

Removal of Phosphate Ions with a Chemically Modified Chitosan/Metal-Ion Complex

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ABSTRACT: The adsorption of metal ions (Mo^{6+} , Cu^{2+} , Fe^{2+} , and Fe^{3+}) was examined on chemically modified chitosans with a higher fatty acid glycidyl (CGCs), and the adsorption of Cu^{2+} was examined on ethylenediamine tetraacetic acid dianhydride modified CGCs (EDTA-CGCs) synthesized by the reaction of the CGCs with ethylenediamine tetraacetic acid dianhydride. The adsorption of phosphate ions onto the resulting substrate/metal-ion complex was measured. Mo^{6+} depicted remarkable adsorption toward the CGCs, although all the Mo^{6+} was desorbed under the adsorption conditions of the phosphate ions. The other metal ions were adsorbed to some extent on CGCs by chelating to the amino group in the substrate, except for CGC-

1, which had the highest degree of substitution (83.9%). Considerable amounts of Fe^{2+} were adsorbed onto CGCs; however, only a limited number of phosphate ions was adsorbed onto the substrate/metal-ion complex. As a result, the following adsorbent/metal-ion complexes gave higher adsorption ability toward phosphate ions: CGC-4/ Cu^{2+} , CGC-4/ Fe^{3+} , and EDTA-CGC-3/ Fe^{3+} . Where, CGC-3 is a chemically modified chitosan with the degree of substitution of 26.5 percentage, and CGC-4 is one with the degree of substitution of 16.0 percentage. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1578–1583, 2008

Key words: adsorption; metal-polymer complexes

INTRODUCTION

The treatment of hyperphosphatemia is necessary for preventing hyperparathyroidism in patients with chronic renal failure undergoing dialysis. To control the serum phosphate levels, aluminum-containing phosphate binders are usually administered for a long period. However, this method results in the risk of aluminum intoxication.¹ On the other hand, phosphate drained from domestic wastewater and agricultural production promotes pollution in environmental surface water. Also, it is quite important to develop an effective method for the recovery of phosphorous species because the phosphorous resources necessary for the growth of crops may be exhausted in the near future. Under these circumstances, we have studied the development of novel adsorbents for the recovery of phosphorous species.

It is well known that chitosan can adsorb various metal ions.² Chitosan is a binary polysaccharide that contains 2-acetoamide-2-deoxy- β -D-glucose and 2-amino-2-deoxy- β -D-glucose residues in various proportions connected through (1 \rightarrow 4)-glucoside linkages; the latter is contained more than the former. In

this study, novel chitosan derivatives were prepared for the adsorption of phosphate ions with the following three-step procedure. First, the base adsorbents, which consisted of chemically modified chitosans, were synthesized by the same procedure described previously,³ and this was followed by further chemical modification with ethylenediamine tetraacetic acid dianhydride (EDTA) as the second step. Finally, the synthesized adsorbents were allowed to adsorb the metal ions for the preparation of the phosphate adsorbents.

EXPERIMENTAL

Materials and reagents

The starting materials for the adsorbents were chemically modified chitosans with a higher fatty acid glycidyl (CGCs)³ synthesized by the reaction of chitosan with a mixture of 9-octadecenic acid glycidyl and 9,12-octadecanedienic acid glycidyl (CG), and ethylenediamine tetraacetic acid dianhydride modified CGCs (EDTA-CGCs) were synthesized by the reaction of the CGCs with EDTA.⁴ CG was donated by Okamura Oil Mill, Ltd. (Osaka, Japan), and it was used without further purification. The degree of substitution of CG and the free amino group contents of the CGCs are listed in Table I. The degree of substitution of EDTA and the content of the EDTA residue

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TABLE I
Chemically Modified Chitosans

Chemically modified chitosan	Degree of substitution (%)	Amino group content (mol/kg)
CGC-1	83.9	0.34
CGC-2	37.1	2.39
CGC-3	26.5	3.01
CGC-4	16.0	3.34

for the EDTA-CGCs are shown in Table II. The chemical structures of those adsorbents are also shown in Schemes 1 and 2, respectively.

Metal-ion solutions were prepared as follows: Fe^{3+} and Cu^{2+} solutions were prepared by the dilution of the corresponding standard solutions (the concentration was 1.0 g/L) for atomic absorption analysis from Wako Pure Chemical (Osaka, Japan). As a diluent, an acetate buffer solution of 0.1 mol/L was used. Fe^{2+} and Mo^{6+} solutions were prepared by the dissolution of Mohr's salt $[(\text{NH}_4)_2\text{SO}_4\text{FeSO}_4 \cdot 6\text{H}_2\text{O}]$ in a dilute sulfuric acid solution of 9×10^{-3} mol/L and by the dissolution of sodium molybdate in an aqueous mixture of hydrochloric acid and sodium acetate of 0.1 mol/L (total electrolyte concentration), respectively. A standard solution of phosphate ions was prepared by the dissolution of potassium dihydrogen phosphate in pure water. The concentration of phosphate ions was determined by the molybdenum blue method.⁵

Adsorption of metal ions onto the chemically modified chitosans

A chemically modified chitosan (0.010 g) was added to 100 mL of a metal-ion solution at the prescribed pH, and the mixture was continued to be stirred at 40°C until the equilibrium was established. The working conditions were selected as optimum on the basis of the results obtained from our previous experiment⁶ and the literature.⁷ After the adsorption process, a part of the solution was poured into a test tube and centrifuged for 30 min. The free-metal-ion concentration of the supernatant liquid was determined by inductively coupled plasma spectroscopy

(SPS 4000, Seiko Electronic Industry Co., Tokyo, Japan).

Adsorption of phosphate ions onto the chemically modified chitosan/metal-ion complexes

All the adsorbent (0.010 g) allowed to adsorb the metal ions was placed in a test tube. To this, a 15 mL phosphate-ion solution was added, and then it was diluted with water until the total volume of the solution was adjusted to 50 mL. The mixture was continuously stirred at 40°C for 24 h. After the adsorption process, a part of the solution was poured into another test tube and centrifuged for 30 min. The free-phosphate-ion concentration of the supernatant liquid was determined by the molybdenum blue method.⁵ For comparison, the adsorption of phosphate ions onto the parent CGCs without the metal-ion treatment was also measured.

Desorption of phosphate ions from the chemically modified chitosan/ Cu^{2+} complex

The chemically modified chitosan/ Cu^{2+} complex containing phosphate ions was stirred in an acetate buffer solution of 0.1 mol/L with a pH value of 6.0 for 48 h at 30°C. The free-phosphate-ion concentration of the solution was determined by the same molybdenum blue method previously mentioned.

RESULTS AND DISCUSSION

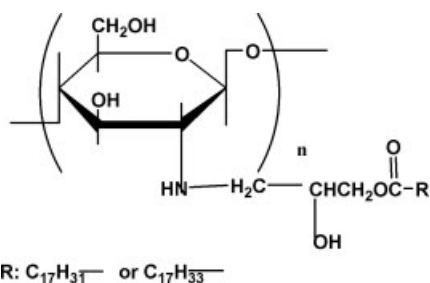
Adsorption of Mo^{6+} onto the chemically modified chitosans and adsorption of phosphate ions onto the resulting adsorbent/metal-ion complex

The adsorption behavior of Mo^{6+} on a chemically modified chitosan (CG-3) was studied in a solution of pH 3.5 at 30°C. The adsorption isotherm is shown in Figure 1.

Figure 1 shows that the adsorption isotherm can be assigned to be a Langmuir type. The saturation value (mol/kg) calculated from a Scatchard plot⁸ was 3.84. This value is similar to the value of the amino group content of CGC-3, suggesting that Mo^{6+} may be binding to the substrate through ionic bonding between the protonated amino group in the

TABLE II
EDTA-Modified CGCs Synthesized by the Reaction of CGCs with EDTA Dianhydride

EDTA-modified CGC	Degree of substitution by CG (%)	Degree of substitution by EDTA (%)	Amino group content (mol/kg)	EDTA residue content (mol/kg)
EDTA CGC-1	13.3	86.0	0.03	1.78
EDTA CGC-2	8.0	62.9	0.96	1.62
EDTA CGC-3	11.2	47.6	1.43	1.30
EDTA CGC-4	13.9	19.7	2.63	0.65



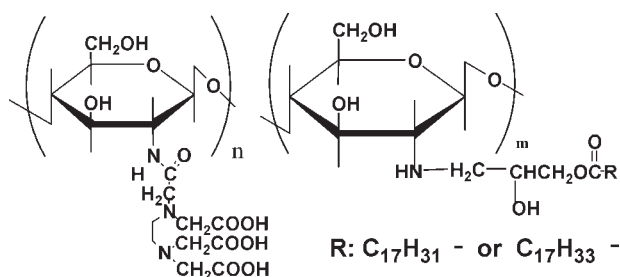
Scheme 1 Chemical structure of CGCs.

substrate and HMoO_4^- . The CGC-3/ Mo^{6+} -ion complex was placed in an acetate buffer solution of pH 6.0, and this was followed by stirring for 24 h at 30°C . Then, the concentration of Mo^{6+} in the solution was determined. As a result, it was found that all the Mo^{6+} ions were desorbed completely. That is, the bonded Mo^{6+} was desorbed during the adsorption process of the phosphate ions.

Adsorption of Cu^{2+} onto the chemically modified chitosans and adsorption of phosphate ions onto the resulting adsorbent/metal-ion complex

The adsorption of Cu^{2+} onto the chemically modified chitosans and that of phosphate ions onto the resulting substrate/ Cu^{2+} complexes were examined. The results are shown in Figures 2 and 3, in which the initial Cu^{2+} concentrations are different.

A measurable amount of Cu^{2+} was not adsorbed on CGC-1 because of steric hindrance. The greater the initial Cu^{2+} concentration and the amino group content were of the chemically modified chitosan, the greater the adsorbed amounts were of both Cu^{2+} and phosphate ions. Therefore, it can be assumed that the resulting substrate/ Cu^{2+} complex could make the chelate easily with phosphate ions if the substrate adsorbs more Cu^{2+} ions. First, the adsorption of Cu^{2+} toward CGC-3 was measured in an acetate buffer solution of pH 6.0. Figure 4 illustrates the adsorption isotherm. Also, Scheme 3 shows the state of chelation of Cu^{2+} ions to the chemically modified chitosan.



Scheme 2 Chemical structure of chemically modified chitosans synthesized by the reaction of CGCs with EDTA.

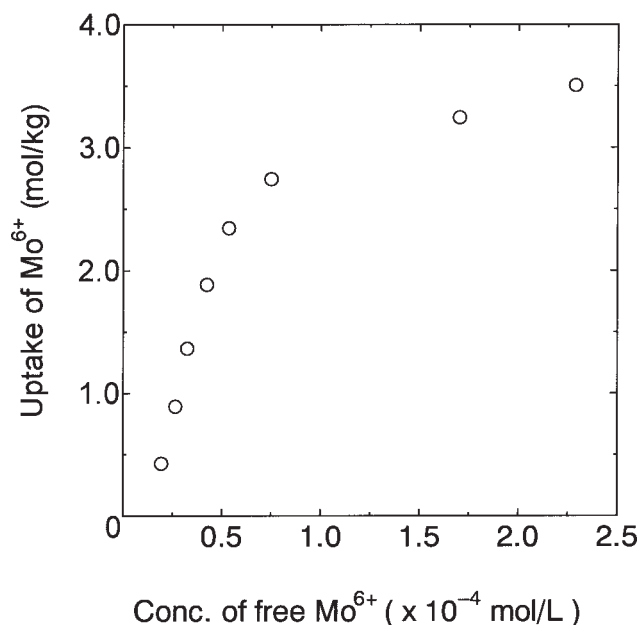


Figure 1 Adsorption isotherm of Mo^{6+} by a chemically modified chitosan (CGC-3) in a buffer solution of pH 3.5 at 30°C . The buffer solution was a mixture of hydrochloric acid and sodium acetate. Its total concentration was 0.1 mol/L.

The saturation value of Cu^{2+} , calculated by the Scatchard equation,⁹ was 1.0 mol/kg. The adsorption of Cu^{2+} onto CGC-3 was performed at the initial concentration of 4.72×10^{-4} mol/L (30 ppm), showing the highest adsorbed amounts here. Next, the phosphate ion was allowed to be adsorbed onto the resulting polymer/metal-ion complex. The obtained results are depicted in Figure 5.

Contrary to expectations, the increase in the adsorbed amount of Cu^{2+} induced a decrease in the adsorption power for phosphate. It can be, therefore, presumed that the chelation of phosphate ions to the substrate/ Cu^{2+} complex requires sufficient space.

For comparison, the adsorption of phosphate ions (the initial concentration was 3 ppm) onto CGCs without Cu^{2+} was measured. No phosphate-ion adsorption was observed for the CGCs. From this fact,

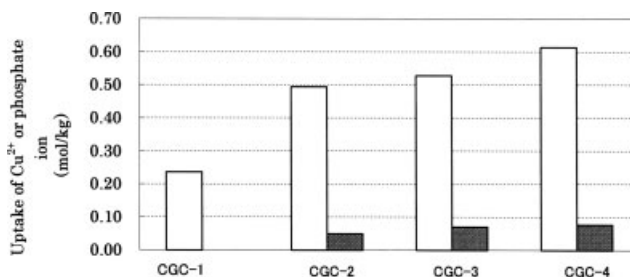


Figure 2 Adsorption of Cu^{2+} and phosphate ions by chemically modified chitosans: (\square) cupric ion and (\blacksquare) phosphate ion. The initial Cu^{2+} concentration was 10 ppm.

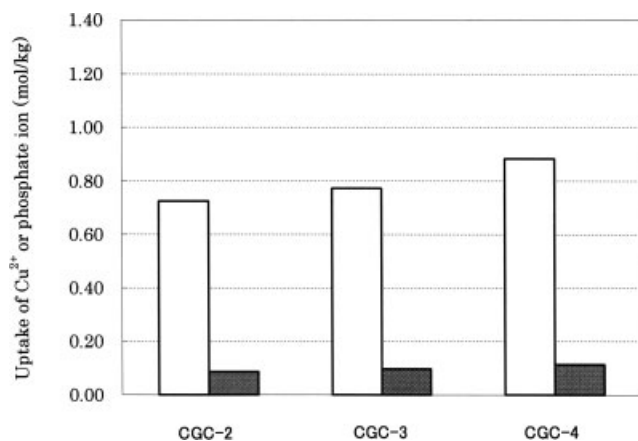


Figure 3 Adsorption of Cu^{2+} and phosphate ions by chemically modified chitosans: (□) cupric ion and (■) phosphate ion. The initial Cu^{2+} concentration was 20 ppm.

it was found that the adsorption of phosphate ions onto CGCs/metal-ion complex was not attributable to ionic bonding, but attributable to the chelation to the metal ion.

Adsorption of Fe^{2+} and Fe^{3+} onto the chemically modified chitosans and adsorption of the phosphate ions onto the resulting adsorbent/metal-ion complex

The adsorption of Fe^{3+} onto the chemically modified chitosans and the adsorption of phosphate ion onto the resulting adsorbent/metal-ion complex were investigated. The results are shown in Figure 6.

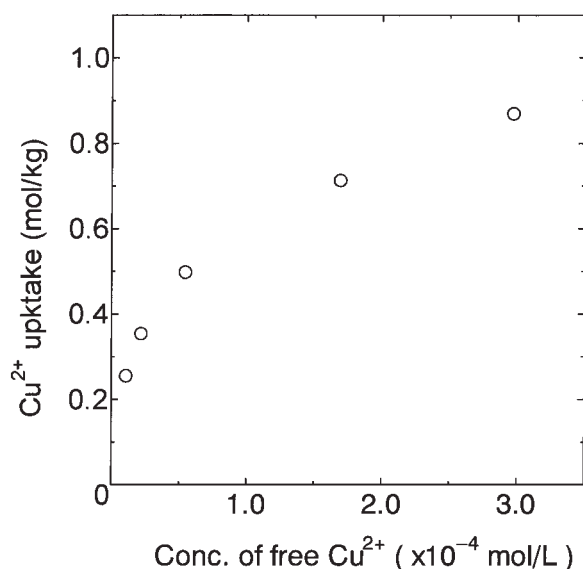
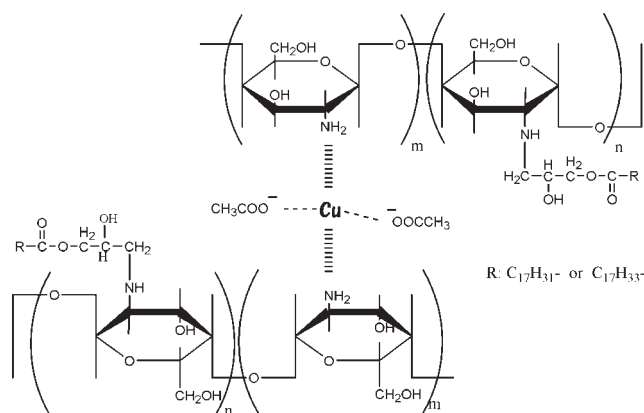


Figure 4 Adsorption isotherm of Cu^{2+} by a chemically modified chitosan (CGC-3) in an acetate buffer solution of pH 6.0 at 30°C.



Scheme 3 Proposed structure of the chemically modified chitosan/ Cu^{2+} complex.

Similarly to the adsorption behavior of Cu^{2+} , steric hindrance could be a reason for the nonadsorption of Fe^{3+} to CGC-1. No significant differences in the adsorbed amounts of both Fe^{3+} and phosphate ions were observed among the substrates, except for CGC-1. The phosphate ion binds nearly stoichiometrically to Fe^{3+} adsorbed onto the chemically modified chitosans. Next, the adsorption of Fe^{3+} onto CGC-3 at the higher Fe^{3+} concentration (the initial concentration was 30 ppm) was studied along with the adsorption of the phosphate ion onto the resulting polymer/ Fe^{3+} complex. As can be found in Figure 7, the adsorbed amount of Fe^{3+} increased; however, an opposite trend was observed for the phosphate ion. The chelation of the phosphate ion to the CGC-3/ Fe^{3+} complex also requires adequate space.

Figure 8 shows the adsorption of Fe^{2+} onto chemically modified chitosans and the adsorption of phosphate ions onto the resulting adsorbent/metal-ion

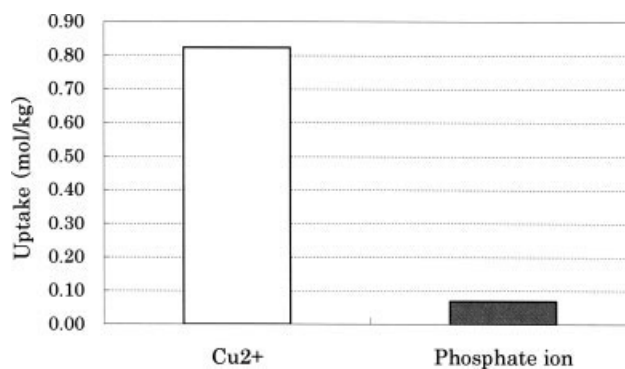


Figure 5 Adsorption of Cu^{2+} and phosphate ions by a chemically modified chitosan (CGC-3): (□) cupric ion and (■) phosphate ion. The initial Cu^{2+} concentration was 30 ppm.

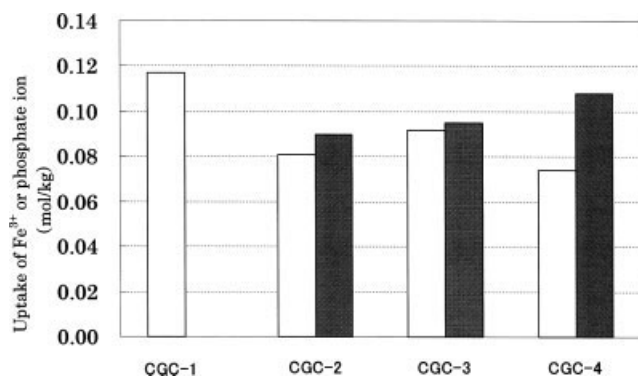


Figure 6 Adsorption of Fe^{3+} and phosphate ions by chemically modified chitosans: (□) ferric ion and (■) phosphate ion. The initial Fe^{3+} concentration was 10 ppm.

complex. The ease of adsorption of Fe^{2+} onto the CGCs increased approximately in the increasing order of the contents of amino groups: $\text{CGC-1} < \text{CGC-2} < \text{CGC-3} < \text{CGC-4}$. Significant amounts of Fe^{2+} were adsorbed onto CGCs. However, the adsorbed amounts of phosphate ions onto the resulting polymer/metal-ion complex were extremely low, suggesting the low chelating power of this ion to Fe^{2+} .

Adsorption of Fe^{3+} onto EDTA-CGCs and adsorption of the phosphate ions onto the resulting adsorbent/metal-ion complex

EDTA-modified CGCs were also introduced as substrates. In Figure 9, the adsorption of Fe^{3+} onto EDTA-CGCs and the adsorption of phosphate ions onto the resulting adsorbent/metal-ion complex are summarized. The adsorption powers of EDTA-CGCs toward metal ions were enhanced with the increase in the EDTA residue content in the substrate. Also, the adsorbed amounts of Fe^{3+} increased significantly with the introduction of the EDTA residue, as can be seen in a comparison of CGC-4 and EDTA-CGC-4, which had nearly equal values for the degree of substitution of the CG group (see Figs. 6 and 9).

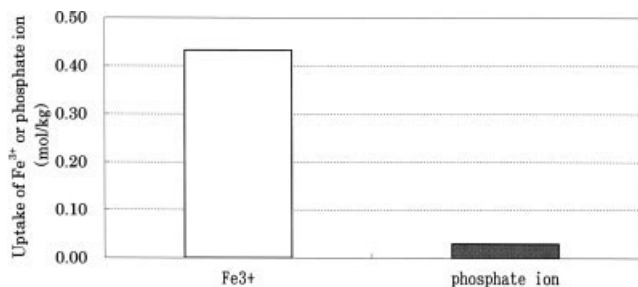


Figure 7 Adsorption of Fe^{3+} and phosphate ions by chemically modified chitosans. The initial Fe^{3+} concentration was 30 ppm.

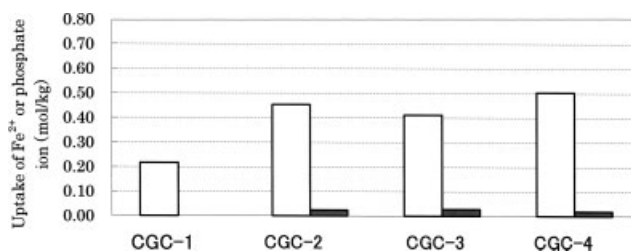


Figure 8 Adsorption of Fe^{2+} and phosphate ions by chemically modified chitosans: (□) ferrous ion and (■) phosphate ion. The initial Fe^{2+} concentration was 11 ppm.

However, such an increase in the adsorbed amounts of Fe^{3+} by the introduction of the EDTA residue could not induce a greater increase for the phosphate ion. This can be interpreted as a strong interaction between the EDTA residue and Fe^{3+} . Therefore, the higher the EDTA residue content was, the lower the adsorbed amount was of the phosphate ion.

Recovery of the phosphate ions from the chemically modified chitosan/ Cu^{2+} /phosphate-ion complex

The desorption behavior of the phosphate ion from the CGC/ Cu^{2+} /phosphate-ion complex was examined. First, Cu^{2+} (the initial concentration was 20 ppm) was allowed to be adsorbed onto CGC-3 (0.01 g), and then the adsorption of the phosphate ion to the resulting complex was studied. The CGC-3/ Cu^{2+} /phosphate-ion complex obtained was placed in an acetate buffer solution (the total concentration was 0.1 mol/L, and its volume was 50 mL) of pH 6.0. It was found that about 93% of the phosphate ions adsorbed by the CGC-3/ Cu^{2+} complex were eluted to the solution by the exchange of the phosphate ions with the acetate ions, which had stronger adsorption power. Therefore, the phosphate ions adsorbed onto the chemically modified chitosan/ Cu^{2+} complex could be recovered easily.

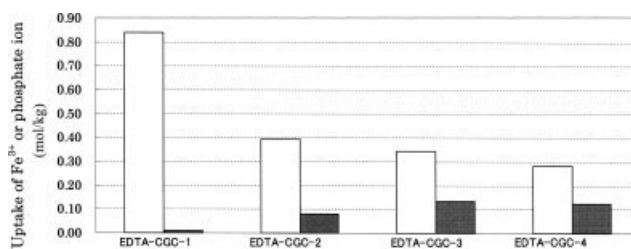


Figure 9 Adsorption of Fe^{3+} and phosphate ions by chemically modified chitosans (EDTA-CGCs): (□) ferric ion and (■) phosphate ion. The initial Fe^{3+} concentration was 10 ppm.

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