Removal of Phosphate Anions from Aqueous Solutions Using Polypyrrole-Coated Sawdust as a Novel Sorbent

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ABSTRACT: This work was focused on the removal of phosphate ions using polypyrrole-coated sawdust as a novel cost-effective sorbent. The phosphate uptake followed the Langmuir sorption isotherm, and the sorption capacity at 20, 35, and 50°C was found to be 17.33, 23.41, and 30.39 mg/g, respectively; this indicated favorable sorption at higher temperatures. The kinetic uptake data were modeled with the Lagergren equation, first-order and second-order kinetic models, and the simple Elovich model. The results indicated that the Lagergren model best described the uptake data. The intraparticle diffusion coefficient, as determined for 250–211- and 630–600-μm sorbent particles at 20°C, was found to be 287.3×10^{-2} and 228.3×10^{-2} mg g^{-1} min^{-1}, respectively. The intraparticle diffusion was also confirmed with the Bangham equation. The sorption mean free energy, calculated with the Dubinin–Radushkevich equation, was found to be 10.98 kJ/mol, thus confirming an ion-exchange regulated sorption process. The positive value of the enthalpy change (i.e., 4.23 kJ/mol) confirmed the endothermic nature of the sorption process. The negative values of the change in the standard free energy were indicative of the spontaneous nature of the sorption process. Finally, the activation energy of the sorption process for 250–212-μm particles, determined with the Arrhenius equation, was found to be 41.68 J/mol. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 3081–3088, 2009

Key words: adsorption; coatings; diffusion

INTRODUCTION

Phosphorus has been recognized as a major nutrient for both plants and microorganisms. However, the adverse effects of phosphorus overload in sensitive aquatic ecosystems, such as streams, rivers, and lakes, have been a major concern of environmental scientists in recent years.[1] Excessive growth of algae and other plants, stimulated by the addition of large quantities of phosphorus to water supplies, is an issue of national concern. In addition to the excessive growth of aquatic plants and microorganism, the deleterious effects of eutrophication include fish kills, filter clogging, unpleasant odor and taste of potable water, and a deterioration of recreational and aesthetic values.[2] Therefore, removal of phosphate from water and wastewater is important to protect public health.

Among various physicochemical methods adopted for the removal of phosphate from aqueous solutions, the sorption process has been recognized to have the greatest potential. Different inorganic materials that have been exploited in the recent past for phosphate removal include ammonium-functionalized mesoporous silica,[3] iron oxide hydroxide,[4] synthetic zeolites,[5] blast furnace slag,[6] activated aluminum oxide,[7] iron containing double hydroxides,[8] and aluminum oxide hydroxide.[9] Moreover, polymeric ligand exchangers (PLEs) have also been used frequently for phosphate removal.[10,11] Recently, Wu et al.[12] prepared a PLE consisting of lanthanum(III) bound to Chelex-100 resin by passing a solution of LaCl$_3$ through a column of Chelex-100. The PLE was found to remove phosphate successfully, even in the presence of chloride and sulfate anions. However, it has been reported recently that the development of PLEs requires a specialty chelating polymer as a substrate, which is quite expensive.[13] Despite their high phosphate selectivity and reusability over many cycles of operations, the higher cost of PLEs has emerged as the primary obstacle against their more frequent applications.[14] Therefore, to overcome this drawback, cost-effective sorbent materials such as agricultural byproducts appear to be the best alternatives for preparing ion exchangers. Agricultural waste/plant residues are renewable and abundantly available at no or little cost.[15] Although lignocellulosic materials have a low ion-exchange or adsorption capacity, chemical modification, graft
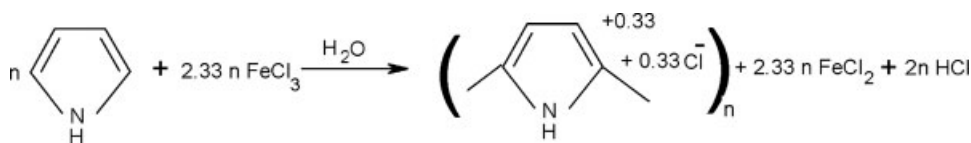
Figure 1 Oxidative chemical polymerization reaction of pyrrole with FeCl₃.

copolymerization, and crosslinking of these materials have resulted in an enhancement of their phosphorous absorptivity.[16–18] In this connection, we report the removal of phosphate ions from aqueous solutions with a novel sorbent material prepared by the coating of chemically synthesized polypyrrole on the surface of sawdust. FeCl₃ has been used as a chemical oxidant for the oxidation of pyrrole into the polymer (polypyrrole/chlorine). Polypyrrole is a well-known conducting electroactive polymer, and its preparation via the chemical polymerization of pyrrole by the oxidant FeCl₃ results in the incorporation of Cl^- ions as counterions into the polymer matrix because of the maintenance of electroneutrality. These Cl^- ions may undergo an ion-exchange process with phosphate anions present in the external solution. The use of sawdust as a substrate makes the overall sorption process cost-effective. The stoichiometry, resulting from the chemical polymerization of pyrrole with FeCl₃ as an oxidant, is shown in Figure 1.

EXPERIMENTAL

Materials

The monomer pyrrole, the oxidant FeCl₃, and trisodium phosphate were purchased from S.D. Fine Chemicals (Mumbai, India). Sawdust was obtained from a local saw mill, was washed thoroughly in hot water for a period of 12 h, and was then dried before use. The double-distilled water was used throughout the investigations.

Preparation of polypyrrole-coated sawdust (PPCSD)

Iron(III) chloride has been reported to be the best chemical oxidant and water has been reported to be the best solvent for the chemical polymerization of pyrrole.[19] Using these facts, we attempted to carry out the polymerization of pyrrole with sawdust as the substrate. In brief, 10.0 g of sawdust was immersed in 100 mL of a freshly distilled 0.2M pyrrole solution for 12 h, and then it was filtered. The pyrrole-soaked sawdust was then put in 100 mL of a 0.5M FeCl₃ solution, and the polymerization reaction was allowed to continue for a period of 6 h at 30°C. Thereafter, the sorbent was filtered, washed three times with distilled water, and dried in an electric oven (Tempstar, New Delhi, India) at 50°C.

To get particles with the desired sizes, a number of standard sieves were placed, one above the other, in such a way that the smallest sieve opening was at the bottom and the largest was at the top. The bottom pan was stacked below the finest sieve, and a definite amount of sawdust was loaded on the top sieve and then closed with the lid. This arranged sieve set was placed in a mechanical sieve shaker, which was operated for 15 min. Then, the amount of the material present in each sieve was collected and weighed accurately to determine the weight percentage based size distribution of the modified sawdust particles.

Fourier transform infrared (FTIR) spectral analysis

The FTIR spectra of plain sawdust and PPCSD were recorded with a Shimadzu 8201 FTIR spectrophotometer (Shimadzu, Japan) with KBr.

PO_4^{3-} uptake studies

The sorbate stock solution was prepared through the dissolution of a precalculated quantity of NaH_2PO_4 in double-distilled water to produce a final concentration of 100 mg/L. The stock solution was diluted to obtain standard solutions with concentrations in the range of 5–30 mg/L. Then, 20 mL of a phosphate solution of a desired concentration was placed in a 125-mL Erlenmeyer flask containing 0.02 g of the PPCSD sorbent, and it was agitated in a thermostatic water bath at 50 rpm for 2 h. At the end of the experiment, the sorbent was separated by filtration, and the supernatant was analyzed spectrophotometrically.[20]

RESULTS AND DISCUSSION

Size distribution of the PPCSD particles

After the dry sieving method was used,[21] the weight percentage based size distribution of the PPCSD particles was determined. The concentrations of the PPCSD particles that were greater than 630 μm in size, that were 630–600, 600–500, 500–355, 355–250, or 250–211 μm in size, and that were less than 211 μm in size were found to be 6.2, 11.4, 21.1, 32.3, 17.4, 7.3, and 4.3 wt %, respectively. However, the particles with particle sizes of 630–600 and 250–211 μm were selected for the adsorption experiments.
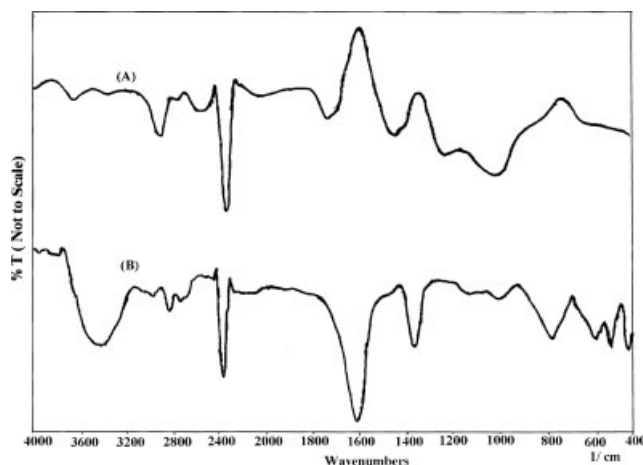
Figure 2 FTIR spectra of (A) plain sawdust and (B) PPCSD particles.

Figure 3 Kinetic data for PO_4^{3-} uptake by PPCSDs of two particle sizes.

FTIR spectral analysis

Figure 2(A,B) shows the FTIR spectra of plain sawdust and PPCSD, respectively. In Figure 2(A), the presence of a band in the region of 3600–3800 cm^{-1} corresponds to the stretching vibration of the OH group, whereas peaks obtained at 2400 and 2900 cm^{-1} refer to the C—H stretching vibration. The band in the region of 1758 cm^{-1} refers to C=O stretching, whereas the peak at 1442 cm^{-1} refers to C—O stretching of plain sawdust. In Figure 2(B), the presence of a strong broad band in the range of 3300–3500 cm^{-1} corresponds to the stretching vibrations of N—H and hydrogen-bonded surface hydroxyls along with chemisorbed water.[22] In addition, a small peak at 1452 cm^{-1} corresponds to typical polypyrrole ring vibrations.[23] Moreover, the C—N stretching (aromatic) at 1360 cm^{-1} also confirms the presence of polypyrrole.[24] The presence of peaks at 2333 and 2797 cm^{-1} refers to the C—H stretching vibrations. Similarly, the benzene ring of lignin molecules of sawdust and C=C stretching of the aromatic ring are characterized by a sharp peak at 1626 cm^{-1}.[24] Finally, a broad band in the range of 1000–1300 cm^{-1} refers to C—O stretching and C—O—C stretching of cellulose in sawdust.[25]
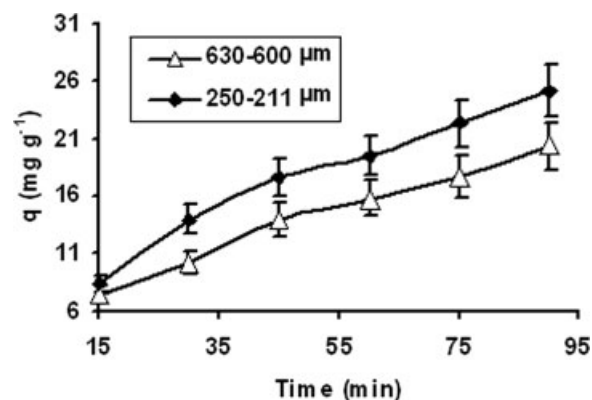
Dynamic uptake of PO_4^{3-} anions

The kinetics of the sorption process describe the solute uptake, which in turn governs the residence time of the adsorption reaction. To understand the kinetic aspects of PO_4^{3-} uptake on PPCSD, the adsorption kinetics were determined with sorbent particles of two different sizes, 630–600 and 250–211 μm, at 20°C with an initial sorbent concentration of 20 mg/L (see Fig. 3). It is clear that the amount of PO_4^{3-} sorbed increased with time, and smaller particles exhibited higher phosphate uptake. This may simply be attributed to the greater surface area of the smaller particles, which provided more binding sites for sorbate uptake. The kinetic uptake data were fitted to some kinetic models,[26,27] such as the Lagergren equation, a second-order equation, and the simple Elovich equation. The estimated models and related kinetic parameters are listed in Table I. On the basis of the linear regression values, it can be seen from Table I that the uptake data are best described by the Lagergren equation.

The following integrated rate expression was used to calculate the Lagergren equation:

$$\ln\left(1 - \frac{q}{q_e}\right) = -k_{ad}t$$

TABLE I
Parameters of Various Kinetic Models Fitted to the Experimental Data

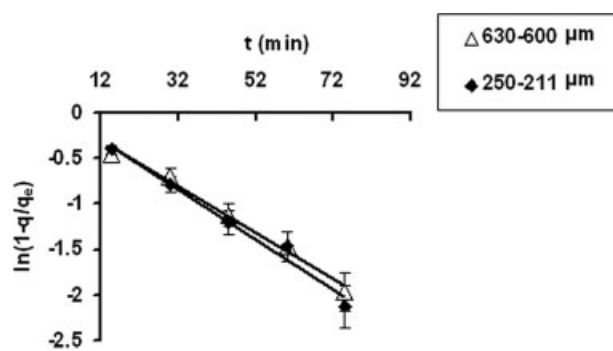| Sample	Kinetic model	Equation	Parameters	
			635-μm particle size	211-μm particle size
1	Pseudo-first-order Lagergren	$\ln\left(1 - \frac{q}{q_e}\right) = -k_1 t$	$R^2 = 0.9893$ $k_1 = 0.0254$	$R^2 = 0.981$ $k_1 = 0.0274$
2	Second-order	$\frac{1}{C} - \frac{1}{C_0} = k_2 t$	$R^2 = 0.978$ $k_2 = 0.0003$	$R^2 = 0.9764$ $k_2 = 0.0004$
3	Simple Elovich	$q = a + 2.303b \log t$	$R^2 = 0.9648$ $a = 7.078$ $b = -12.58$	$R^2 = 0.9889$ $a = 8.994$ $b = -16.26$

Figure 4 Lagergren equation for PO_4^{3-} uptake by PPCSD.

where q and q_e are the amounts of phosphate sorbed at time t and at equilibrium, respectively, and k_{ad} is the adsorption coefficient. From the slopes of the linear plots depicted in Figure 4, the k_{ad} values for two particle sizes, 630–600 and 250–211 μm, at 20°C were calculated and found to be 2.5×10^{-2} and 2.7×10^{-2} L mg^{-1} min^{-1}, respectively. The almost linear nature of the plots clearly indicates that PO_4^{3-} uptake follows the Lagergren equation.

Because of the porous nature of the sorbent, intraparticle diffusion (pore diffusion) is also expected. Knocke and Hemphill[28] stated that because diffusion is an endothermic process, the rate of adsorption will increase with an increased solution temperature when pore diffusion is the rate-limiting step. Therefore, in this study, we also expected the PO_4^{3-} uptake process to be pore-diffusion-controlled. To further confirm this, graphs were plotted of the logarithm of the adsorption percentage versus the logarithm of time, and they yielded straight lines (data not shown), thus confirming the occurrence of intraparticle diffusion. The rate constant of intraparticle diffusion (k_{id}) was calculated from the slopes of linear plots of q (mg/g) versus the square root of time at room temperature for two particle sizes (Fig. 5) with the Weber–Morris equation:
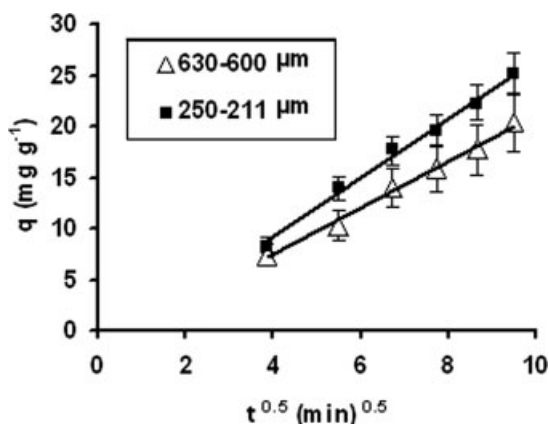

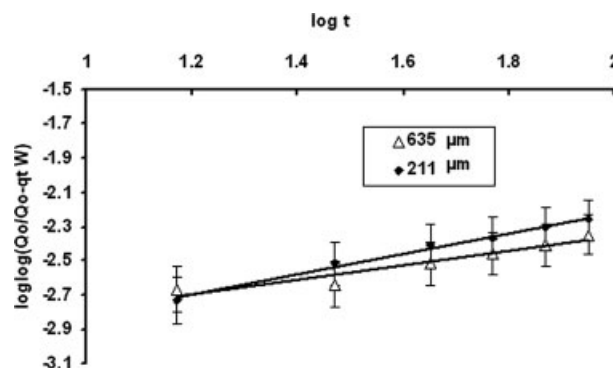**Figure 5** Plot of q (mg/g) versus $t^{0.5}$ for the determination of k_{id}.

Figure 6 Bangham equation showing the intraparticle diffusion of PO_4^{3-} at room temperature for different particle sizes.

$$q = k_{id}t^{0.5}$$

The values of k_{id} for the 630–600- and 250–211-μm particles were found to be 228.2×10^{-2} and 287.3×10^{-2} mg g^{-1} min$^{-0.5}$, respectively.

To further confirm the occurrence of intraparticle diffusion, the Bangham equation, as suggested by Rehman et al.,[29] was applied to the sorption data in the following form:

$$\log \log \frac{Q_0}{Q_0 - q_t W} = \log \frac{k_0 W}{2.303 V} + \alpha \log t$$

where Q_0 is the initial concentration of metal ions in the solution (g/dm^3), V is the volume of the sorbate solution (dm^{-3}), W is the weight (g) of the sorbent, q_t is the amount of metal ions sorbed (g/g) at time t, and α and k_0 are constants.

Straight lines (see Fig. 6) were obtained from the plotting of $\log \log \frac{Q_0}{Q_0 - q_t W}$ against $\log t$, thus indicating the validity of the Bangham equation. The values of α and k_0 at 20°C for two particle sizes, 630–600 and 250–211 μm, as calculated from the slopes and intercepts of the plots shown in Figure 6, were found to be 0.418 and 1.47×10^{-3} and 0.596 and 0.88×10^{-3}, respectively. The linear nature of the plots confirmed intraparticle diffusion.

The energy of activation was determined with the Arrhenius equation and was found to be 41.68 J/mol. The relatively low value suggests that PO_4^{3-} sorption takes place by an activated or diffusion-controlled process. In addition, the positive value suggests that sorption is favored by a rise in the solution temperature.

Sorption isotherms

The equilibrium sorption of PO_4^{3-} anions onto PPCSD was studied for different initial concentrations of the sorbate in the range of 10–60 mg/L at
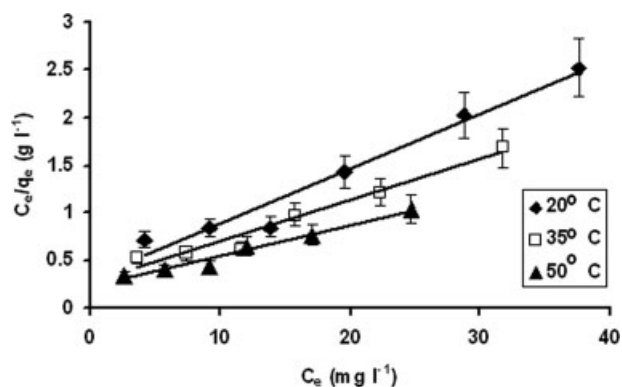
Figure 7 Langmuir isotherms for PO_4^{3-} uptake at three different temperatures.

three temperatures (20, 35, and 50°C), and the obtained data were fitted into the rearranged Langmuir isotherm:

$$C_e/q_e = C_e/Q_0 + 1/Q_0 b$$

where C_e and q_e are the equilibrium concentrations of phosphate ions in solution (mg/L) and on the sorbent (mg/g), respectively, and Q_0 and b are Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. For the sorbent particles with the particle size of 250–211 μm, the isotherms at three temperatures are depicted in Figure 7. The values of Q_0 and b were also calculated with the least-square method through a regression analysis and are presented in Table II along with the experimental values. It is clear from Table II that the graphical values are in close agreement with the regression values, and this indicates the suitability of the Langmuir isotherm for the experimental sorption data. It is also clear that the value of Q_0 increases with temperature, and this suggests that uptake is favored at higher temperatures. In addition, the magnitude of exponent b gives an indication of the favorability and capacity of the sorbent/sorbate system.

To investigate the nature of the sorption process, the sorption data at room temperature were applied to the Dubinin–Radushkevich (D–R) isotherm model. The D–R equation is

$$C_{ad} = C_m \exp(-B\varepsilon^2)$$

where C_{ad} is the amount of PO_4^{-3} adsorbed onto PPCSD, C_m is the maximum PO_4^{-3} uptake, and B is a constant with a dimension of energy. The Polyanyi potential (ε) is determined as follows:

$$\varepsilon = RT \ln(1 + 1/C_e)$$

where R is the gas constant (kJ mol^{-1} K^{-1}), T is the absolute temperature, and C_e is the equilibrium concentration of PO_4^{3-} in solution. The obvious linearized form of the D–R isotherm is

$$\ln C_{ad} = \ln C_m - B\varepsilon^2$$

When $\ln C_{ad}$ values were plotted against ε^2, a straight line was obtained (see Fig. 8). The computed value of B, as determined from the slope of the linear plot, was 4.2×10^{-3} kJ/mol. From the calculated value of B, the mean sorption energy (E) was computed as follows:

$$E = 1/\sqrt{-2B}$$

E is the free energy transfer of 1 mol of the solute from infinity to the surface of PPCSD. The numerical value of E was found to be 10.98 kJ/mol, which lies in the expected range of 8–16 kJ/mol, thus indicating that the ion-exchange process[30] is responsible for phosphate uptake.

Evaluation of the thermodynamic parameters

Thermodynamic parameters were calculated with the following relation:

$$K_c = \frac{C_0 - C_e}{C_e}$$

where K_c is an equilibrium constant, C_0 is the equilibrium concentration of phosphate ions on the sorbent (mg/L), and C_e is the equilibrium concentration

TABLE II
Values of Q_0 and b at Different Temperatures

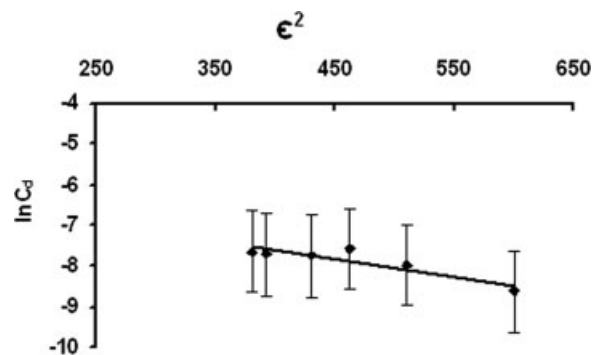| Temperature (°C)	Graphical values		Regression values	
	Q_0 (mg/g)	b (L/mg)	Q_0 (mg/g)	b (L/mg)
20	17.33	0.187	17.33	0.192
35	23.41	0.153	23.41	0.154
50	30.39	0.152	30.48	0.15

Figure 8 D–R isotherm for the evaluation of B.

in the solution (mg/L). The change in the standard free energy (ΔG^0) was calculated as follows:

$$\Delta G^0 = -RT \ln K_c$$

Finally, the standard enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated with the slope and intercept of the linear Vant Hoff plot, respectively, with the following relation:

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T}$$

All the thermodynamic parameters are shown in Table III. The positive value of ΔH^0 indicates the endothermic nature of the process. The negative values of ΔG^0 indicate the spontaneous nature of the sorption process. The positive value of ΔS^0 also indicates increased randomness during the uptake of PO_4^{3-} onto PPCSD particles. During the sorption process, the sorbed water molecules, which are displaced by PO_4^{3-} species, gain more translational entropy than is lost by the PO_4^{3-} ions, and this allows the prevalence of randomness in the system.

Effect of the presence of co-ions

It is almost unlikely that only a single type of metal ion [i.e. PO_4^{3-}] will be present in industrial effluents or domestic water. For example, there are some regions in India where the ground water contains other metal ions along with phosphate. Therefore, it may be interesting to see the effect of the presence of co-ions on PO_4^{3-} uptake by PPCSD. To investigate this, various amounts of sodium fluoride were added to a PO_4^{3-} solution with an initial concentration of 40 mg/L to yield fluoride concentrations in the range of 10–50 mg/L, and sorption studies were carried out with the same amount of 250–211-μm sorbent particles. The results, as depicted in Figure 9, clearly indicate that there was a drastic decrease in the uptake of PO_4^{3-} due to the presence of F^- ions in the sorption system. The observed findings may be attributed to the fact that F^- ions compete with PO_4^{3-} ions and bind at the available sorption sites, and this results in the availability of fewer sites for
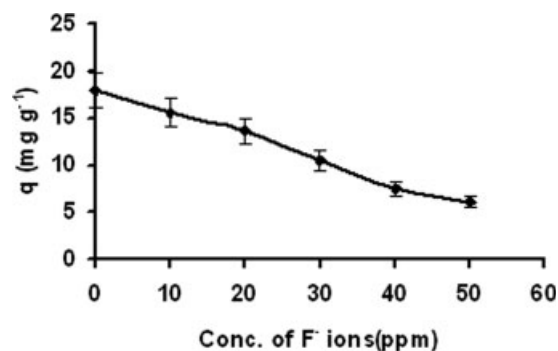

Figure 9 Effect of the presence of F^- ions on PO_4^{3-} uptake by PPCSD particles.

PO_4^{3-}. Therefore, PO_4^{3-} uptake gradually decreases with an increase in the concentration of F^- ions in the sorption system.

Effect of pH on the phosphate uptake

To find out the optimum pH for maximum phosphate removal, the experiments were conducted with 25 mL of a 40 mg/L sorbate solution containing 0.02 g of the sorbent at different pHs in the range of 1.0–8.5 at 20°C. The results, as depicted in Figure 10, reveal that phosphate uptake increases with the pH of the phosphate solutions. The amount of sorbed phosphate (mg/g of sorbent) was in the range of 13.6–56.2 for the sorbate solutions with pHs in the range of 1.0–11.0. The observed findings may be explained as follows. The pK values for sodium phosphate are 2.1, 7.2, and 12.3, respectively.[31] Therefore, at these pH values, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} species are predominant.

When the pH of the phosphate solution is 1.0, phosphate exists mainly as phosphoric acid, and this causes almost minimum phosphate uptake. When the pH of the phosphate solution exceeds 2.0, $H_2PO_4^-$ species become predominant, and hence the phosphate uptake increases because of the ion exchange of these ions with Cl^- ions present within
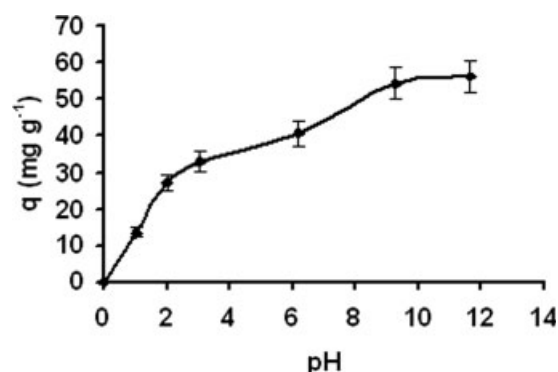
TABLE III
Values of ΔG^0, ΔH^0, and ΔS^0

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J K^{-1} mol^{-1})
293	−0.112		
313	−1.092	16.29	55.73
323	−2.228		

Figure 10 Effect of the pH on PO_4^{3-} uptake by PPCSD particles.

Sample	Sorbent material	Q_0 (mol/g)	Reference
1	PPCSD	18.2×10^{-5}	This work
2	Iron(III)-loaded, polyacrylamide-grafted sawdust	9.70×10^{-5}	18
3	Acid-mine-drainage-treated juniper fiber	2.29×10^{-5}	17
4	Iron and aluminum oxide coated sand	0.03×10^{-5}	32
5	Activated carbon	1.86×10^{-5}	33
6	Synthetic-polymer-based anion-exchange resin (Dowex)	20.9×10^{-5}	18

the polypyrrole matrix. As the pH of the phosphate solution increases beyond 7.0, the predominant HPO_4^{2-} species, being divalent, are subjected to a greater attractive force by positive residual charges on pyrrole rings, and this causes an enhancement of the ion-exchange process. Likewise, when the pH of the solution reaches 11.0, the presence of PO_4^{3-} ions in the sorbate solution results in a further increase in the electrostatic attraction toward positive-charge residues, thus finally resulting in a further increase in phosphate uptake.

CONCLUSIONS

On the basis of this study, it can be concluded that PPCSD is a potential cost-effective sorbent for the removal of phosphate ions from aqueous solutions. The sorption follows the Langmuir isotherm model and is endothermic in nature. The sorption capacity increases with the pH of the sorbate solution. The phosphate uptake appears to be governed by an ion-exchange mechanism. Finally, the values of the maximum sorption capacity (i.e., Q_0) obtained for phosphate ion uptake with various types of sorbents are shown in Table IV. A close look at the values reveals that the polymer-based ion-exchange resin Dowex demonstrated a maximum sorption capacity of 20.9×10^{-5} mol/g, which may simply be attributed to the fair ion-exchange capacities of this commercial synthetic resin. Interestingly, the sorbent PPCSD exhibited the second highest value of 18.2×10^{-5} mol/g, which establishes its superiority. Table IV also shows that sorbents such as aluminum oxide coated sand and activated carbon had poor uptake values, and this can probably be attributed to the fact that in the former case, the sorbent particles above their pH_{ZPC} might have undergone less ion exchange with sorbate ions. Likewise, the smaller value of Q_0 for activated carbon may also be due to poor van der Waals attraction forces between sorbate and sorbate species. In fact, apart from the chemical nature of the sorbent, experimental conditions (e.g., pH and temperature of the sorbate solu-

tion and particle size of the sorbent) also play a crucial role in governing the extent of uptake. In this study, as sawdust is a very cheap and easily available material, the overall process may be considered cost-effective and fairly effective.

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