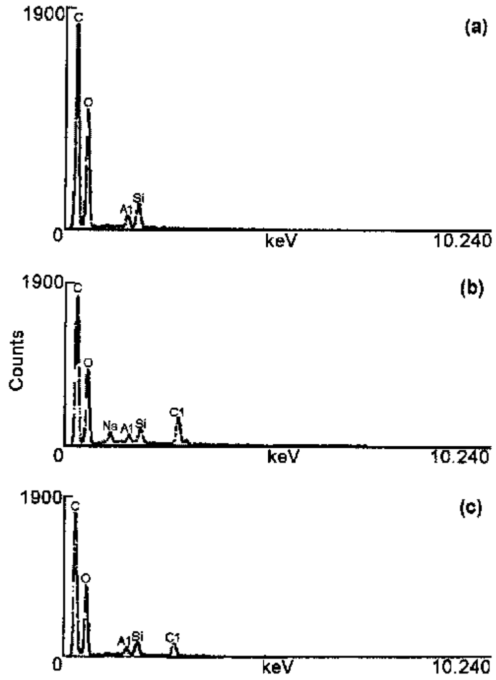

Figure 2 Representative EDXA spectra of (a) control extracted bark, (b) PAA HCl treated bark, and (c) PAA HCl treated bark after rinsing. Note disappearance of Na peak after treated bark was exhaustively rinsed with deionized water. Intensity of Na peak decreased from 463 counts to 0, while that of Cl peak decreased from 1,793 to 1,034 counts.

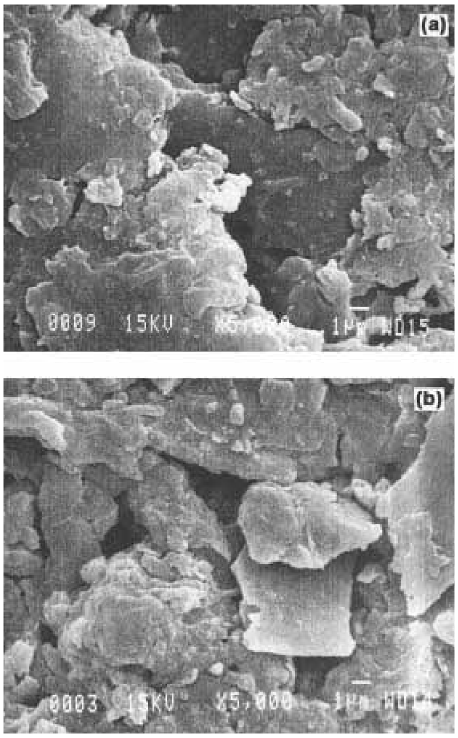

Figure 3 SEM images of bark treated with (a) PAA HCl and (b) control extracted bark.

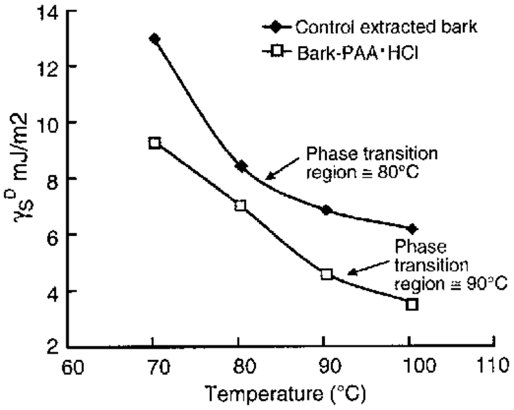

Figure 4 Plots of dispersive component $\gamma_S{}^D$ of surface energy as function of temperature for bark treated with PAA HCl and control extracted bark.

where T_c is column temperature (K), W is amount (g) of sample packed into column, F is flow rate of helium carrier gas, and t_r and t_{Ar} are retention times of probe and marker gas, argon, respectively. Retention times at a given column temperature were determined in quadruplicate.

The dispersive component of the surface energy, $\gamma_S{}^D$, is calculated from eq. (2):

$$\gamma_S^D = (1/\gamma_{(CH2)})[\Delta G_{(CH2)}/2Na]^2 \tag{2}$$

where $\gamma_{(CH2)}$ is surface tension of a methylene group, $\Delta G_{(CH2)}$ is free energy of a methylene group, N is the Avogadro number, a is estimated surface area occupied by a methylene group and is equal to 0.06 nm^2, $\gamma_{(CH2)} = 35.6 + 0.058(293.15 - T_c)$ (mJ/m^2), and $\Delta G_{(CH2)}$ is obtained from the slope of ln V_g as a function of the number of carbon atoms of a series of alkanes.[35]

Figure 4 shows $\gamma_S{}^D$ as a function of temperature for control extracted bark and bark–PAA HCl. The bark–PAA HCl exhibited lower values for the dispersive component of the surface energy compared to the values of control extracted bark. In addition, the plot for bark–PAA HCl showed an inflection point at ~ 90°C compared to ~ 80°C for control extracted bark. The shift in the inflection point is probably related to the different glass transition temperatures of the different surface polymers of bark–PAA HCl and control extracted bark. The shifted inflection point indicates that the surface energy characteristics of bark–PAA HCl are clearly different from those of control extracted bark.

The surface acid–base characteristics of bark–PAA HCl and control extracted bark were evaluated by comparing the values obtained by dividing the surface acceptor number, AN_s, by the surface donor number, DN_s. Values for AN_s and DN_s were estimated from the free energy of adsorption–desorption, ΔG_a, of a polar probe by assuming that ΔG_a of a polar probe having an acidic character yields DN_s, whereas that of a polar probe having a basic character yields AN_s.[36]

TABLE II
Physicochemical Properties of Study IGC Probes

Probe	a (Å^2)	γ_L^D (mJ · m^{-2})	AN	DN (Kcal · mol^{-1})	MW (g · mol^{-1})	Specific character
n-Hexane	51.5	18.4	0	0	86.18	Neutral
n-Heptane	57	20.3	0	0	100.21	Neutral
n-Octane	63	21.3	0	0	114.23	Neutral
Chloroform	44	25.9	23.1	0	119.38	Acidic
Tetrahydrofuran	45	22.5	8.0	20.1	72.11	Amphoteric

a is surface area of probe; γ_L^D is dispersive component of surface energy of probe, AN and DN are acceptor and donor numbers, respectively, of acid–base probes as defined by Gutmann [34]; MW is molecular weight of probe.

TABLE III
Surface Acid–Base Properties of Treated and Untreated Bark

Sample	*AN*s/*DN*s	Surface acid–base properties
Control extracted bark	1.1 ± 0.01	Acidic surface
Bark treated with PAA HCl	1.2 ± 0.03	Acidic surface

The free energy of adsorption–desorption of an acidic or basic IGC probe is estimated from eq. (3):

$$\Delta G_a = -RT_c \ln V_g \quad (3)$$

where R is the gas constant, T_c is the column temperature (K), and V_g is the specific retention volume of an acid–base probe.

Tetrahydrofuran (THF) and chloroform (CHL) were used as the basic and acidic IGC probes, respectively. The ratio of AN_s/DN_s was estimated from the following relationship:[36]

$$AN_s/DN_s \equiv \Delta G_a^{\text{THF}}/\Delta G_a^{\text{CHL}} \quad (4)$$

As shown in Table III, the ratio AN_s/DN_s is practically the same for both bark–PAA HCl and control extracted bark. We had expected the AN_s/DN_s ratio for bark–PAA HCl to be much higher than 1.2. However, since this ratio is greater than 1.1, the surfaces of both bark–PAA HCl and control extracted bark are considered to be acidic.[36] Note that, although these ratios are nearly equal, this does not necessarily imply that the surface acidity of bark–PAA HCl and control extracted bark arises from similar surface groups. It is conceivable that the surface acidity of bark–PAA HCl arises from the surface quaternary ammonium groups, $\sim RNH_3^+$, while that of control extracted bark arises from surface phenolic groups. Thus, the barely measurable increase in surface acidity together with a measurable decrease in the dispersive component (γ_S^D) of the surface energy of bark after treatment with PAA HCl supports our proposition that reaction of bark with PAA HCl results in a surface network of fixed cationic sites of quaternary ammonium ($\sim RNH_3^+$) that have mobile chloride ions as counter anions (Cl^-).

Although differences in the IGC surface acidity of bark–PAA HCl and control extracted bark were barely measurable, differences in their surface charge were clearly distinguishable. Figure 5 shows plots of zeta potential as a function of pH of aqueous suspension of bark–PAA HCl and control extracted bark. The control extracted bark had a negative zeta potential that corresponded to its surface charge in the pH range of 2.5 to 9. The surface charge of the bark–PAA HCl was positive at low pH and changed to negative at high pH. The point of zero charge (pH_{ZPC}), defined as the pH at which the surface charge is zero, was around pH 7.9 for bark–PAA HCl. At pH < pH_{ZPC}, bark–PAA HCl had a positively charged surface due to the presence of quaternary ammonium cationic sites ($\sim RNH_3^+$), and at pH > pH_{ZPC}, it had a negatively charged surface. The negative charge developed as a result of neutralization of the surface $\sim RNH_3^+$ to $\sim RNH_2$, accompanied by ionization of the surface phenolic groups to phenolate anions.

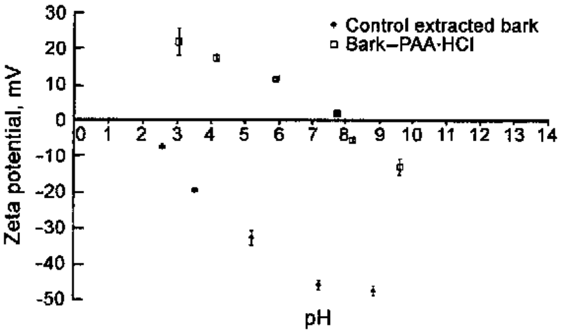

Figure 5 Zeta potential versus pH of aqueous suspensions of bark–PAA HCl and control extracted bark.

Compared to other inorganic phosphorus sorbents,[37] such as SiO_2 (pH_{ZPC} 2.5), SnO_2 (pH_{ZPC} 4.5), kaolinite (pH_{ZPC} approximately 4.6), ZrO_2 (pH_{ZPC} 6.7), goethite (pH_{ZPC} 6.7), and lanthanum-impregnated silica gel (pH_{ZPC} 6.7) that have lower pH_{ZPC}, bark–PAA HCl has a higher pH_{ZPC}, which makes it an attractive sorbent for orthophosphate anions over a wide pH range.

Phosphate adsorption

Figure 6 shows a plot of the percentage of phosphate adsorbed by bark–PAA HCl and the corresponding plot of adsorption capacity versus the initial phosphate concentration (C_0) in solution. The adsorption capacity is defined as milligrams of phosphorus ad-

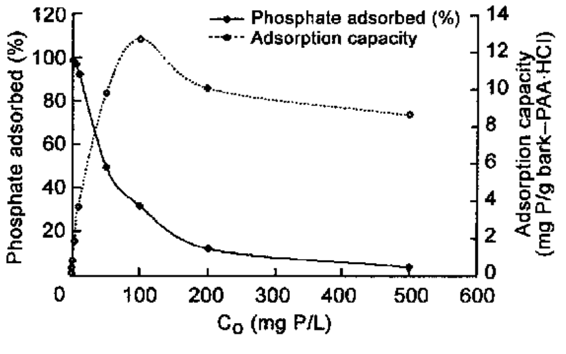

Figure 6 Percentage of phosphate adsorbed by bark–PAA HCl and adsorption capacity of bark–PAA HCl versus initial phosphate concentration (C_0) in solution. Equilibrium pH value was 4.5 ± 0.25.

sorbed per grams of bark–PAA HCl after equilibration for 24 h in a phosphate solution. At $C_0 \leq 10$ mg/L, the percentage of phosphate adsorbed was greater than 90%. At $C_0 > 10$ mg/L, the percentage of phosphate adsorbed gradually decreased, dropping to approximately 10% at $C_0 = 200$ mg/L. Correspondingly, the adsorption capacity plot showed a maximum at approximately $C_0 = 100$ mg/L. Thus, the maximum adsorption capacity is estimated to be approximately 12.65 mg phosphorus/g bark–PAA HCl.

We expected the plot of adsorption capacity as a function of C_0 to remain constant after reaching a maximum at $C_0 = 100$ mg/L. But since this plot showed an apparent decrease with further increase in phosphate C_0 above 100 mg/L, it is likely that at such high concentrations no additional sites are available on bark-PAA HCl to adsorb orthophosphate anions. Additional experiments are currently in progress to determine adsorption isotherms and to elucidate the precise adsorption mechanism of orthophosphate anions on bark– PAA HCl.

CONCLUSION

We have demonstrated the potential for converting low-cost, abundantly available, and renewable lignocellulosic materials such as bark to sorption media for removing dissolved phosphorus from water. Future work will focus on designing filtration systems that use cationized milled bark to capture dissolved phosphorus in surface water runoff from urban and agricultural areas. Proposed experiments will focus on determination of the service life of such filtration systems as well as the recyclability of the sorption media.

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