A Novel Thermosensitive Gel Adsorbent for Phosphate Ions

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Summary: A novel thermosensitive gel adsorbent for phosphate ions was developed and its adsorption/desorption properties were investigated. The gel adsorbent was made by the copolymerization of *N*-isopropylacrylamide (NIPA) and *N*-[3-(dimethylamino)propyl]acrylamide (DMAPAA). The adsorbent has a volume phase transition temperature (VPTT), below which it becomes hydrophilic. The tertiary amino groups of DMAPAA were ionized and showed a cationic state when the gel swelled. Phosphate ions were adsorbed onto the ionized tertiary amino groups in the gel network below the VPTT and were desorbed above the VPTT because of the suppression of the ionization of the tertiary amino groups of gel and the shrinkage of the gel.

Keywords: adsorption; hydrogel; phosphate ion; thermo-sensitive

Introduction

The eutrophication of closed bodies of water such as lakes, ponds or bays by an influx of phosphorus has become a serious problem. On the other hand, phosphorus is one of the essential elements for life, and should be recovered and reused, as it is a valuable, limited resource. Various methods for the removal and/or recovery of phosphate from wastewater have been proposed.[1–5] However, the purity of the recovered phosphorus has not been high enough to permit its reuse. Thus, a simple process to purify the recovered phosphate is needed to enhance phosphorus recovery from wastewater. Ion exchange is one of the methods used to purify the recovered phosphorus, but the regeneration and disposal of the used ion-exchange resins is a costly process. The physical and chemical properties of thermosensitive hydrogel have been studied both experimentally and theoretically by many researchers [6–10]. Studies concerning the application of these gels for extraction,[11] adsorption,[12] drug delivery systems,[13] and dewatering systems,[14] also are ongoing. Poly(*N*-isopropylacrylamide) (PNIPA) is a typical thermosensitive polymer. It is well known that PNIPA has a lower critical solution temperature (LCST) and shows reversible phase transition at 32 °C.[15] This copolymer of NIPA is comprised of an ionic monomer that is temperature- and pH-sensitive, and its qualities of adsorbency[9] and chromatography have been studied.[16] In the present study, a novel thermosensitive gel adsorbent for phosphate ions was developed and its adsorption/desorption properties were investigated.

Concept of Adsorption/Desorption of Phosphate Ions in A Thermosensitive Gel

The gel adsorbent prepared in this work had tertiary amino groups in the thermosensitive gel network. The gel was composed of *N*-[3-(dimethylamino)propyl]acrylamide (DMAPAA) and *N*-isopropylacrylamide (NIPA) as monomers with methylenebisacrylamide (MBAA) as a cross-linker. The adsorbent had a volume phase transition temperature (VPTT),

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above which it became hydrophobic. When the gel adsorbent swelled to below the VPTT, the tertiary amino group of DMAPAA was ionized and showed a cationic state expressed as follows:

$$\begin{aligned}&CH_2CHCONH(CH_2)_3N(CH_3)_2\\&+H_2O \leftrightarrow CH_2CHCONH(CH_2)_3N\\&+H(CH_3)_2+OH^-\end{aligned} \qquad (1)$$

The ionized tertiary amino group worked as an adsorption site. When the gel swelled to below the VPTT, the tertiary amino group of DMAPAA was ionized by the water. Then, anionic phosphate ions were adsorbed onto the ionized tertiary amino groups. On the other hand, the ionization of the amino groups was suppressed above the VPTT because the amino groups of the DMAPAA were surrounded by hydrophobic NIPA and the water molecules could not easily access the amino groups. The phosphate ions were detached from the adsorption site because the ionization of the amino groups in the gel network was suppressed and they were expelled from the gel by its shrinkage.

Materials and Methods

The *N*-isopropylacrylamide (NIPA) and *N*-[3-(dimethylamino)propyl]acrylamide (DMAPAA) was kindly supplied by Kohjin Co. (Japan). The NIPA was purified by recrystallization from n-hexane and DMAPAA was purified by reduced distillation. All other chemicals were purchased from Sigma-Aldrich Co. (USA). They were reagent grade and used without further purification. The preparation condition of the gel is shown in Table 1. The molar ratios of DMPAA in total monomer concentration were 2.5, 5 and 10%, respectively, and those of the cross-linker were 3, 5 and 7.5%. The copolymerization of NIPA and DMAPAA was conducted by radical polymerization in Teflon tubes with 6 or 12 mm inner diameters at 50 °C, which was higher than the LCST of NIPA polymer, to make the gel porous for quick swelling and shrinking.[17] After completion of the reaction, cylindrical gels were pushed out from the tubes then washed with methanol by Soxhlet extraction to remove unreacted chemicals. Then they were cut into pieces. The copolymerization of the NIPA and DMAPAA was confirmed by the FTIR spectrum.

The swelling degree of the gel was determined by measuring the swelling diameter of the cylindrical gel in 6 mm lengths at desired temperatures using a cathetometer. The pH of the gel in deionized water was measured by sticking a pH electrode directly in gel that had reached a diameter of 12 mm at the desired temperature. The pH of 1 wt.% DMPAA polymer aqueous solution was measured with the same pH electrode. The pH electrode used was a needle-type electrode equipped with a thermometer (6252-10D, HORIBA Ltd., Japan) connected to a pH meter (Type D-51, HORIBA Ltd., Japan). The temperatures of the gel and the solution were measured by a thermometer equipped with the pH meter. The temperature bias of the electrode was corrected with a pH meter. The gels with 6 mm diameters were then sliced into pieces 1.5 mm thick and dried at room temperature for the adsorption/desorption experiment. The adsorbate solution was prepared using 5 ml of aqueous solution of potassium

Table 1.
Preparation conditions of the gel

	Material	[mmol/L]
Monomer	*N*-isopropylacrylamide	1350, 1425, 1462.5
Co-monomer	*N*-[3-(dimethylamino)propyl]acrylamide	150, 75, 37,5
Cross-linker	*N,N'*-methylenebisacrylamide	45, 75, 112.5
Accelerator	*N,N,N',N'*-tetraethylmethylenediamine	10
Initiator	Ammonium peroxodisulfate	0.5

dihydrogenphosphate. The desired amount of the dried gels was mixed with the solution in a test tube. The test tube was shaken in a water bath at a desired temperature for 24 hours, and then the concentration of the phosphate ions in the solution was measured. The temperature of the solution was then raised to 50 °C for desorption of the phosphate ions, and their concentration was measured. The amount of phosphate adsorbed onto the gel was determined from the decrease in the concentration of phosphate in the solution. The concentration of the phosphate was measured by using a conductivity detector (COD-10A, Shimadzu Co., Japan).

Results and Discussions

Fig. 1 shows the FT-IR spectra of the gels. Weak C-N stretching attributed to amino groups of DMAPAA and C-H stretching attributed to propyl groups of DMAPAA was observed for the DMAPAA/NIPA gel, at around 1100 cm^{-1} and 2800 cm^{-1}, respectively.

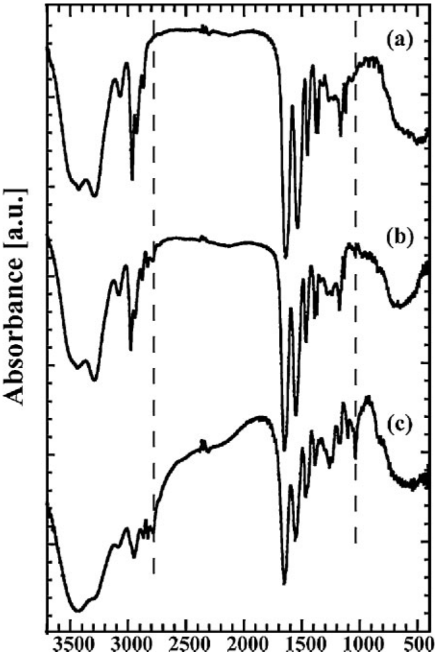

Figure 1.
FT-IR spectra of the gels. (a) NIPA (b) NIPA-DMAPAA = 9:1 (c) DMAPAA.

The effects of the gel composition on the thermosensitive properties are shown in Figure 2. Figure 2(a) shows the effect of the DMAPAA concentration in the preparation of the gel on the swelling diameter of the gel. The swelling diameter of the gel gradually decreased as the temperature increased. The swelling diameter of the gel increased with an increase in the DMAPAA concentration. This result suggests that hydrophilicity and ionic repulsion of the gel network are increased with an increase in the DMAPAA concentration.

The copolymerized gels swelled larger below 50 °C. This result suggests that the VPTT of the copolymerized gels is higher than that of the NIPA gel, ca. 32 °C,[18] because of the copolymerization with a hydrophilic DMAPAA monomer. Figure 2(b) shows the effect of the cross-linker concentration in the preparation of the gel on the swelling diameter of the gel. It is noted that the difference in the swelling diameter between 20 °C and 50 °C increased as the concentration of the cross-linker decreased.

The effects of the preparation composition of the gel on its pH are shown in Figure 3. The pH change of an aqueous solution of DMAPAA polymer (1 wt. %) with temperature is also shown in Fig. 3. The pH in the gel is abruptly decreased above the transition temperature of the gel and the values of pH in the gel are smaller than that of the polymer. Those results suggest that the pH in the gel is influenced by the hydrophilic-hydrophobic transition of poly-NIPA. Figure 3(a) shows the effect of the DMAPAA concentration on the pH of the gel. The pH of the gel increased with the increase of the DMAPAA concentration of the gel because the amino groups in the gel were ionized and became cationic in water. Figure 3(b) shows the effect of the cross-linker concentration on the pH of the gel. The difference in pH of the gel did not change very much when the cross-linker concentration changed. These results show that the pH

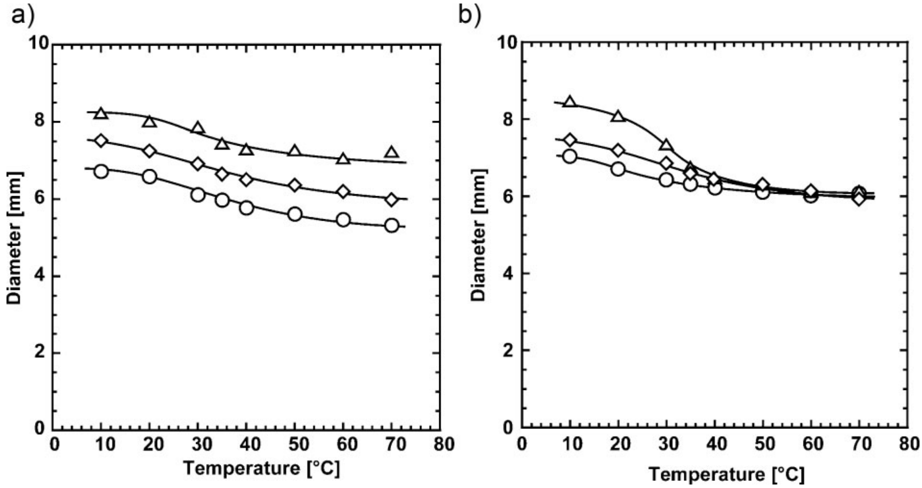

Figure 2.

(a): The effect of the DMAPAA concentration in the preparation of the gel on the swelling diameter of the gel. NIPA/DMAPAA/MBAA [mmol/L]; Δ=1350/150/75, ◇ = 1425/75/75, ○ = 1462.5/37.5/75. (b): The effect of the cross-linker concentration in the preparation of the gel on the swelling diameter of the gel. NIPA/DMAPAA/MBAA [mmol/L]; Δ=1425/75/45, ◇ = 1425/75/75, ○ = 1425/75/112.5.

in a gel depends not only on the water content of the gel but also on the DMPAA concentration and hydrophilic-hydrophobic transition of poly-NIPA of the gel. This suggests that a lower cross-linker concentration with a higher DMPAA concentration will increase the pH of the gel at low temperature. The amount of ionizable amino groups in the gel was determined by the DMAPAA concentration of the gel, and the ratio of ionization for the amino groups was provided by the water content of the gel.

The effect of the cross-linker concentration of the gel on the adsorption rate is shown in Fig. 4. The amount of adsorption

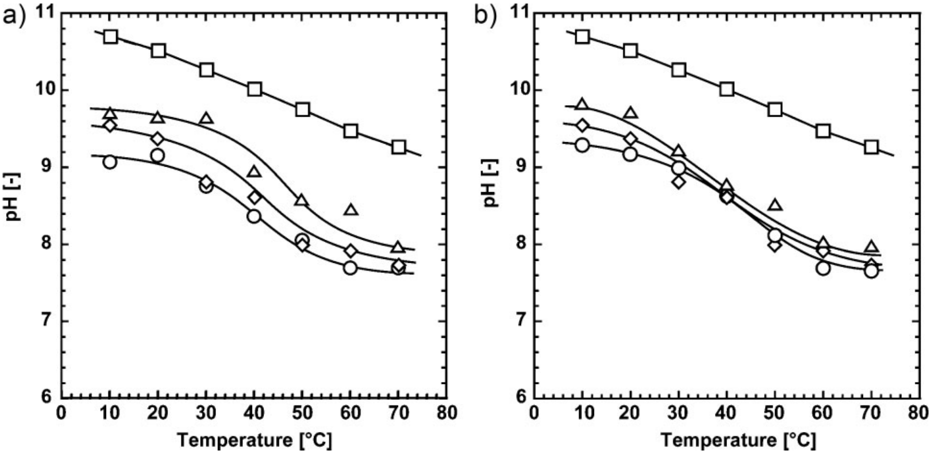

Figure 3.

(a): The effect of DMAPAA concentration on the pH of the gel. NIPA/DMAPAA/MBAA [mmol/L]; Δ=1350/150/75, ◇ = 1425/75/75, ○ = 1462.5/37.5/75. (b) The effect of cross-linker concentration on the pH of the gel. NIPA/DMAPAA/MBAA [mmol/L]; Δ=1425/75/45, ◇ = 1425/75/75, ○ = 1425/75/112.5. Square keys express the pH of the DMPAA polymer aqueous solution (1wt. %).

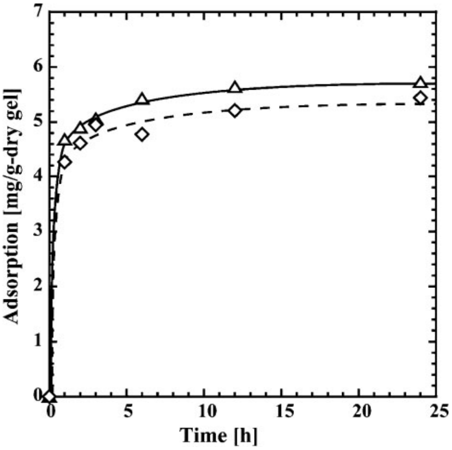

Figure 4.
The adsorption rate of phosphate ions at 20°C; NIPA/DMAPAA/MBAA [mmol/L]; Δ=1425/75/45, ◇ = 1425/75/75,

reached equilibrium within 24 hours. The adsorption rate was not largely influenced by the cross-linker concentration.

The effects of the cross-linker concentration of the gel on the adsorption were examined. The adsorption isotherms of phosphate ions at 20 and 50 °C are shown in Figures 5.

The amount of adsorption increased with an increase in the concentration of the phosphate ions in the solution. The amounts of adsorption at 20 °C were larger than those at 50 °C. This result suggests that the ratio of the ionized amino groups was increased at a lower temperature by the increase in the water content of the gel.

Figure 6 shows the effects of the cross-linker concentrations on the time course of the ratio of adsorption of phosphate ions by

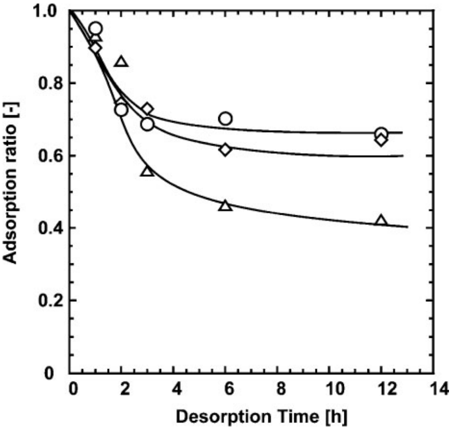

Figure 6.
The effects of the cross-linker concentrations on the time course of the ratio of adsorption of phosphate ions; adsorption time= 24 hr, adsorption temperature = 20 °C desorption temperature = 50 °C, adsorbate = 5 mM KH_2PO_4, NIPA/DMAPAA/MBAA [mmol/L]; Δ=1425/75/45, ◇ = 1425/75/75, ○ = 1425/75/112.5.

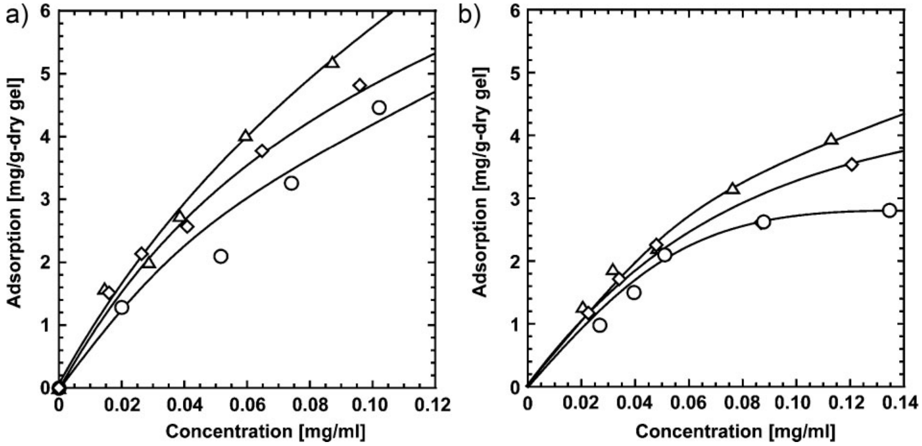

Figure 5.
The adsorption isotherms of phosphate ions at 20°C (a) and at 50°C (b); NIPA/DMAPAA/MBAA [mmol/L]; Δ=1425/75/45, ◇ = 1425/75/75, ○ = 1425/75/112.5.

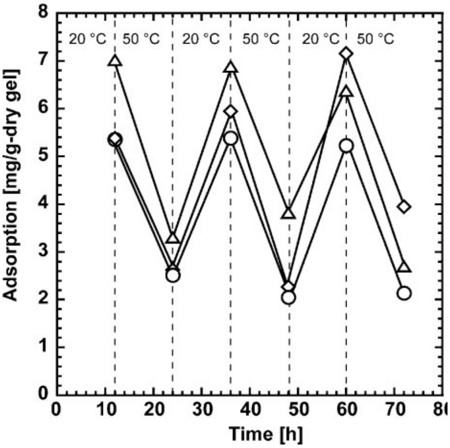

Figure 7.
Adsorption/desorption of phosphate ions in response to temperature swings between 20 and 50 °C; adsorbate = 5 mM KH_2PO_4, NIPA/DMAPAA/MBAA [mmol/L]; Δ=1425/75/45, ◇ =1425/75/75, ○ =1425/75/112.5.

the gel. The adsorption ratio is the amount of adsorption at a certain time compared with that of an equilibrium state. The adsorption ratio decreased largely as the concentration of the cross-linker decreased. As shown in Figure 2(b), when the cross-linker concentration decreased, the difference in the swelling diameter of the gel between 20 and 50 °C increased. This suggests that a large amount of expelled water from the gel enhanced desorption of the phosphate ions from the gel.

Figure 7 shows the change in the adsorption of phosphate ions on the gel by temperature swing. The phosphate ions repeatedly adsorbed and desorbed as the temperature fluctuated between 20 and 50 °C.

Conclusion

A novel thermosensitive gel adsorbent for phosphate ions was developed. The gel was composed of thermosensitive and ionizable components. Phosphate ions were adsorbed onto the gel at a lower temperature than the VPTT of the gel because the tertiary amino groups of DMAPAA of the gel were ionized at low temperature by the swelling of the gel. The phosphate ions were desorbed from the gel by the suppression of ionization of the tertiary amino groups of the gel by shrinkage of the gel network above VPTT. The adsorption increased with an increase in the ratio of the DMAPAA in the gel. The adsorption also increased as the cross-linker ratio decreased. Therefore, the gel with a higher DMAPAA concentration and with a lower cross-linker concentration was favorable as an adsorbent because the ionization of adsorption sites and the change of water content of the gel were required for adsorbing and desorbing the phosphate ions through the temperature swing. Phosphate ions were repeatedly adsorbed and desorbed by temperature swings between 20 and 50 °C. These results suggest that this novel thermosensitive gel is applicable as an absorbent of phosphate ions from wastewater.

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