

# Removal of Phosphate by Using Copper-Loaded Poly(*N*-vinylimidazole) Hydrogels as Polymeric Ligand Exchanger

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**ABSTRACT:** Polymeric ligand exchangers (PLE) are generally composed of a crosslinked hosting resin that can firmly hold a transition metal ion which can act as terminal functional groups. In this study, poly(*N*-vinylimidazole) (PVIm) hydrogels were synthesized by free radical polymerization/crosslinking of *N*-vinylimidazole in aqueous solution. Swelling behavior of PVIm hydrogels was investigated and the gel with minimum amount of crosslinking agent, hence showing maximum swelling was selected as the optimum gel system for further studies. To prepare the corresponding PLE for the removal of phosphate, PVIm hydrogels were loaded with Cu(II) ions. Copper loading capacity of PLE was determined to be 5 mmol of Cu(II)/g of dry gel. For removal of phosphate, adsorption experiments were performed in batch mode at differ-

ent pH (3–9) and phosphate concentrations. It was found that phosphate adsorption capacity did not change significantly within this pH range. The effect of initial concentration of phosphate on the adsorption behavior of PLE was determined for 10 different phosphate concentrations (0.1–1000 mg/L) at pH 7. NaCl solution was used for regeneration of phosphate adsorbed Cu(II) loaded PVIm hydrogels with 100% regeneration efficiency. The new PLE showed high affinity for phosphate; the highest uptake was found to be 218 mg/g dry PLE from 1000 mg/L phosphate solution. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 613–619, 2011

**Key words:** poly(*N*-vinylimidazole); PVIm hydrogels; polymeric ligand exchanger; phosphate removal

## INTRODUCTION

Phosphorus is an essential nutrient for all living organisms. Phosphates are not toxic to people or animals unless they are present in very high levels. Digestive problems could occur from extremely high levels of phosphate. Phosphorus is recognized as one of the major nutrients contributing to the increased eutrophication of lakes and other natural waters. Phosphorus concentrations in excess of 0.03–0.05 mg/L have been associated with algae blooms, which lead to the eutrophication of lakes and rivers, the only potential risk that phosphorus represents.<sup>1–3</sup> To decrease eutrophication in lakes and other water sources, concentration of phosphorus must be limited to 0.01 mg/L as or less.<sup>4</sup> In wastewater treatment technology, various techniques have been used for phosphate removal. Inorganic and polymeric sorbents, such as clay minerals, zirconia,<sup>4</sup> titania, polymeric ligand exchangers (PLE),<sup>5</sup> and activated alumina<sup>6</sup> have been investigated as adsorbents of nutrients (especially  $\text{PO}_4^{3-}$ ) in water. However, these conventional adsorbents may not be feasible in prac-

tical wastewater treatment because their adsorption capacities are limited and the processes using these sorbents have not been fully developed. Recently, the use of PLE to remove anions in water has attracted much attention.<sup>7–12</sup> A PLE consists of a polymer with chelating functional groups that can bind tightly to a transition metal, which can remove anions from water by complex formation.

The aim of this study is to prepare a special PLE to remove phosphate from aqueous system. For this purpose, poly(*N*-vinylimidazole) (PVIm) hydrogels were first synthesized by using a free radical initiator and crosslinking agent for simultaneous polymerization/crosslinking. Then copper ions were loaded to PVIm hydrogels to get a PLE. Eventually, the adsorption properties of Cu-loaded PVIm hydrogels were investigated for phosphate and relevant results pertaining to this novel PLE are given.

## EXPERIMENTAL PART

### Materials and methods

All chemicals used in this study were of analytical grade. *N*-vinylimidazole (VIm) was obtained from Fluka (Germany) and used as the monomer. Crosslinking agent, *N,N'*-methylenebisacrylamide (MBAAm) was purchased from Aldrich (USA). Azobisisobutyronitrile (AIBN) obtained from Merck (Germany) was

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recrystallized from methanol before use and used as the initiator.  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  obtained from BDH (England) was used in copper loading experiments. Phosphate salt used in the adsorption experiments  $\text{KH}_2\text{PO}_4$  was supplied by Fluka (Switzerland).

### Synthesis of poly(*N*-vinylimidazole) hydrogel

PVIm hydrogels were synthesized through free radical polymerization/crosslinking of VIm in aqueous solution by using azobisisobutyronitrile (AIBN) as the polymerization initiator and *N,N'*-methylenebisacrylamide (MBAAm) as the crosslinking agent. Four different amounts of crosslinking agent ranging from 0.05 to 0.3 g were used for the preparation of PVIm hydrogels.

The synthesis of PVIm hydrogels was performed by using the following procedure. AIBN (0.16 g) was dissolved in VIm (10 mL), then water (10 mL) was added to this mixture. Different amounts of MBAAm (0.05, 0.1, 0.2, and 0.3 g) were added to these aqueous solutions afterward. These mixtures were poured in a glass tubes with 5 mm in diameter and 10 cm long and placed in a water bath at 65°C for different time periods to follow the conversion with time. Hydrogels reaching 100% conversion were taken out, cut into pieces, and washed repeatedly with an excess amount of deionized water. Purified hydrogels were dried in air and in a vacuum oven at ambient temperature to constant weights and ground into fine particles. The sizes of the particles were 100–150  $\mu\text{m}$ . The hydrogel particles were stored in vials in dark and at room temperature for further use in swelling and adsorption experiments.

### Determination of conversion percent of PVIm into hydrogel

The percentage conversion of monomers into an insoluble network was based on the total weight of monomer and crosslinking agent used in the initial mixture ( $m_0$ ), and calculated by using eq. (1).

$$\text{Conversion}(\%) = \frac{m}{m_0} \times 100 \quad (1)$$

where  $m_0$  is the total mass of monomer and crosslinking agent mixture in the initial mixture, and  $m$  is the mass of PVIm hydrogel after drying.

### Swelling behavior of PVIm hydrogels

Swelling extent of PVIm hydrogels was determined gravimetrically by using hydrogels having cylindrical form cut in the shape of disks 1 mm in thickness and 10 mm in diameter. Dry PVIm hydrogels were first weighed and then immersed in deionized water. Swollen hydrogels were removed from swell-

ing media at regular time intervals, dried superficially with filter paper, weighed, and placed in the same bath. The measurements were continued until a constant weight was reached for each sample.

The swelling degree (%*S*) of PVIm hydrogels in deionized water was calculated using eq. (2) given below.

$$\%S = \frac{S_t - S_0}{S_0} \times 100 \quad (2)$$

where  $S_t$  is the weight of swollen gel at time  $t$  and  $S_0$  is the weight of the dry gel at zero time.

### Preparation of Cu-loaded PVIm hydrogels

To prepare Cu-loaded PVIm hydrogel, first the adsorption kinetics of Cu(II) ion from 100 mg/L Cu(II) ion solution was followed at pH 4. For this purpose, the amount of Cu(II) ion adsorbed by hydrogel particles was checked at different time intervals. After the adsorption equilibrium time was determined, 0.05 g of PVIm hydrogel particles were contacted with solutions containing different concentrations (100, 250, 500, 750, 1000, 1250, and 1500 mg/L) of Cu(II) ion at pH 4 with continuous stirring at 6 h.

Preparation of PLE was conducted by loading Cu(II) onto PVIm hydrogel particles. For this purpose, ~ 0.2 g PVIm hydrogel particles prepared by using the minimum amount of crosslinking agent was placed into 200 mL, 1500 mg/L Cu(II) ion solution at pH ~ 4 in a bottle stirred magnetically at moderate rpm for predetermined time period. To determine the amount of Cu(II) ions adsorbed onto PVIm particles, Cu(II) ion concentration remaining in the solutions was determined by using Carry 100 UV-vis spectrophotometer and ammonia as complexing agent. The amount of Cu(II) ion adsorbed per unit mass of PVIm hydrogel was evaluated by using the following expression,

$$q_e = \frac{(C_e - C_0) \times V}{W} \quad (3)$$

where  $q_e$  is the amount of Cu(II) ions adsorbed onto unit dry mass of PVIm hydrogel (mg/g),  $C_0$  and  $C_e$  are the concentrations of Cu(II) ion solutions (mg/L) initially and after treatment for a certain period of time, respectively;  $V$ , is the volume of aqueous phase (L) and  $W$  is the amount of dry PVIm hydrogel used (g).

### Phosphate anions adsorption experiments

Phosphate anions adsorption studies at different initial concentrations

Cu-loaded PVIm hydrogel of 0.05 g was treated with phosphate anions ion solution (50 mL) to get information on the relative performance of Cu-loaded

PVIm hydrogel. The adsorption kinetics of phosphate anion from 100 mg/L phosphate solution was followed at pH 7. For this purpose, the amount of anion adsorbed was checked at different time intervals. After the adsorption equilibrium time was determined, the Cu-loaded polymer ligand exchangers were contacted with 10 different concentrations of phosphate ion solutions (0.1, 0.5, 1, 5, 10, 50, 100, 250, 500, and 1000 mg/L) at pH 7 with continuous stirring for predetermined time periods. Phosphate ion concentrations remaining in the solution after every adsorption stage were determined by colorimetric ascorbic acid method using UV-vis spectrophotometer.<sup>13</sup> The amounts of phosphate adsorbed per unit mass of the Cu-loaded PVIm hydrogel were evaluated by using eq. (3). Regeneration of phosphate was performed by 4% NaCl solution. There was no Cu(II) leakage during treatment with 4% NaCl solution as checked with ammonia test.

#### Phosphate adsorption studies at various pH values

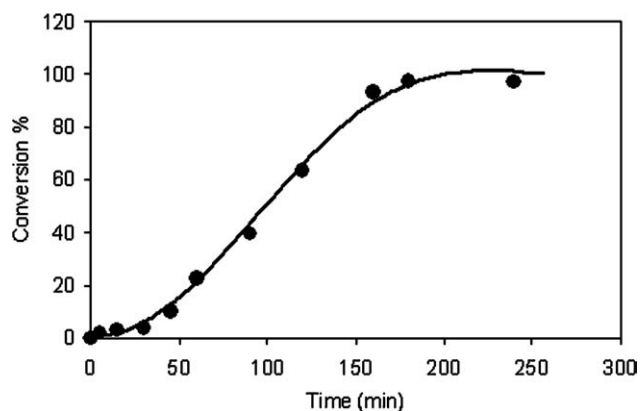
The effect of pH on phosphate removal by using PLE was investigated at different pH values. The pH was adjusted by using NaOH and HCl solutions. Cu-loaded PVIm hydrogel particles of 0.05 g were treated with 100 mg/L of phosphate solution at different pH values ranging from 3 to 9 at 8 h. Phosphate ion concentrations remaining in solution after adsorption were determined by using UV-vis spectrophotometer.

#### Selectivity studies

Selective phosphate adsorption tests were performed by using three different mixtures of aqueous anion solutions. The first solution mixture contained 50 mg/L of phosphate, bromide, fluoride, and nitrite, and 500 mg/L of sulfate, chloride, and nitrate; the second one was composed of 10 mg/L of phosphate, bromide, fluoride, and nitrite, and 100 mg/L of sulfate, chloride, and nitrate; third one was prepared from 1 mg/L of phosphate, bromide, fluoride, and nitrite, and 10 mg/L of sulfate, chloride, and nitrate.

The Cu-loaded polymer ligand exchangers were contacted with those solutions with continuous stirring for predetermined time periods. The hydrogel particles were filtered and the filtrate was used in ion chromatography to determine percent adsorption and adsorbed milligram of phosphate per gram of dry Cu-loaded hydrogels. Dionex ICS-1000 model ion chromatography was used for the quantitative determination of anions. The properties of Dionex ICS-1000 model ion chromatography system are given below.

Suppressor: ASRS-ULTRA II 4-mm,  
Column: ION Pac AS9-HC,  
Eluent: 9 mM Na<sub>2</sub>CO<sub>3</sub>,



**Figure 1** Conversion percentage versus time for PVIm hydrogels prepared by using 0.05 g of MBAAM.

Dedector: ED50 Electrochemical detector,  
Flow: 100 mL/min,  
Supresor current: 66 mA,  
Total pressure: 1950 psi, and  
Ejection volume: 200  $\mu$ L.

## RESULTS AND DISCUSSIONS

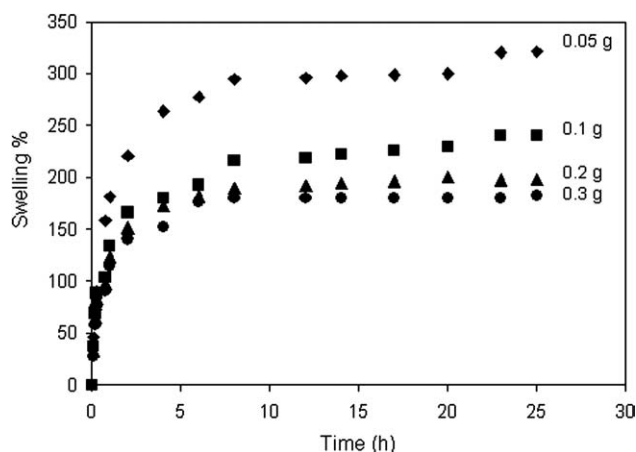
### Synthesis of PVIm hydrogels

Crosslinked PVIm hydrogels were synthesized by free radical polymerization of VIm in aqueous solution by using azobisisobutyronitrile as the initiator and *N,N'*-methylenebisacrylamide (MBAAM) as the crosslinking agent. The synthesis of PVIm hydrogels was performed at four different amounts of crosslinking agent ranging from 0.05 to 0.3 g.

The conversion percentage of monomers into an insoluble network was determined gravimetrically. Figure 1 shows the conversion of monomer and crosslinking agent mixture to PVIm hydrogels as a function of time. In the reaction conditions described in the experimental part, 100% conversion to gel was achieved at about 200 min.

To identify hydrogel system to be used in adsorption studies, the swelling behaviors of the hydrogels prepared with different amount of crosslinking agent was investigated in deionized water and given in Figure 2. Swelling capacity and stability in the swollen state are particularly important for environmental applications of hydrogels. As can be seen from Figure 2,  $\sim$  300% and 180% swelling were observed for the PVIm hydrogels prepared from minimum (0.05 g) and maximum (0.3 g) amount of crosslinking agent in deionized water, respectively. These values show that swelling percentage increases with decreasing amounts of crosslinking agents in PVIm hydrogels as a result of decreasing density of crosslinks.

The PVIm hydrogels with minimum MBAAM content were selected as the optimum gel system and were used in the remaining part of this study.

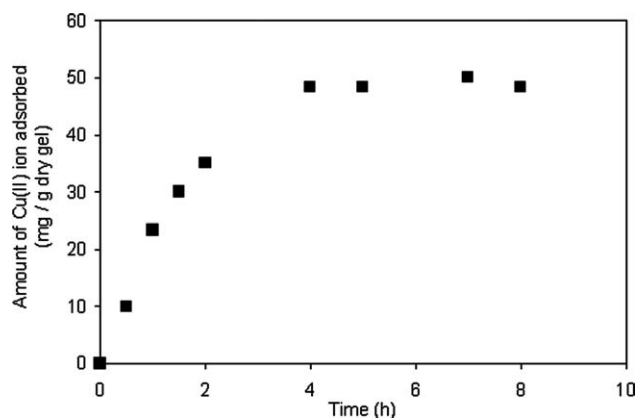


**Figure 2** Swelling percentage versus time for PVIIm hydrogels prepared by different amounts of MBAAm.

### Preparation of Cu-loaded PVIIm hydrogels

To prepare PLE for the removal of phosphate, PVIIm hydrogels were loaded with Cu(II) ions. For this purpose, the adsorption kinetics of Cu(II) ions onto PVIIm hydrogels was investigated by contacting  $\sim 0.05$  g of hydrogel particles with 100 mg/L Cu(II) ion solution. Figure 3 shows the adsorption kinetics of Cu(II) ion onto PVIIm hydrogels under these conditions.

High-adsorption rate was observed within 2 h and the plateau value (i.e., adsorption equilibrium) was quickly reached at around 4 h. The PVIIm hydrogels adsorbed 50 mg Cu(II) per gram of dry hydrogel particles from 100 mg/L Cu(II) ion solution. The adsorption kinetics for Cu(II) ion by PVIIm hydrogels prepared in this work is better than that of the PVIIm hydrogels that were prepared by irradiating of binary mixtures of VIm-water using  $^{60}\text{Co}$ - $\gamma$  source by Pekel and Güven.<sup>14</sup> It was found that 50 h was needed to reach adsorption equilibrium for Cu(II) ion by using PVIIm hydrogel particles. A total of 200 mg of Cu(II) per gram of dry gel was adsorbed from 250 mg/L initial Cu(II) solution by Pekel and Güven.



**Figure 3** Adsorption kinetics of Cu(II) ion onto PVIIm hydrogels.

The effect of initial concentration of Cu(II) ion on the adsorption behavior of PVIIm hydrogels was determined for seven different Cu(II) ion concentrations (100, 250, 500, 750, 1000, 1250, and 1500 mg/L) and given in Figure 4 as mg adsorbed Cu(II) ion per gram of dry gel and millimolar adsorbed Cu(II) ion per gram of dry gel. These curves show that the Cu(II) adsorption increased with increase in initial metal ion concentration. PVIIm hydrogels exhibited very high affinity for Cu(II) ion, the highest value was found to be 325 mg/g from 1500 mg/L Cu(II) ion solution.

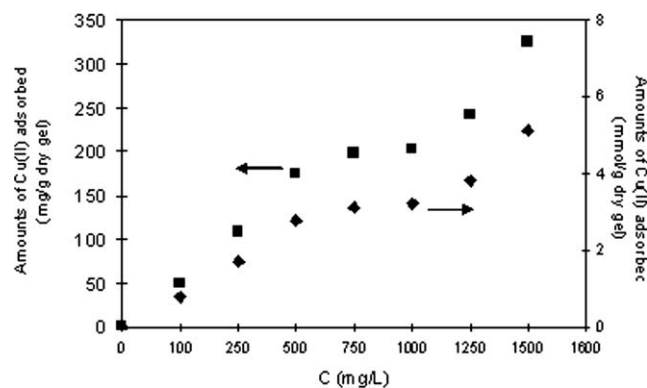
PVIIm hydrogel particles were converted to Cu-loaded form by using 1500 mg/L Cu(II) solution at about pH 4 for 6 h. As can be seen from Figure 4, PVIIm hydrogels adsorbed 5.1 mmol Cu(II) ion per gram of dry gel. Cu(II) ion loading onto PVIIm hydrogels takes place very effectively. The metal ion binding property of VIm is due to the electron donor nitrogen atom at position 3 of the imidazole ring. Acidic Cu(II) ions easily react with the basic chelating unit of PVIIm.<sup>15</sup> Highest amount of Cu-loaded hydrogels were used in all phosphate adsorption experiments. In the highest loaded systems, the stoichiometry of Cu(II) ions to vinylimidazole repeating units was found to be 2 : 1.

The interaction between PVIIm hydrogel particles and Cu(II) ion, and furthermore, phosphate with Cu(II) ion loaded PVIIm hydrogels could be easily seen by observing respective changes in color. The color of untreated PVIIm hydrogels is pale yellow. After Cu(II) loaded onto PVIIm hydrogels, the color became dark blue. When Cu(II) loaded PVIIm hydrogels adsorbed phosphate, the color was observed to change to light blue.

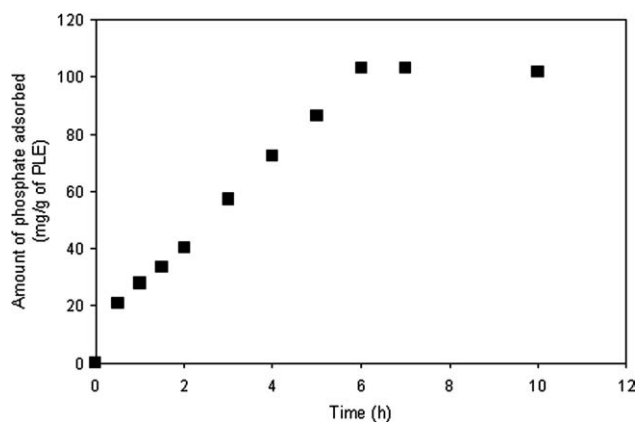
### Phosphate adsorption studies

Phosphate adsorption studies at different initial concentrations

In this part of the study, the performance of PLE is investigated with respect to adsorption kinetics,



**Figure 4** Dependence of Cu(II) uptake on the initial concentrations of Cu(II) ion as milligram of adsorbed Cu(II) per gram dry gel and millimolar of adsorbed Cu(II) per gram dry gel.



**Figure 5** Adsorption kinetics of phosphate uptake onto Cu-loaded PVIm hydrogel.

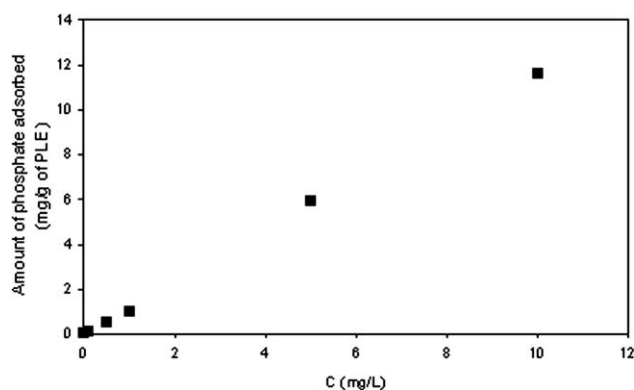
adsorption and desorption behavior, and pH effects toward target phosphate anions. The phosphate anions species present in aqueous solutions such as  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{H}_3\text{PO}_4$  are highly dependent on the pH of the solution. For the sake of convenience, these phosphorus species are simply called as phosphate hereafter.

To investigate adsorption kinetics of phosphate anion onto Cu-loaded PVIm hydrogel particles (PLE),  $\sim 0.05$  g PLE was contacted with 50 mL of 100 mg/L phosphate solution at about pH 7. Figure 5 shows the adsorption kinetics of phosphate anion onto PLE. High-adsorption rate was observed within 6 h, and the plateau value (i.e., adsorption equilibrium) was reached approximately at a removal efficiency of 100 mg phosphate per gram of PLE within this period.

The effect of initial concentration of phosphate on the adsorption behavior of Cu-loaded PVIm hydrogels (0.05 g) was determined in 8 h contact time for 10 different phosphate concentrations (0.1, 0.5, 1, 5, 10, 50, 100, 250, 500, and 1000 mg/L) at pH 7, and the adsorption amounts were given in Figures 6 and 7.

Figure 6 shows that adsorption of phosphate at low-concentration increased almost linearly with increasing initial phosphate concentration. The new PLE exhibited very high affinity for phosphate at low-concentration levels reaching a value of 12 mg of phosphate per gram, dry PLE from 10 mg/L phosphate solution. Adsorptions (95%) of phosphate have been reached easily for all concentration studies.

Figure 7 shows the effect of high-initial phosphate concentrations on the adsorption behavior of Cu-loaded PVIm hydrogels. It was found that adsorption of phosphate by Cu-loaded PVIm hydrogels increased with increasing phosphate concentration and 218 mg/g dry PLE (2.3 mmol/g dry PLE) of phosphate adsorption was obtained from 1000 mg/L



**Figure 6** Phosphate uptakes onto PLE at low-concentration levels.

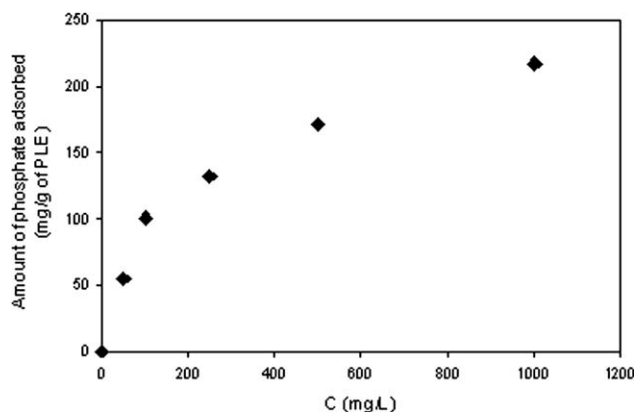
phosphate solution. The adsorption test was also performed by using unmodified PVIm hydrogel particles. No phosphate adsorption was observed from 100 mg/L phosphate solution at predetermined time period by PVIm alone.

Adsorption isotherms of Cu-loaded PVIm hydrogels were analyzed according to the linear form of Langmuir isotherms for phosphate by using eq. (4),

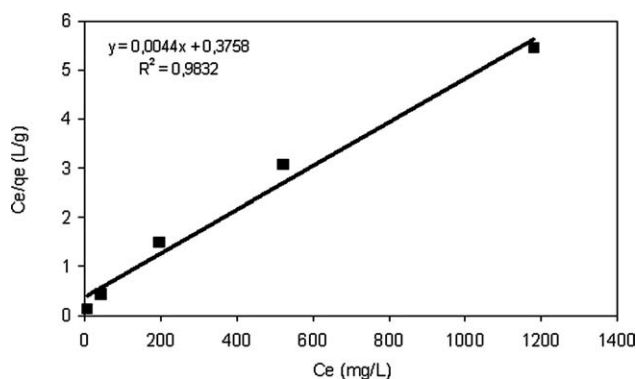
$$\frac{C_e}{q_e} = (1/K_L q_{\text{mon}}) + (1/q_{\text{mon}})C_e \quad (4)$$

where  $C_e$  is the equilibrium concentration of adsorbate in solution,  $q_e$  represents the adsorbed phosphate per unit mass of adsorbent at equilibrium.  $q_{\text{mon}}$  denotes the amount of adsorption corresponding to complete monolayer coverage.  $K_L$  is the Langmuir constant. A plot of  $C_e/q_e$  versus  $C_e$  would give  $K_L$  and  $q_{\text{mon}}$ .<sup>16</sup>

The isotherm shown in Figure 8 seems to be linear over the whole concentration range studied.  $K_L$  and  $q_{\text{mon}}$  values were calculated from Langmuir equation. The constant ( $K_L$ ) contains enthalpic interaction of the binding of phosphate with PLE, and can be found from the intercept of the lines given in Figure 8.  $K_L$  value of PLE indicates the favorable



**Figure 7** Phosphate uptake onto PLE at high-concentration levels.



**Figure 8** Langmuir isotherms for phosphate adsorption on PLE.

interaction of accessible Cu(II) sites on the surface of the polymer.  $q_{\text{mon}}$  is a quantity representing adsorption capacity, also known as monolayer coverage of the surface.  $K_L$  and  $q_{\text{mon}}$  values of PLE from the Langmuir equation for phosphate were found to be  $1.17 \times 10^{-2}$  and 228 mg/g, respectively.  $q_{\text{mon}}$  value is very good accordance with the result previously found as 218 mg/g and reported above.

#### Effect of pH on the phosphate uptake

The species present in a phosphate solution and corresponding acid dissociation constants of the parent acidic forms are as follows:<sup>17</sup>

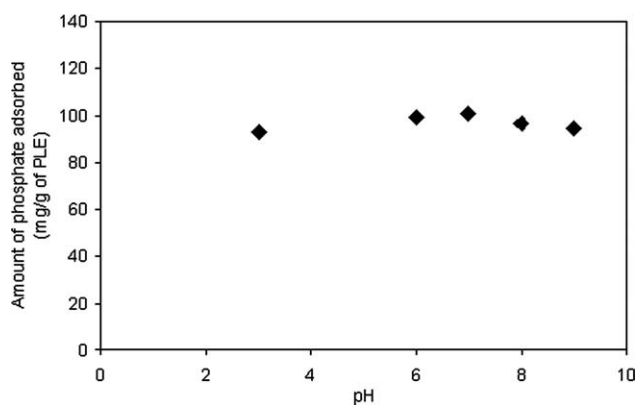


For a municipal wastewater, pH normally ranges from 6.5 to 7.3. Under this condition,  $\text{H}_2\text{PO}_4^-$  is the major phosphate species. Between  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$  is a monodentate ligand with one negative charge, whereas  $\text{HPO}_4^{2-}$  is a bidentate ligand with two negative charges. Understandably, from both electrostatic and Lewis acid–base interaction view-points, the PLE will exhibit greater affinity toward  $\text{HPO}_4^{2-}$  over  $\text{H}_2\text{PO}_4^-$ .

Figure 9 shows equilibrium phosphate uptakes of Cu(II) loaded PVIm hydrogel particles at different pH values for an initial aqueous phosphate concentration of 100 mg/L. It was found that phosphate adsorption did not change virtually within pH values of 3–9.

#### Selectivity studies

Figure 10 shows the results of the selectivity experiment for Cu(II) loaded PVIm hydrogels. The order of decreasing selectivity is phosphate  $\geq$  sulfate  $\geq$  nitrite  $\geq$  nitrate  $>$  bromide  $\gg$  fluoride for 1 mg/L

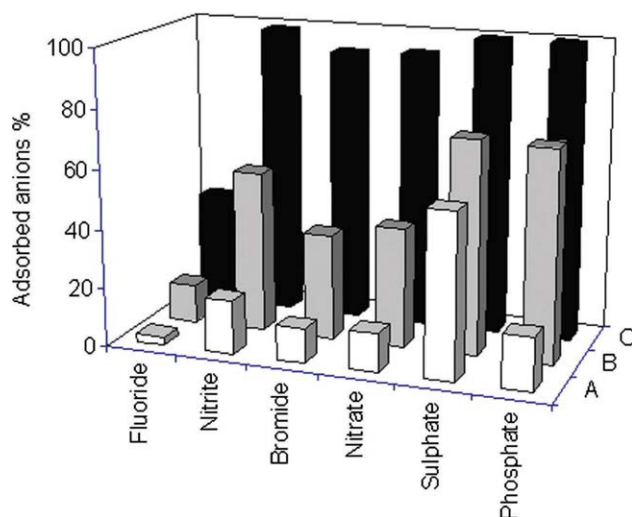


**Figure 9** pH effects on phosphate uptake onto Cu-loaded PVIm hydrogel.

and 10 mg/L solutions of anions mixtures [Fig. 10(B,C)]. The adsorption percentage calculated for phosphate and sulfate anions showed that their adsorption from 1 mg/L phosphate, 10 mg/L sulfate mixture solution is higher than adsorption from 50 mg/L phosphate, 500 mg/L sulfate mixture solution. These results show that the new adsorbent is suitable for the removal of trace amounts of phosphate and sulfate anions from aqueous media.

#### Regeneration of phosphate adsorbed Cu(II) loaded PVIm hydrogels

The PLE should be suitable for efficient regeneration so that they can be used for multiple cycles of operations. An ideal regenerant should have the following



**Figure 10** Adsorption selectivity of Cu-loaded PVIm hydrogels for the indicated anions: solution mixture included (A) 50 mg/L of phosphate, bromide, fluoride, and nitrite, and 500 mg/L of sulfate and nitrate; (B) 100 mg/L of phosphate, bromide, fluoride, and nitrite, and 10 mg/L of sulfate and nitrate; (C) 1 mg/L of phosphate, bromide, fluoride, and nitrite, and 10 mg/L of sulfate and nitrate. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

characteristics: easily available, inexpensive, and environmentally benign high-regeneration efficiency, the newly loaded ion form after regeneration should be easily exchangeable and nontoxic when discharged.<sup>11</sup>

Sodium chloride meets all of the above requirements, hence 4% of NaCl solution was used for regeneration of phosphate adsorbed Cu(II) loaded PVIm hydrogels. Dionex ICS-1000 model ion chromatography was used for the determination of regeneration amount. The regeneration process was performed at 2 h. High-regeneration efficiencies were achieved and the phosphate recovery efficiency was 100%. The regenerated hydrogel was used in the repeated adsorption experiment and nearly 100% adsorption was observed.

### CONCLUSIONS

A new PLE was synthesized by Cu(II) loading onto PVIm hydrogels. This PLE exhibited high affinity for phosphate together with high-removal efficiencies for other anions. Phosphate uptake 218 mg/g from 1000 mg/L phosphate solution was achieved. NaCl solution (4%) was used for regeneration of phosphate adsorbed Cu(II) loaded PVIm hydrogels with 100% regeneration efficiency.

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