

Orthophosphate Sorption onto Lanthanum-Treated Lignocellulosic Sorbents

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Inorganic/organic hybrid adsorbents for removing orthophosphate from water were prepared by lanthanum (La) treatment of bark fiber, a lignocellulosic material obtained from juniper (*Juniperus monosperma*). The La was anchored to the juniper bark (JB) fiber by ion exchange with Ca in the bark and was responsible for removing orthophosphate. Two La concentrations (0.01 and 0.1 M) were used that resulted in loadings of 0.198 (La/JB01) and 0.302 (La/JB02) mmol of La g⁻¹ of fiber, respectively. At circumneutral pH conditions, La exhibited a strong affinity for bark, but significant La desorption occurred under acidic conditions (pH < 4.5). For La/JB02, 86% of the initial La loading was released at pH 2.5, and only 0.1% at pH 7.3. Initial La loading in the bark fiber significantly influenced its orthophosphate sorption capacity, which was determined for La/JB01 and La/JB02, respectively, to be 0.188 and 0.233 mmol of P g⁻¹ (sorption envelopes) and 0.211 and 0.351 mmol of P g⁻¹ (sorption isotherms when surface site saturation occurred). The P-to-La molar ratio on the bark surface was extremely high (0.12–1.77 for La/JB01 and 0.13–2.58 for La/JB02), implying that orthophosphate removal occurred by other mechanisms in addition to surface complexation. From the orthophosphate surface loading levels and the shape of the sorption isotherms, it appears that adsorption occurred at low sorbate-to-sorbent (P-to-La-treated JB) ratios and transitioned to surface precipitation at higher ratios. When surface precipitation occurred, orthophosphate uptake continued to increase with increasing initial P levels. Results from X-ray diffraction and infrared spectrometric analyses are also suggestive of the occurrence of surface precipitation during the interaction of orthophosphate with La-treated lignocellulosic materials.

Introduction

Forest and agricultural residues have been evaluated as sorbents for removing potential environmental pollutants (both cationic and anionic) in surface waters (1–4). These

renewable biosorbents, including algae (5, 6), sugar beet (7), peat moss (8, 9), and bark (10, 11), appear to have a natural affinity for some cations because they possess surface functional groups (–COOH) that can bind cations by ion exchange. With appropriate surface modification, some of these biosorbents can be used to bind anions in water and, therefore, could be used for removing anionic pollutants such as orthophosphate or arsenate. Different approaches for grafting surface positive charges on selected lignocellulosic materials such as bark or sawdust to enhance their sorption capacity for anionic contaminants have been attempted (1, 2, 12–14). Those approaches were based on the use of quaternary amines and polyamines for surface cationization (1, 2) or impregnation of these lignocellulosic materials with metals that could serve as binding sites for anions in water (12–14). The latter approach resulted in a high sorption capacity per unit metal loading because the impregnated metal particles were well dispersed inside the support and existed in a chemical environment different from that of commercial inorganic material adsorbents (15, 16). The impregnation method, therefore, presents an added advantage over simply producing cationic sorption sites by surface modification.

In this study, we introduced lanthanum (La) as an inorganic material into bark fiber, an organic substrate, to develop an inorganic/organic hybrid adsorbent for anions. Lanthanum is a rare earth element (REE) that is considered to be environmentally friendly and is relatively abundant in the earth's crust compared to other REEs (17). Lanthanum compounds have been used in water treatment processes, since La is less expensive compared to other REEs and the point of zero charge of lanthanum oxide is higher than that of other well-known adsorbents. Examples include application of La salts for precipitative removal of arsenic (As) ions (18, 19) and the use of lanthanum oxide and La-impregnated alumina/silica gel for As removal by adsorption (20, 21). Recently, lanthanum oxide was infused into mesoporous silicates for removal of arsenate ions from water (22).

Juniper bark (JB) and wood fibers have been evaluated as sorption media for removal of cationic pollutants such as cadmium (Cd) from water (3, 4, 23). Sulfonation or treatment with a base improved the sorption capacity of wood fiber by producing additional surface anionic sites for binding cations. In a recent study (23) we compared the sorption characteristics of juniper wood and bark fibers, and showed that JB had a greater sorption capacity for Cd in water than juniper wood fiber. Thus, in the present study, bark fiber was selected for investigation as the organic support for La cations, which then in turn serve as the adsorption sites for binding anions in water.

Excess phosphorus (P) in surface water bodies causes eutrophication that leads to serious impairment of water quality (2, 24). Phosphorus exists in water bodies in particulate-bound and/or dissolved forms. Dissolved P, the immediately bioavailable fraction, is composed of orthophosphate anions, inorganic polyphosphate, and some organic P compounds (25). In this study, we focused on the removal of orthophosphate anions from water by JB treated with La, and paid particular attention to sorption behavior and interaction mechanisms. The extent of orthophosphate sorption and La desorption as a function of pH was also monitored. The proposed mechanism for orthophosphate sorption on La-treated bark fiber is based on data from adsorption isotherms and from infrared and X-ray diffraction (XRD) spectrometric analyses.

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Materials and Methods

Materials. Small-diameter logs of juniper were randomly collected in New Mexico, and reduced into small chips at the USDA Forest Products Laboratory (FPL), Madison, WI. Bark was separated from wood chips and ground in a Wiley mill to pass through an 0.18 mm screen. Lanthanum-treated JB adsorbents were prepared by soaking in aqueous solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich Chemical Co., Milwaukee, WI). A 10 g portion of JB was soaked for 1 d at room temperature in a 600 mL solution containing two different La salt concentrations, 0.1 or 0.01 M, and the solution pH was adjusted to be between 7.0 and 8.0 using 0.1 M KOH/HNO_3 . The solids were filtered and washed with distilled water several times and finally dried at room temperature for 2 d. The adsorbents were designated as La/JB01 and La/JB02 for La salt concentrations corresponding to 0.01 and 0.1 M, respectively. To determine the extent of La loading, the supernatants were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Ultima ICP-AES instrument, Jobin Yvon, Inc., Edison, NJ) at the USDA FPL. The infrared (diffuse reflectance infrared Fourier transform spectrometry, DRIFT) spectra were obtained on a Mattson Galaxy 5020 (Mattson Instruments, Madison, WI) fitted with a Harrick Scientific diffuse reflectance accessory (Harrick Scientific Co., Ossining, NY). The XRD patterns were obtained on a Scintag PAD V X-ray diffractometer, equipped with $\text{Cu K}\alpha$ radiation. The infrared spectra and XRD patterns of La-treated bark fiber, after interaction with orthophosphate, were compared to those of freshly formed lanthanum phosphate precipitate, which was prepared in our laboratory from $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ (Fisher Scientific, Fair Lawn, NJ) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ by adding 10.80 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to 500 mL of 0.05 M $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ solution. The solution was stirred overnight, filtered, and then dried overnight in an oven at 383 K.

Sorption Experiments. Orthophosphate sorption isotherms were acquired through batch experiments. A sorbent mass of 0.035 g was reacted with 35 mL solutions containing different initial orthophosphate concentrations (0.032–14.5 mmol of P L^{-1} , C_0) in 40 mL polypropylene (PP) tubes. The orthophosphate solutions were prepared by serial dilution of a stock solution containing 1000 mg of P L^{-1} prepared from $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$. The initial solution pH was adjusted to 6.1 ± 0.1 . The mixtures were equilibrated on a platform shaker for 12 h at room temperature. After equilibration, the supernatant was filtered through a 0.45 μm PP syringe filter and analyzed for P concentration using ICP-AES. Since P analysis was performed on filtered solutions, all the measured P was assumed to be in the form of orthophosphate. The final solution pH ranged from 5.9 to 6.5.

Sorption kinetics were evaluated using 0.60 g of sorbent with a C_0 of 0.32 mmol of P L^{-1} and an initial pH of 6.0 in a 600 mL solution. The suspension was continuously stirred by a magnetic bar, and aliquots (~ 5 mL) were taken at various times during the 30 h experiment. The total volume sampled for the entire kinetics experiment was only 50 mL, which had a minimal impact on the solid-to-solution ratio (increased it from 1:1000 to 1:917). The orthophosphate concentration in the filtrate was measured using ICP-AES. Orthophosphate uptake (q_e) and sorption rate constants (k) were determined from the pseudo-second-order rate equation (9), which assumes that adsorption follows the Langmuir model. The kinetic rate equation can be written as follows:

$$dq_t/dt = k(q_e - q_t)^2 \quad (1)$$

where q_t and q_e are the amounts of orthophosphate adsorbed at time t and equilibrium (mmol g^{-1}), respectively, and k is the equilibrium rate constant for second-order sorption ($\text{g mmol}^{-1} \text{min}^{-1}$). Besides the pseudo-second-order equation,

TABLE 1. Correlation Coefficient Values for the Description of Experimental Data by Several Kinetic Rate Models

sample	R^2 (correlation coefficient)				
	pseudo-second-order	pseudo-first-order	power function	simple Elovich	parabolic diffusion
La/JB01 ^a	0.999	0.758	0.996	0.996	0.945
La/JB02 ^a	0.999	0.843	0.894	0.964	0.947

^a La/JB01 and La/JB02 are La-treated juniper bark sorbents.

several other kinetic rate models including the pseudo-first-order, the parabolic diffusion, the power function, and the simple Elovich models were used to describe the experimental data. As shown in Table 1, the pseudo-second-order model had the highest correlation coefficients for both La/JB01 and La/JB02.

Sorption envelope experiments were conducted as a function of solution pH. A sorbent mass of 0.035 g was placed in 40 mL PP tubes containing 35 mL of 0.32 mmol of P L^{-1} solution. The solutions were shaken for 12 h at room temperature. After equilibration, the final pH of the solutions was measured with an AR50 pH meter (Fisher Scientific, Pittsburgh, PA). The supernatant was also filtered with a 0.45 μm PP syringe filter and analyzed for orthophosphate concentration using ICP-AES.

La Desorption Tests. Desorption tests were conducted to assess the pH-dependent stability of La in the La-treated sorbents. The desorption tests were performed between pH 2.5 and pH 7.0. A sorbent (La/JB01 or La/JB02) mass of 0.3 g was added to a 1 L beaker containing 600 mL of deionized water adjusted to different pH values using 0.1 M KOH/HNO_3 . Supernatant samples were collected at several incremental time periods during the 2 h experiment, and the filtrate (0.45 μm) was analyzed for La.

Spectroscopic Measurements. Samples of control bark fiber (JB) and bark fiber treated with La (La/JB01 and La/JB02), before and after equilibration in orthophosphate solutions, as well as a reference sample of freshly precipitated La phosphate were analyzed by XRD and DRIFT spectroscopy. The XRD patterns were obtained at a wavelength of 0.154 nm with a scan speed of 1.5 deg min^{-1} , from 10° to 50°. To acquire the infrared spectra, the DRIFT spectrometer was set to collect 4000 scans at 4 cm^{-1} resolution in the range 4000–400 cm^{-1} . Prior to analysis, samples were finely ground using a Wiley mill and sieved with an 0.18 mm screen. For comparison, each spectrum was baseline corrected at 400, 840, 2000, and 4000 cm^{-1} and normalized against the 1320 cm^{-1} band associated with the C–H bending mode (26). In addition, energy-dispersive X-ray analysis (EDXA) was performed on a Tracor-Noran TN-5500 energy-dispersive X-ray analyzer (ThermoNoran, Middleton, WI) to characterize changes in JB after treatment with La and subsequent reaction with orthophosphate.

Results and Discussion

Treatment of Bark with La. The pH-dependent interaction between La and bark is highlighted in Figure 1 (data obtained by reacting 500 mL of 0.01 M $\text{La}(\text{NO}_3)_3$ solution in a 1 L beaker with and without JB). A sharp decrease in La concentration in solution was observed in the absence of bark only at pH > 8.5. Such a sharp pH dependence is normally noticed during homogeneous precipitation of cationic elements. In the presence of bark, a completely different pH-dependent trend was obtained. Soluble La concentration decreased gradually above pH 4.5, likely attributable to sorption, since the bark fiber has an intrinsic affinity for cations. On the basis of these results, a pH value of 7.0 was chosen for the preparation of La-treated JB sorbents.

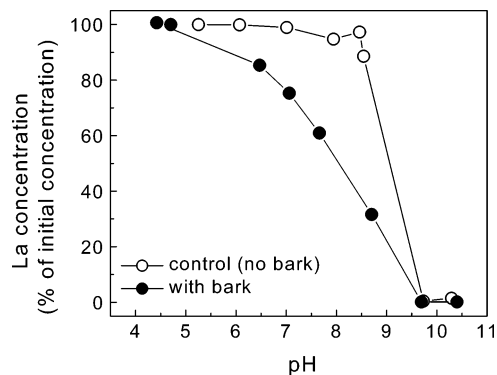


FIGURE 1. Effect of pH on lanthanum loading onto *Juniperus monosperma* bark.

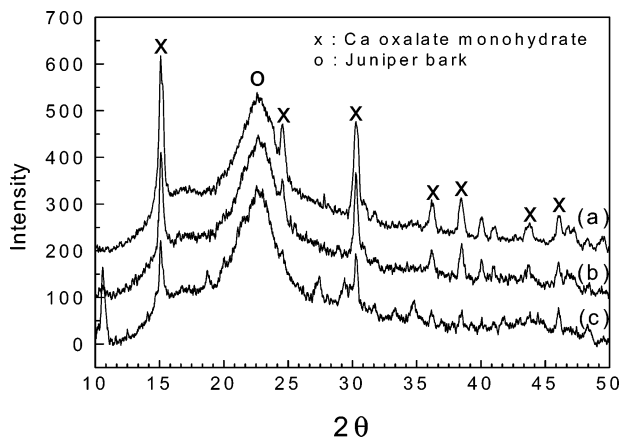


FIGURE 2. X-ray diffraction patterns of (a) JB, (b) La-treated JB La/JB01, and (c) La-treated JB La/JB02.

The use of two different initial La salt concentrations, 0.01 and 0.1 M, resulted in different La contents in the bark fiber, namely, 0.198 (for La/JB01) and 0.302 (La/JB02) mmol of La g⁻¹ of fiber, respectively. These La surface loading amounts are comparable to those in La-impregnated alumina (0.237–0.256 mmol of La g⁻¹) when a similar wet impregnation method was used for La infusion (20). A proportional increase in surface La loading corresponding to an increase in initial La concentration was not obtained; a 10 times higher initial La concentration (14.2 times higher final solution La concentration) increased the La loading in JB only by a factor of 1.5. Therefore, it can be inferred that La attachment to the bark fiber was achieved primarily through binding in the plateau region of a Langmuir-type isotherm, rather than surface precipitation of a La phase on JB, where uptake is nearly independent of the final La concentration.

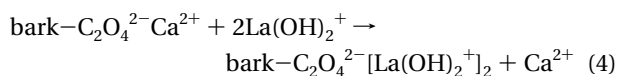
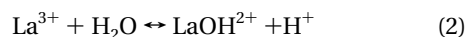
The XRD patterns of JB, La/JB01, and La/JB02 shown in Figure 2 suggest that La is attached to the bark by exchanging places with some of the intrinsic calcium (Ca) in the bark. The characteristic peak for the JB structure occurs at a 2θ of 22.78°. Sharp peaks appearing at 2θ values of 15.06°, 24.51°, 30.25°, 36.16°, 38.38°, and 45.99° in JB match very well with those of calcium oxalate monohydrate (whewellite); the characteristic peaks for whewellite are at 2θ values of (in decreasing order of intensity) 14.93°, 24.37°, 30.11°, 15.29°, 38.18°, 35.98°, 43.58°, 38.32°, 30.64°, 45.84°, and 46.53° (27). Calcium oxalate is known to be an important inorganic constituent in bark fibers (28). After La treatment, the height of the Ca peak relative to the characteristic JB peak in the diffractograms decreased (Figure 2). In addition, measured Ca levels in solution after La treatment of JB also increased significantly (by more than an order of magnitude compared to those for untreated JB). These observations support our

TABLE 2. EDXA Peak Intensity Ratios of Elements on Untreated and La-Treated Bark Samples

peak ratio	juniper bark (untreated)	La-treated juniper bark La/JB02	La/JB02 after orthophosphate sorption
Ca/C	0.4	0.2	0.2
La/C	0	0.2	0.2
P/C	0	0	0.2

hypothesis that La attachment to the bark takes place by a La–Ca ion exchange mechanism.

The displacement of the Ca by La from the bark was also confirmed by EDXA analysis of the bark fiber before and after treatment with La. As shown in Table 2, the ratio of the EDXA peak intensity of the Ca relative to the carbon (C) peak intensity (Ca/C) decreased from approximately 0.4 in JB to approximately 0.2 in La/JB02, while the La/C ratio increased from 0 in JB to approximately 0.2 in La/JB02. Since the dominant La species under neutral solution pH conditions is La(OH)₂⁺ (20), on the basis of the above information, the following scheme is proposed for La–Ca exchange in JB:



Desorption of La from the Sorbents. To evaluate the leachability of La from La-treated bark fiber, desorption kinetics were performed under a number of pH conditions (Figure 3). Table 3 summarizes the extent of pH-dependent La desorption under our experimental conditions for La-treated bark. The extent of La desorption was a function of both pH and the La content, with the former exerting a greater influence. Desorption of La is insignificant around neutral pH conditions, which is desirable for the use of these materials for water and wastewater treatment. The stability was significantly affected under acidic conditions with up to 45.6% and 29.5% of La desorbed for La/JB02 (pH 4.1) and La/JB01 (pH 4.4), respectively.

Lanthanum release from the sorbents during orthophosphate uptake at different pH conditions is shown in Figure 4. Figure 3 and Table 3 provide information on La desorption in the absence of orthophosphate ions. The extent of La desorption from La-treated bark was unaffected by the presence of orthophosphate ions (Figure 4). Under circumneutral conditions, La desorption was negligible, whereas a large amount of La was desorbed from the treated bark under acidic conditions (pH < 4.5). The tendency of La to desorb from the bark at pH ≤ 4.5 is identical to the behavior of La(OH)CO₃ when it was exposed to low pH conditions (19). Tokunaga et al. (19) observed that release of La from La-(OH)CO₃ was significant below pH 4.3 and it was not influenced by the presence of anions such as arsenate.

Orthophosphate Sorption onto La-Treated Bark. The untreated JB sorbed negligible amounts (<5%) of orthophosphate from solution. On the other hand, orthophosphate sorption by La-treated bark increased with increasing pH (Figure 4), a trend opposite that commonly observed for its sorption to oxides and clay minerals (29). Maximum sorption occurred around pH 6, above which it leveled off. The pH-dependent trend can be attributed to the strong relationship between orthophosphate uptake and the extent of La release (Figures 3 and 4). Therefore, it is apparent that orthophos-

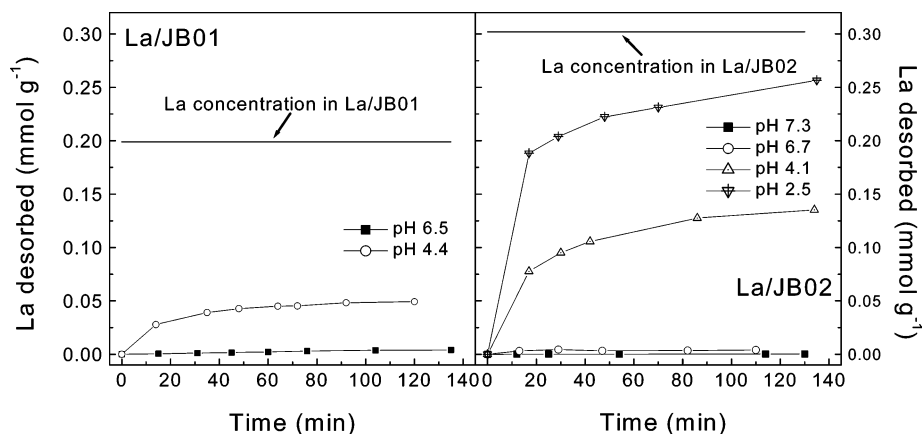


FIGURE 3. Lanthanum desorption kinetics of La-treated JB sorbents La/JB01 and La/JB02 at different solution pH conditions. The solution concentration of La normalized on the basis of sorbent mass is represented in the y-axis.

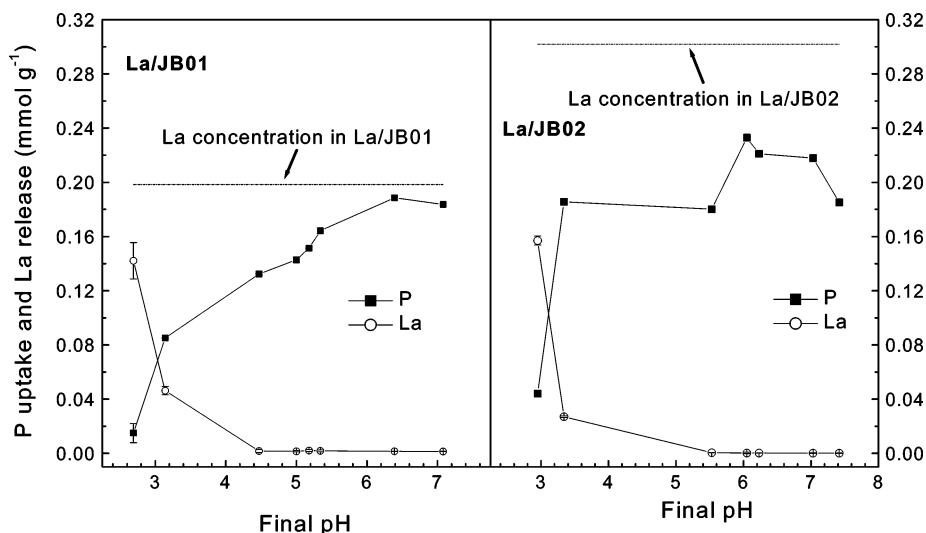


FIGURE 4. Orthophosphate sorption curves for La-treated JB sorbents La/JB01 and La/JB02 ($C_0 = 0.32 \text{ mmol P L}^{-1}$, equilibration time 12 h). Concomitant La release during orthophosphate uptake is also highlighted.

TABLE 3. Lanthanum Desorption from La-Treated Bark

sample	La loading level (mmol g^{-1})	final pH	La desorbed (mmol g^{-1})	% desorption
La/JB01 ^a	0.198	6.5	0.00684	3.4
		4.4	0.0514	29.5
La/JB02 ^a	0.302	7.3	0.000336	0.1
		6.7	0.00395	1.3
		4.1	0.138	45.6
		2.5	0.261	86.4

^a La/JB01 and La/JB02 are La-treated juniper bark sorbents.

phate reacted mainly with surface-bound La and not with La ions in solution. Use of these sorbents around neutral pH would not only result in maximum orthophosphate uptake but also overcome problems associated with La desorption. The maximum orthophosphate uptake ($C_0 = 0.32 \text{ mmol of P L}^{-1}$) was 0.188 (pH 6.39) and 0.233 (pH 6.05) mmol of P g^{-1} for La/JB01 and La/JB02, respectively.

A comparison of the molar ratio of orthophosphate (as P) sorbed to surface-bound La determined in this study and for other sorbents is illustrative. At 0.188 and 0.233 mmol of P g^{-1} the surface P-to-La molar ratio was extremely high and corresponded to 0.95 and 0.77, for La/JB01 and La/JB02, respectively. In comparison the P-to-Fe molar ratio was 0.13 for an Fe-impregnated juniper fiber (WNF03) (30). Even for

an Al-impregnated mesoporous silicate adsorbent ($\text{Al}_{10}\text{SBA-15}$) where Al is well dispersed within mesopores, the P-to-Al molar ratio was found to be 0.23 (15). Such a high P/La ratio obtained in this study indicates the possibility of reactions other than adsorption occurring during the interaction between orthophosphate and the La-treated sorbents. In a study on As adsorption to ferrihydrite (31, 32), the authors suggested the occurrence of inner-sphere ligand bonding of arsenate at the maximum sorption density (As(V)/Fe) of 0.25, but for arsenite the maximum sorption density of 0.6 (As(III)/Fe) was attributed to surface polymerization. Similarly, while surface complexation could have dominated orthophosphate sorption processes with Fe- and Al-impregnated adsorbents (WNF03 (30) and $\text{Al}_{10}\text{SBA-15}$ (15), respectively), only formation of a surface precipitate of the phosphate phase at high equilibrium orthophosphate levels could explain the extremely high P-to-La molar ratio obtained for the La-treated JB.

The shape of sorption isotherms generated in this study (Figure SI-1 in the Supporting Information and Figure 5a) is suggestive of the importance of surface precipitation in controlling P uptake at higher equilibrium orthophosphate concentrations. The orthophosphate sorption isotherms for La/JB01 and La/JB02 expressed in terms of mmol of P g^{-1} of sorbent (double logarithmic format) and P-to-La molar ratios are presented in parts a and b, respectively, of Figure 5. The isotherms for both these sorbents were nearly parallel over the entire C_e range (Figure 5a), with La/JB02 having a higher

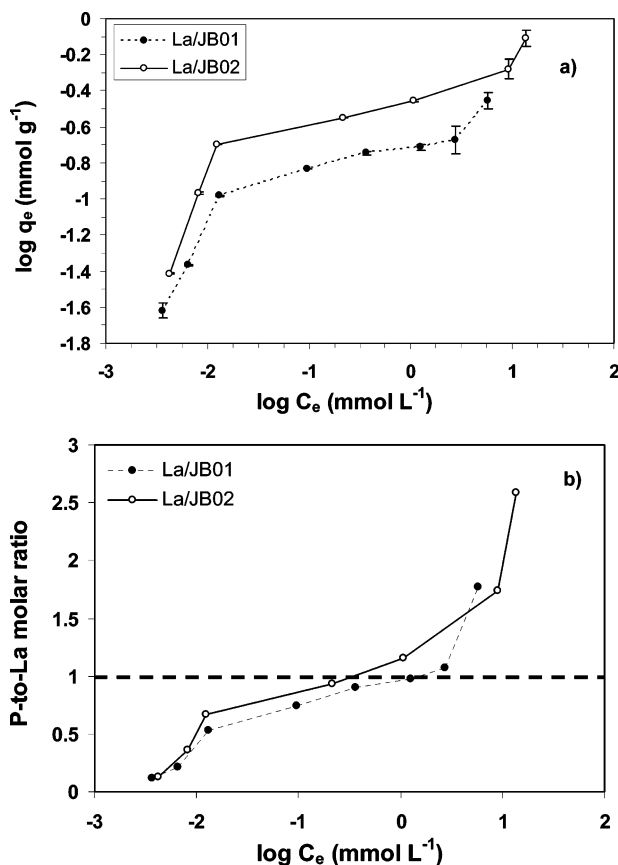


FIGURE 5. Isotherms for orthophosphate sorption onto La-treated JB sorbents La/JB01 and La/JB02 plotted on the basis of the (a) millimoles of P sorbed per gram of sorbent (q_e) and (b) surface-bound orthophosphate-to-La (P-to-La) molar ratio (mol of P mol⁻¹ of La). C_e is the equilibrium orthophosphate concentration, and q_e is the amount of orthophosphate sorbed onto La-treated juniper bark. $C_0 = 0.032$ – 14.5 mmol of P L⁻¹, the equilibration time was 12 h, and the initial pH was 6.1 ± 0.1 . Error bars if not shown are within the symbols.

sorption capacity (on a mmol g⁻¹ basis), primarily due to the presence of a higher La content. Isotherms normalized on the basis of the surface La content revealed minimal differences between the sorbents (Figure 5b). The isotherms reveal several interesting trends. For both La/JB01 and La/JB02, the initial region at low orthophosphate concentrations (low sorbate-to-sorbent ratios) resembled that typically observed for the adsorption process. A steep initial region (break point around log C_e of -1.9) at low orthophosphate concentration resembled an H-curve isotherm, which is indicative of a very high affinity for orthophosphate (33). This initial region is followed by relatively small increases in sorption capacity with increasing C_e , and saturation of surface sorption sites occurred around a log C_e of 0.5.

However, a further increase in C_e beyond the saturation region produced a significant (and sharp) increase in orthophosphate uptake, signaling the onset of surface precipitation. Such behavior during the sorption of heavy metals (Cu, Cd), at high surface coverages, with hydrous iron and aluminum oxides has been shown elsewhere (34, 35). Sorption capacities at saturation of surface sites were 0.211 and 0.351 mmol of P g⁻¹ for La/JB01 and La/JB02, respectively. With the onset of surface precipitation, orthophosphate uptake continued to increase and the P-to-La molar ratio even significantly exceeded 1.0. A plot of C_e (mmol of P L⁻¹) vs sorption density q_e (mmol of P g⁻¹ of fiber) along with corresponding model fits of the Langmuir adsorption isotherm equation are included in Figure SI-1 in the Supporting

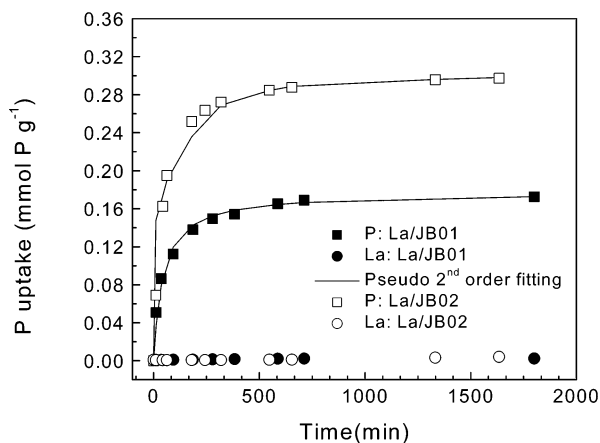


FIGURE 6. Orthophosphate sorption kinetics for La-treated JB sorbents La/JB01 and La/JB02 ($C_0 = 0.32$ mmol of P L⁻¹, initial pH 6.0 ± 0.1).

TABLE 4. Parameters for P Uptake from the Fit to the Pseudo-Second-Order Kinetic Model

sample	k (g (mmol·min) ⁻¹)	q_e (mmol g ⁻¹)	R^2	adsorption density (P/La or Fe)
La/JB01 ^a	0.126	0.177	0.999	0.893
La/JB02 ^a	0.087	0.304	0.999	1.00
WNF03 ^b	0.146	0.039	0.991	0.128

^a La/JB01 and La/JB02 are La-treated juniper bark sorbents. ^b Fe-deposited lignocellulosic adsorbents (30).

Information. Although a reasonable fit ($r^2 > 0.9$) to the experimental data was obtained with the Langmuir equation, the model fit deviated significantly from the measurements, especially at high C_e levels when surface precipitation is likely to occur.

Time-dependent sorption (up to 30 h) of orthophosphate to these La-treated JB sorbents ($C_0 = 0.32$ mmol L⁻¹) is shown in Figure 6. The parameters obtained by fitting the kinetic data to the pseudo-second-order model (eq 1) are summarized in Table 4, highlighting the rate constants and the orthophosphate sorption capacities. For comparison purposes, results obtained for WNF03 (Fe-impregnated juniper fiber) are shown as well. Uptake of orthophosphate onto the sorbents was fairly slow, since apparent equilibrium removal levels were observed only after 10 h. The pseudo-second-order rate constants for La/JB01 and La/JB02 are 0.126 and 0.087 g (mmol·min)⁻¹, respectively, which is comparable to that obtained for WNF03 (30). The orthophosphate sorption capacity of La-treated JB (Table 4), which is a function of the La content, was much higher than that of the Fe-impregnated material and also compared well with those of other anionic adsorbents prepared from lignocellulosic materials (2, 20, 30).

Spectroscopic Analyses. Spectroscopic experiments were conducted to elucidate the mechanisms responsible for orthophosphate removal by La-treated JB. Only the EDXA spectra of La/JB02 after equilibration with orthophosphate contained a peak for P. As shown in Table 2, the EDXA peak intensity of P/C was 0 for JB and La/JB02, but increased to 0.2 for La/JB02 reacted with orthophosphate.

The nature of the lanthanum phosphate species formed on the La-treated bark was investigated by XRD. The diffraction patterns shown in Figure 7 suggest that the lanthanum phosphate species formed on the La-treated bark is very similar to freshly formed lanthanum phosphate precipitate. After orthophosphate sorption, new peaks emerged in the XRD patterns of La/JB01 and La/JB02 (Figure

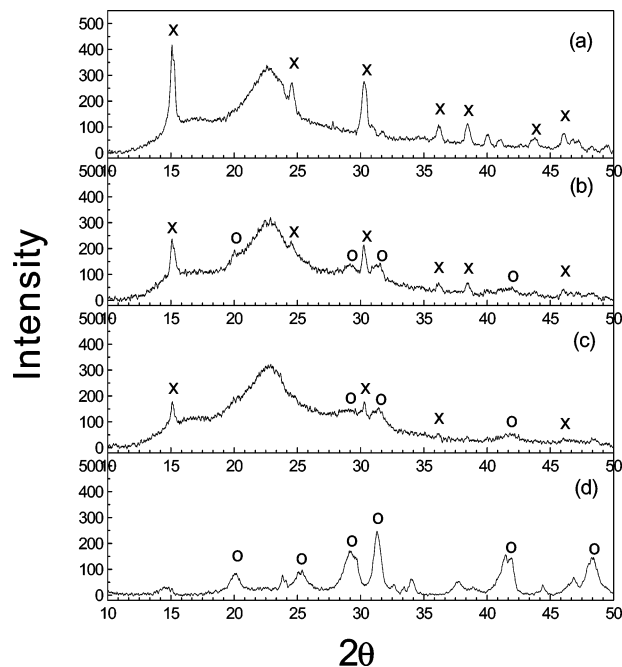


FIGURE 7. X-ray diffraction patterns of (a) JB, (b) La-treated JB La/JB01 after orthophosphate sorption, (c) La-treated JB La/JB02 after orthophosphate sorption, and (d) freshly precipitated lanthanum phosphate (x, characteristic peaks of calcium oxalate monohydrate; o, characteristic peaks of freshly precipitated lanthanum phosphate).

7b,c) at 2θ values of 29.22° , 31.31° , and 41.89° (o labels in Figure 7). These peak positions matched reasonably well with the characteristic XRD peaks of freshly precipitated lanthanum phosphate (Figure 7d). The complex nature of the bark matrix makes it extremely difficult to unambiguously resolve all the peak positions corresponding to freshly precipitated lanthanum phosphate. The XRD diffractogram for freshly precipitated lanthanum phosphate (Figure 7d) matched well (in terms of peak positions) with that of LaPO_4 , but the peaks were broader possibly because of a lower degree of crystallinity. According to Mooney (36), the major peaks for crystalline LaPO_4 occur at 2θ values of (in decreasing order of intensity) 29.36° , 41.58° , 14.56° , 25.28° , 48.38° , 20.12° , 31.36° , 46.79° , 37.77° , and 39.05° . The XRD data are indicative of the occurrence of a poorly crystalline lanthanum phosphate surface precipitate on La-treated JB at high orthophosphate concentrations.

Infrared spectra of the sorbents in the wavenumber range of 700 and 1900 cm^{-1} are shown in Figure 8. For JB, IR bands between 1600 and 1800 cm^{-1} correspond to carbonyl groups, but it is difficult to definitively assign the IR bands below 1550 cm^{-1} due to the inherent complexity of the JB matrix. Bands of $\text{P}=\text{O}$ and $\text{P}-\text{O}$ stretching emerge around $1000\text{--}1200$ and $950\text{--}1100\text{ cm}^{-1}$, respectively (37–39). Therefore, the IR bands for freshly precipitated lanthanum phosphate (Figure 8d) were assigned as follows: bands at 1018, 1156, and 1632 cm^{-1} correspond to $\text{P}-\text{O}$ stretching, $\text{P}=\text{O}$ stretching, and water bending, respectively. While the IR pattern of La/JB02 was not different from that of JB (Figure 8a,b), the IR pattern of La/JB02 after orthophosphate sorption (Figure 8c) contained a tiny shoulder around 1015 cm^{-1} which could correspond to $\text{P}-\text{O}$ stretching. It was difficult to resolve the $\text{P}=\text{O}$ stretching peak around 1156 cm^{-1} in La/JB02 after orthophosphate sorption. The IR data provide relatively weak evidence that, at high surface coverages, the orthophosphate species exists on the La-treated bark in a form similar to freshly precipitated lanthanum phosphate. It is, therefore, very likely that orthophosphate, which at our experimental pH of ~ 6.1 exists predominantly as H_2PO_4^- , reacts with the

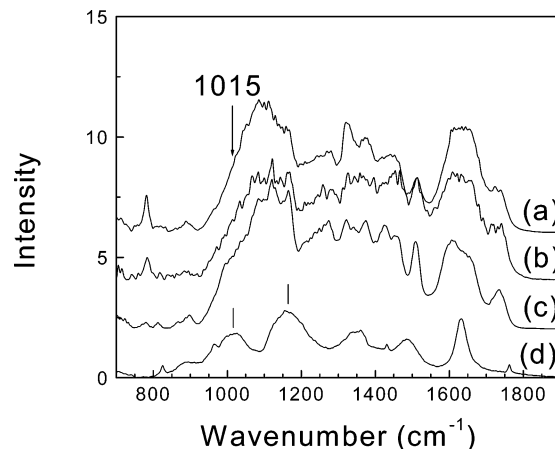
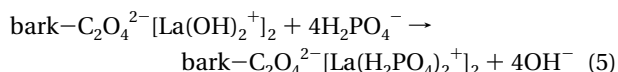


FIGURE 8. DRIFT spectra of (a) JB, (b) La-treated JB La/JB02, (c) La-treated JB La/JB02 after orthophosphate sorption, and (d) freshly precipitated lanthanum phosphate.

surface-bound La on the bark according to the following scheme:



The results in this study indicate the ability of La-treated JB to function as a sorbent for the removal of orthophosphate from water. The orthophosphate sorption capacity of La-treated JB compares favorably with those of other well-known P adsorbents. Sorption behavior and spectroscopic results suggest that a surface precipitation mechanism could be responsible for orthophosphate binding onto the sorbents at high equilibrium orthophosphate levels. The ability of this novel sorption medium to function around neutral pH conditions will enhance its applicability for water and wastewater treatment.

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Supporting Information Available

Isotherms for orthophosphate sorption (pdf). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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