

# Synthesis of Crosslinked Oxidized Starch and Its Adsorption Behavior for Calcium Ion

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Received 30 May 2005; accepted 28 September 2005

DOI 10.1002/app.23323

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Cornstarch, after crosslinking with epichlorohydrin (4%, v/w, dry basis of the starch), was oxidized with hydrogen peroxide over the catalyst Cu(II). The newly synthesized products were applied to examine the calcium ion removal activity from water, under various conditions. Removal efficiency of calcium ion from aqueous solution increased proportionally with carboxyl content and the dose of crosslinked oxidized starch in the solution. Ionization of carboxyl groups in starch was necessary for the effective calcium removal. When the pH of the solution was adjusted below 4.0, the starch was no longer an effective calcium-sequestering agent. Adsorption isotherm models were developed, wherein the best fit was obtained in the Langmuir

model. Thermodynamic study indicated that the adsorption process was exothermic, and the enthalpy change ( $\Delta H^\theta$ ), the entropy change ( $\Delta S^\theta$ ), and free energy change ( $\Delta G^\theta$ ) of the adsorption process were calculated with adsorption isotherm data and basic thermodynamic relations. It was assessed that adsorption occurred by strong electrostatic interactions with the negative adsorption enthalpy ( $\Delta H^\theta$ ). The regeneration and reusability of oxidized starch were also assessed and were found to retain the adsorption capacity. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1539–1546, 2006

**Key words:** crosslinked oxidized starch; adsorption; calcium ion; Langmuir isotherm; thermodynamics

## INTRODUCTION

The tripolyphosphate has been used for many years as a builder in detergents. Since the substance is responsible for the eutrophication of water, its use is controlled in many countries. As a result, intensive research has taken place to identify new builders to completely or partially replace the action of tripolyphosphate. Naturally, for having good capabilities for sequestering calcium and magnesium, new builders must be biodegradable, nontoxic, and must be of low cost. In this respect, many natural polysaccharides and their derivatives containing various functional groups may have some potential.

Starch, a natural low-cost polymer, has been a subject of academic as well as industrial interest for the past few decades, because of its renewability and biodegradability. However, starch by itself could not be satisfactorily applied in detergents to sequester calcium and magnesium ions to replace tripolyphosphate, because it has inherently no sequestering or metal-interaction capacity. Hence, new approaches must be made to utilize starch as metal binder, by introducing the functional groups of chelating activity. The use of modified starch to remove metal ions

from wastewater has been reported.<sup>1–8</sup> However, using crosslinked oxidized starch as an adsorbent to remove calcium ion from aqueous solution, the Langmuir constant and thermodynamic parameters of adsorption at different temperature are not found so far in relevant literature.

In this work, cornstarch, after crosslinking, was oxidized by hydrogen peroxide over the catalyst Cu(II) at a relatively high degree of oxidation, and its adsorption capacity for calcium ion from their aqueous solution was investigated under various conditions. The Langmuir constant and thermodynamic parameters of adsorption at 25–50°C were also studied.

## EXPERIMENTAL

### Materials

Common cornstarch (industrial grade) was purchased from Dacheng Corn starch Co. Ltd. (Jilin, China) Epichlorohydrin, hydrogen peroxide, copper sulfate, calcium chloride, and other chemicals used in this study were of analytical grade. All aqueous solutions were prepared using deionized water.

### Synthesis of crosslinked oxidized starch

Cornstarch (50 g) was slurried in 150 mL water, containing sodium sulfate (1.66 g) and epichlorohydrin (2 mL), in a three-necked round-bottomed flask,

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equipped with a reflux condenser. The pH of the starch slurry was adjusted to 11.0 with 0.1M NaOH, and the mixture was stirred for 5 h at 45°C. Then, the pH was adjusted to 7.0 with 0.1M HCl, and the reaction temperature was cooled to 40°C. The starch slurry was supplemented with copper sulfate (either with 1, 1.5, 2, 2.5, 3, or 4 mL, 0.4% aqueous solution). Hydrogen peroxide (40 mL, 30% aqueous solution) was slowly added into the starch slurry for over 30 min, and the mixture was stirred for 3 h at 40°C. The pH of the slurry was maintained at 7.0 throughout the oxidation reaction. After reaction, the slurry was cooled, filtered, and washed with deionized water, until the filtrate was free from chlorine ion. The products were dried at 40°C. The dried samples were stored in a desiccator at room temperature before use.

### Measurements

The carboxyl content of oxidized starch was determined according to the modified procedure.<sup>9</sup> About 5 g of oxidized starch sample was mixed with 25 mL of 0.1M HCl, and the slurry was stirred continually for 30 min with a magnetic stirrer. The slurry was then vacuum-filtered through a 100 mL medium porosity fritted glass funnel and washed with 400 mL of distilled water. The starch cake was then carefully transferred into a 600 mL beaker, and the volume was adjusted to 300 mL with distilled water.

The starch slurry was heated in a boiling water bath, with continuous stirring for 8–10 min, to ensure complete gelatinization. The hot starch dispersion was then adjusted to 300 mL with distilled water, and then standard NaOH solution was dripped into the sample solution slowly, and the titration end point was judged by potentiometer (pH 8.3). A blank test was performed with unmodified starch. The carboxyl content was calculated as follows:

$$-\text{COOH} (\%) = \left( \frac{V_1}{m_1} - \frac{V_0}{m_0} \right) \times c \times 0.045 \times 100 \quad (1)$$

where  $V_1$  and  $V_0$  are the volumes of the consumed standard NaOH solution (mL) for the titration of samples and blank,  $m_1$  and  $m_0$  are the masses of the sample and unmodified starch, and  $c$  is the concentration of NaOH (mol/L), respectively.

The hydroxylamine method described by Wing and Willett<sup>10</sup> was used for the determination of carbonyl content. 5 g of oxidized starch was dispersed in 100 mL of distilled water, and the suspension was gelatinized by heating in a boiling water bath and then cooled to 40°C. The pH was adjusted to 3.2, and 60 mL of hydroxylamine reagent was added (the hydroxylamine reagent was prepared by dissolving 25 g of reagent grade hydroxylamine hydrochloride in water

and adding 100 mL of 0.5M NaOH. The solution was then made up to 500 mL with distilled water). The sample was covered with aluminum foil and placed in a water bath at 40°C. After 4 h, the excess hydroxylamine was determined by rapid titration of the reaction mixture to pH 3.2, with 0.1M HCl. A blank test was performed with unmodified starch. Carbonyl content was calculated as follows:

$$-\text{C=O} (\%) = \frac{(V_1 - V_0) \times c \times 0.028}{m} \times 100 \quad (2)$$

where  $V_1$  and  $V_0$  are the volumes of the consumed HCl standard aqueous solution (mL) for the titration of sample and blank,  $m$  is the mass of the sample, and  $c$  is the concentration of HCl (mol/L), respectively.

The apparent viscosity of the cooked samples (6%) was measured by using coaxial rotary viscometer, with a rate of shear of 2000 or 350  $\text{s}^{-1}$  at 40°C.

The residual copper was estimated by the atomic adsorption spectrometry.

### Adsorption studies

An aqueous solution of calcium ion was prepared by dissolving calcium chloride in deionized water. Crosslinked oxidized starch (0.1–0.5 g, dry basis) was added in the calcium solution (100 mL), and the dispersion was stirred for 15 min for the starch to form a complex with the calcium ion. The starch–calcium complex was removed by filtration, and the residual calcium ion in the filtrate was measured by using Digital Ion Concentration Meter (PXD-3).

From the calcium concentration before and after the adsorption ( $C_0$  and  $C_e$ , respectively) and the dry weight of oxidized starch ( $m$ ), as well as the volume of aqueous solution ( $V$ ), the amount of adsorption ( $Q$ ) was calculated according to the following equation:

$$Q = \frac{(C_0 - C_e) \times V}{m} \quad (3)$$

All the experiments were repeated three times, and the average values are presented in this communication. Blank experiments were carried out to ensure that no adsorption was taking place on the walls of the apparatus used.

### Desorption and repeated use

Desorption of calcium ion from each of the loaded material was carried out in 0.1M HCl solution. Oxidized starch, used to remove calcium ion, was redispersed in deionized water, and the dispersion was adjusted to pH 2.0 by adding 0.1M HCl solution. After stirring for 120 min at 25°C, the dispersion was fil-

TABLE I  
Carboxyl and Carbonyl Contents, Viscosity, and Residual Copper in Oxidized Starch

Concentration of the catalyst (%)	Carboxyl content (%)	Carbonyl content (%)	Viscosity (mPa s)	Residual copper ( $\mu\text{g/g}$ of dry sample)
0	0.32	0.06	490	
0.008	1.17	0.42	230	0.06
0.012	1.37	0.73	120	1.42
0.016	1.62	0.95	54	1.82
0.020	2.10	1.42	27	2.40
0.024	1.86	1.56	80	3.20
0.032	1.47	1.78	120	5.40

tered. Then, they were immersed in 0.1M NaOH solution and stirred for 30 min at 25°C to convert carboxylic acids to carboxylic salts. The oxidized starch was filtered again. The starch residue was washed with deionized water until the filtrate was free from chlorine ion, and dried at 40°C for repeated use.

## RESULTS AND DISCUSSION

Initially, the concentration of the Cu(II) catalyst affecting oxidation of crosslinked starch was studied. The work was further extended to study the adsorption capacity of calcium ion on crosslinked oxidized starch. In the adsorption experiments, three kinds of crosslinked oxidized starch were used, of which the carboxyl contents were 1.62, 1.86, and 2.10%, respectively. The three starches were denoted as OS1, OS2, and OS3, respectively. The results obtained along with their appropriate discussion were presented later.

### Effect of the amount of catalyst on the degree of oxidation

The number of carbonyl and carboxyl groups on oxidized starch reflects the degree of oxidation. Table I showed that carboxyl and carbonyl contents dramatically rose after the addition of copper sulfate. Evidently, such high figures are due to consumption of Cu(II). During the oxidation reaction, hydroxyl groups of glucose are initially oxidized to carbonyl groups, and thereafter to carboxyl groups. The carbonyl content for oxidized starch increased from 0.06 to 1.78% (Table I), as the amount of the catalyst increased. It was found that the carboxyl content increased the catalyst concentration up to 0.02%, and then decreased by further raising the amount of the catalyst. Addition of low doses of Cu(II) to starch increased the carboxyl content. It is well known that the oxidation reaction system of starch is heterogeneous, which contains starch granules of relatively large size (about 10  $\mu\text{m}$ ), and the overall rate of reaction depends on the rate of supply of oxidant to the substrate. In this system, oxidant is dissociated in the aqueous phase, but oxidation reaction has to occur at

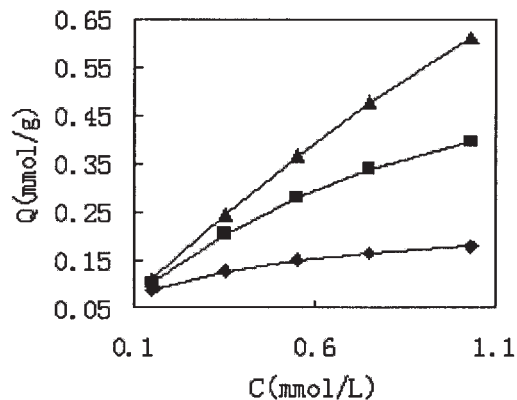
the surface of starch particles. An active site may be formed at the starch surface by starch-copper complexes between Cu(II) and two hydroxyl groups located at the starch surface, which break the hydrogen bond between starch molecules and decrease resistance of oxidation reaction. Moreover, Cu(II) facilitates the form of active oxygen atoms. In this situation, more catalysts will produce more active sites at the starch backbone and more active oxygen atoms, which increase the chance of collision of oxidant and the starch, and it will result in more number of carbonyl and carboxyl groups per starch particle. However, higher doses of Cu(II) decreased the carboxyl content. This can be reasonably explained as follows: because excess copper ions can cause fast decomposition of  $\text{H}_2\text{O}_2$ , bringing the excessive depletion of active oxygen atoms in the form of oxygen, and at the same levels of  $\text{H}_2\text{O}_2$ , the number of active oxygen atoms that will participate in oxidation reaction can decrease rapidly, and so the remaining active oxygen atoms are not enough to oxidize carbonyl groups to carboxyl groups, which result in the decline of carboxyl content and continuous increase of carbonyl content.

The residual copper on the granule surface could be recognized by the atomic absorption spectrometry (Table I). Although crosslinked oxidized starch was intensive-washed with distilled water to eliminate Cu(II), one may see a small deposit of copper ions on the granule surface. The copper content in starch was dependent of the additional amount of the copper catalyst, which increased from 0.06 to 5.4  $\mu\text{g}$  per 1.0 g of crosslinked oxidized starch, as seen in Table I. Copper ions were taken by crosslinked oxidized starch from solution, and it could reside in granules in the form of starch-copper complexes or as the copper carboxylate.<sup>11</sup> These results strongly exhibited the adsorption of copper ions on crosslinked oxidized starch. Residual amount of the catalyst left in the reaction product can seriously influence estimations of the degree of oxidation. Under such circumstances, estimation of the carboxyl groups by common methods would be obscured, which decreased the degree of oxidation.

The apparent viscosity of the samples, as measured by coaxial rotary viscometer (NDJ-7) at pH 7.0, was presented in Table I. The viscosity of oxidized starch decreased with increase of the degree of oxidation and then increased. The decrease in viscosity after oxidation could be attributed to a partial cleavage of the glycosidic linkages resulting from oxidation, and this led to a decrease in molecular weight of starch molecules. The degraded starch was not resistant to shear and could not maintain the integrity of starch granule, and thereby produced a lower viscosity. When hot pastes are being cooled, the extent of increase in viscosity is governed by reassociation tendency of the starch. This phenomenon is largely determined by the affinity of hydroxyl groups of one molecule to another. Oxidized starch, having been subjected to conformational reordering and rearrangement, is less prone to such reassociation. Introduction of carboxyl and carbonyl groups, to replace hydroxyl groups, limits formation of such binding forces, and this accounts for reduction in viscosity. The most notable differences for catalysis-oxidized starch ( $\geq 0.02\%$  copper ions for catalyst concentration) compared with the modified counterparts ( $< 0.02\%$  copper ions) were the fact that the apparent viscosity of oxidized starch slightly increased. The increase may be attributed to the decline in depolymerization of the starch chains because of the decrease of the extent of oxidation. On the other hand, the increase was the characteristic of slightly bonding Cu(II) to produce a random crosslinking (Cu(II) formed insoluble complexes), because of the improved starch integrity from chemical crosslinking. However, unlike the conventional chemically crosslinked starch, which usually exhibits a higher viscosity, oxidized starch had lower viscosity. It was further suggested that the residual copper formed complexes on the granule surface. The complexes crosslinks may have two possible structures, and form internal complexes crosslinks and external complexes crosslinks. The formation of external complexes crosslinks might be an evidence of increasing apparent viscosity of oxidation starch. The formation of internal complexes crosslinks is more energetically favored over metal-adsorption of oxidized starch.

#### Effect of initial concentration of calcium ion on adsorption capacity

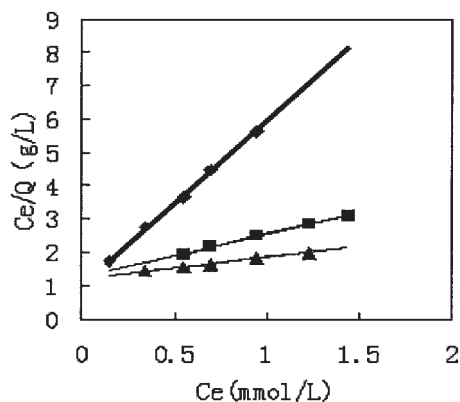
As showed in Figure 1, the adsorption capacity of calcium ion on oxidized starch was dependent on the initial calcium ion concentration in the solution. When initial concentration increased from 0.15 to 1.03 mM, the adsorbed amount of calcium ion on OS2 materials increased from 0.102 to 0.395 mmol/g, which was equivalent to 16.52 and 63.99 mmol/AGU, respec-



**Figure 1** Effect of initial concentration of calcium ion on adsorption capacities, OS1 ( $\blacklozenge$ ); OS2 ( $\blacksquare$ ); OS3 ( $\blacktriangle$ ). (Conditions: the dose of starch, 0.1%; temperature, 30°C; pH, 8; time, 15 min.)

tively. The degree of oxidation for oxidized starch (carboxyl content 1.86%, DS 0.0682) indicates that starch theoretically have 68.2 mmol of carboxyl groups per AGU. If calcium ions interact with carboxyl groups on the oxidized starch, a DS of 0.0682 will bind 34.10 mmol of calcium ion per AGU. The adsorption capacity in the experiments showed a value less than their theoretical value at low concentration. It could be interpreted that the low initial concentration, as well as the electrostatic repulsion and steric hindrance of oxidized starch, leads to an unsaturated adsorption. However, in the range of higher concentration up to 1.03 mM, the adsorption capacity of calcium ion appeared higher than their theoretical value for OS2 and OS3. Mao and Liu<sup>12</sup> investigated the adsorption of calcium ions by carboxymethyl starch (DS 0.45) and found that the adsorption capacity toward calcium ion was 0.340 mmol/g under the same conditions. The adsorption capacity in carboxymethyl starch was lower than those reported in the present experiment. This result might indicate that the adsorption between the oxidized starch and calcium ion was not only from ionic interactions but also from physical entrapments. Considering the porous structure of the starch granule, some of the free metal ions still remained inside the granule, possibly interacting electrostatically with the starch chains. Therefore, the physical entrapments of metal ions could be an additional mechanism for calcium removal by starch.

Figure 1 showed the effect of carboxyl content of oxidized starch on adsorption capacity. Higher carboxyl content resulted in higher adsorption capacity. The ionic interaction between the negative carboxyl groups in the starch and positive calcium ion is the important factor in the adsorption procedure, and so the adsorption is more effective when the carboxyl content is higher.



**Figure 2** Langmuir adsorption isotherm for OS1 (◆); OS2 (■); OS3 (▲). (Conditions: the dose of starch, 0.1%; temperature, 30°C; pH, 8; time, 15 min.)

### Adsorption isotherm

Langmuir or Freundlich adsorption models are used to characterize the adsorption of metal ions on polymer.

Langmuir:

$$\frac{C_e}{Q} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$$

where  $C_e$  presents the equilibrium concentration of calcium ion (mmol/L) in the solution,  $Q$  the adsorbed amount of calcium ion (mmol/g),  $Q_m$  the maximum amount of adsorbed calcium ion (mmol/g), and  $b$  is a constant related to the energy of adsorption (L/mmol).

Freundlich:

$$\log Q = \log K_f + \frac{1}{n} \log C_e$$

where  $K_f$  is the proportionality constant, which is indicative of bond strength, and  $n$  is a dimensionless exponent related to bond energies between metal ion and the adsorbents.

The Langmuir plot and Freundlich plot of the data of adsorbed calcium ion on crosslinked oxidized starch at 30°C were showed in Figures 2 and 3, respectively. The values of  $Q_m$ ,  $b$ ,  $n$ , and  $K_f$  were obtained from the plot. All these values along with those of the correlation coefficient for Langmuir and Freundlich isotherms for adsorption of calcium ions on oxidized starch are given in Table II.

The  $R^2$  values for Langmuir isotherms for adsorption of calcium ion on OS1, OS2, and OS3 were above 0.99, which indicates that adsorption behavior between calcium ion and crosslinked oxidized starch followed the Langmuir isotherm. Consequently, this suggests that the calcium ion forms a monolayer cov-

erage on the adsorbent surface. The correlation coefficient for Freundlich indicated a poorer fit to the experimental data when compared with the Langmuir treatment for OS1, OS2, and OS3. Higher  $Q_m$  values, giving maximum adsorption capacity, were observed for OS3 materials when compared with OS1 and OS2 materials. The highest  $b$  value was observed in the case of OS3 materials, which indicated a stronger affinity of the adsorbent toward the adsorbate, resulting in a stable adsorption product.

### Thermodynamic studies

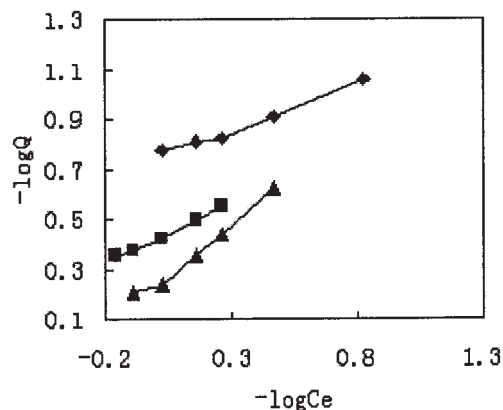
To explain the effect of temperature on the adsorption, adsorption capacity of crosslinked oxidized starch for calcium ion with varying temperatures (25–50°C) was determined. A plot of the relation of the two variables showed a downward trend (Fig. 4), which implied that the adsorption process is exothermic. To verify the conclusion,  $\log(Q/C_e)$  was plotted *versus*  $1/T$  (Fig. 5) to give apparent enthalpy change ( $\Delta H^\theta$ ) and entropy change ( $\Delta S^\theta$ ) according to the equation as follows:

$$\log \frac{Q}{C_e} = -\frac{\Delta H^\theta}{2.303RT} + \frac{\Delta S^\theta}{R}$$

The free energy change ( $\Delta G^\theta$ ) was calculated using the relationship mentioned later and was listed in Table III:

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$$

It can be observed that the adsorption capacities decrease as the temperature increases. As it is reflected from the negative value of  $\Delta H^\theta$ , the adsorption process was exothermic that is responsible for reduction in adsorption as the temperature increased.



**Figure 3** Freundlich adsorption isotherm for OS1 (◆); OS2 (■); OS3 (▲). (Conditions: the dose of starch, 0.1%; temperature, 30°C; pH, 8; time, 15 min.)

TABLE II  
Langmuir and Freundlich Parameters at 30°C

Adsorbents	R <sup>2</sup> value		Q <sub>m</sub> (mmol/g)	B (L/mmol)	n	(mmol <sup>(1-1/n)</sup> L <sup>1/n</sup> /g)
	Langmuir	Freundlich				
OS1	0.9985	0.9813	0.203	0.207	2.77	5.64
OS2	0.9948	0.9895	0.768	0.956	2.08	2.65
OS3	0.9923	0.9800	1.561	1.850	1.29	1.77

Thermodynamic considerations tell us that at constant temperature and pressure, free enthalpy change ( $\Delta G^\theta$ ) during the spontaneous adsorption process always has a negative sign. However, from a more random stage (in solution) to a more orderly stage (on the surface of the adsorbent) for calcium ions, the entropy change of adsorption ( $\Delta S^\theta$ ) also has a negative sign. As known from thermodynamics, the negative values of  $\Delta G^\theta$  and  $\Delta S^\theta$  require a negative adsorption enthalpy ( $\Delta H^\theta$ ), which eventually implies that the adsorption phenomenon is exothermic. In Table III, negative  $\Delta G^\theta$  values showed the spontaneity of the adsorption process.  $\Delta G^\theta$  was more negative with decreasing temperature, which suggested that lower temperature makes the adsorption easier.

The  $\Delta H^\theta$  value can be used as a measure of the interaction force between the adsorbate and the adsorbent. In the adsorption of metal ions, the net enthalpy and entropy changes of the adsorption are the result of different processes. The dehydration form of the metal ion with water generally involves a positive enthalpy variation ( $\Delta H^\theta > 0$ ) as a result of the breakage of ion-water bonds and a positive entropy variation ( $\Delta S^\theta > 0$ ) because of an increase of disorder in the system by the release of bonded water. However, complexes formed with two of the carboxyl groups result in a negative enthalpy change ( $\Delta H^\theta < 0$ ) as a consequence of replacing relatively weak hydrogen bonds with

stronger metal bonds, and as well as in a negative entropy change ( $\Delta S^\theta < 0$ ) because of the increase of order caused by the new bonds. The  $\Delta H^\theta$  and  $\Delta S^\theta$  values found in this experiment showed that the newly formed bond between calcium ions and oxidized starch is stronger than the bond between the hydrogen ion and the oxidized starch. Also, the calcium ion binding mechanism can be explained by the interaction between calcium ion and carboxyl groups derived from Coulombic force, and the adsorption reaction took place with the replacement of protons by the calcium ion. These findings agreed with the experimental results.

The calcium ion-adsorbed materials when placed in pure water and in NaCl solution did not release the adsorbed calcium ions, whereas when the calcium ion-adsorbed oxidized starch is treated with 0.1M HCl acid solution, the calcium ions were released (in highly acidic solutions, protons are replaced by adsorbed calcium ions), that is, the electrostatic interaction between the calcium ion and the carboxyl groups vanished without any destruction of adsorbent.

Adsorption on solid is classified into physical adsorption and chemical adsorption. Physical adsorption is nonspecific, and the enthalpy changes for chemical adsorption are usually substantially greater in magnitude than those for physical adsorption. As is seen from Table III, enthalpy changes ( $\Delta H^\theta$ ) for OS1, OS2, and OS3 are  $-12.25$ ,  $-6.65$  and  $-9.69$  kJ/mol, respec-

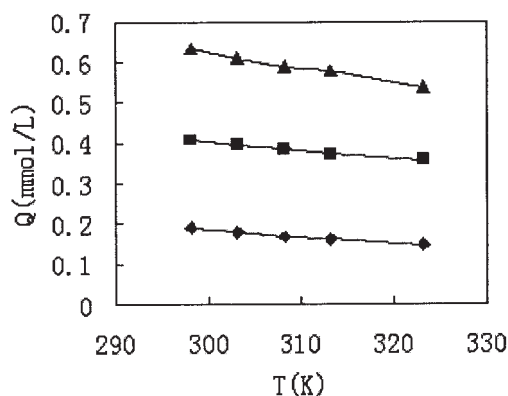


Figure 4 Effect of temperature on adsorption capacities for OS1 ( $\blacklozenge$ ); OS2 ( $\blacksquare$ ); OS3 ( $\blacktriangle$ ). (Conditions: calcium ion concentration, 1.03 mM; the dose of starch, 0.1%; pH, 8; time, 15 min.)

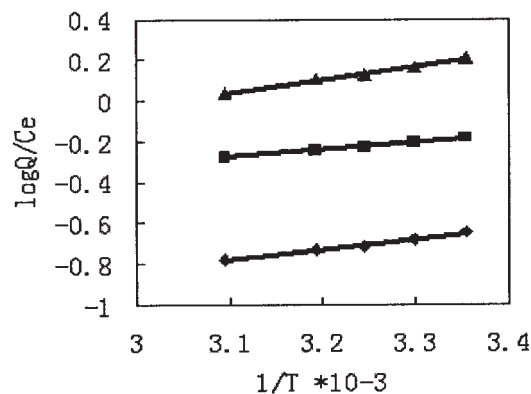


Figure 5  $\log(Q/C_e) \sim 1/T \times 10^3$  for OS1 ( $\blacklozenge$ ), OS2 ( $\blacksquare$ ); OS3 ( $\blacktriangle$ ). (Conditions: calcium ion concentration, 1.03 mM; the dose of starch, 0.1%; pH, 8; time, 15 min.)

TABLE III  
Thermodynamic Parameters for OS1, OS2, and OS3

Sample	Temperature (°C)	$\Delta G^\theta$ (kJ/mol)	$\Delta H^\theta$ (kJ/mol)	$\Delta S^\theta$ (J/mol/K)	Correlation coefficient
OS1	25	-7.43	-12.25	-16.15	0.9896
	30	-7.35			
	35	-7.27			
	40	-7.19			
	50	-7.03			
OS2	25	-3.30	-6.65	-11.24	0.9980
	30	-3.24			
	35	-3.19			
	40	-3.13			
	50	-3.02			
OS3	25	-3.87	-9.69	-19.52	0.9919
	30	-3.77			
	35	-3.67			
	40	-3.58			
	50	-3.38			

tively, which are slightly higher than those from the lower limit of corresponding physical adsorption, but lower than those corresponding chemical adsorption. This would indicate that physical adsorption process is involved in the calcium sorption on the oxidized starch.

### Effect of pH

Owing to the protonation and deprotonation of carboxyl groups on the surface of the oxidized starch, its adsorption behavior for calcium ion was influenced by the pH values, as shown in Figure 6. The tests were limited to the pH range of 2.0–10.0, because of the precipitation of  $\text{Ca}(\text{OH})_2$  at pH 12.6 ( $\text{p}K_{\text{sp}} = 5.89$ ). For calcium ion, the adsorption capacity increased with

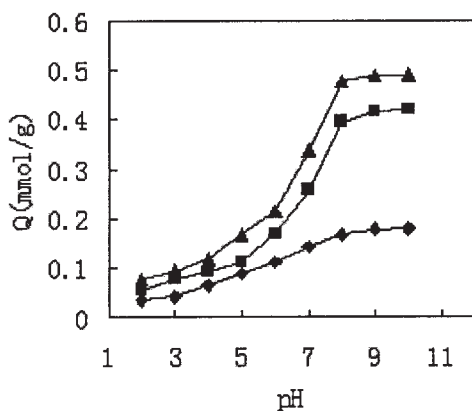


Figure 6 Effect of pH on adsorption capacity for OS1 (◆); OS2 (■); OS3 (▲). (Conditions: calcium ion concentration, 1.03 mM; the dose of starch, 0.1%; temperature, 30°C; pH, 8; time, 15 min.)

increasing pH, reaching a plateau value at around pH 9.0. It was found from Figure 6 that, at strongly acidic pH, oxidized starch has lower adsorption capacity. This can be explained by the fact that in this case most of the carboxyl groups are protonated. Then, cationic repulsion can occur between calcium ion species and protonated starch chains.

As the pH value of the solution was  $\sim 2.0$ , the carboxyl groups existed in the free acid form. The adsorption surface will be highly protonated, and the proton concentration in the medium increased. The protonated carboxyl groups cannot effectively interact with the metal ions, because of the loss of negative charge. Thus, the increased proton concentration inhibited the metal–chelate property of the adsorbent. However, when pH value of the solution was 5.0 or higher, the carboxyl groups theoretically existed as sodium salts. For effective ion exchange activity, the ionization of carboxyl groups was needed, and this explained why at pH 2.0 the oxidized starch did not show good calcium-binding activity.

The pH effect on the calcium removal efficiency revealed that the carboxyl groups behaved as ion exchangers for calcium ions in the solution. The results demonstrated that carboxyl groups played an important role in forming the chelates with calcium ions, and the ionized carboxyl groups were not as effective as protonated carboxyl groups in maintaining the starch integrity, possibly due to their negative charge repulsion.

### Effect of the dose of crosslinked oxidized starch

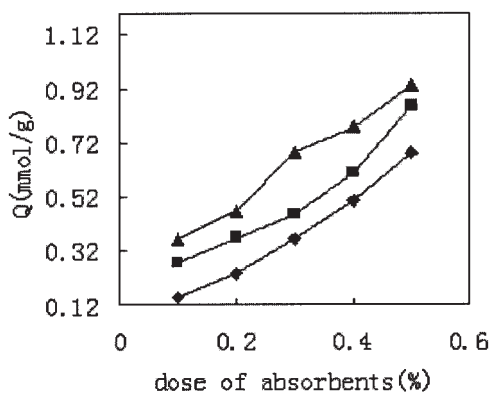
In Figure 7, the effect of varying the dose of oxidized starch on the adsorption capacity was shown, and it

was seen that the adsorption capacity of calcium ion increased as the dose of crosslinked oxidized starch increased. It could be interpreted that the active sites increase with increasing dose. For OS3, calcium ions in the solution were almost completely removed with 0.5% starch addition, based on the solution volume. The degree of oxidation for OS2 (DS 0.0682) at 0.5% addition indicates that starch theoretically will adsorb 0.105 mmol calcium ions, while the experimental adsorption capacity (0.428 mmol) showed that the number of removed calcium ion was more than their theoretical value at higher dose of starch. It was assumed that some of the calcium ion might be physically entrapped inside the starch granules. Therefore, using a small quantity of a high DS starch or a large quantity of a low DS starch might be equally applicable.

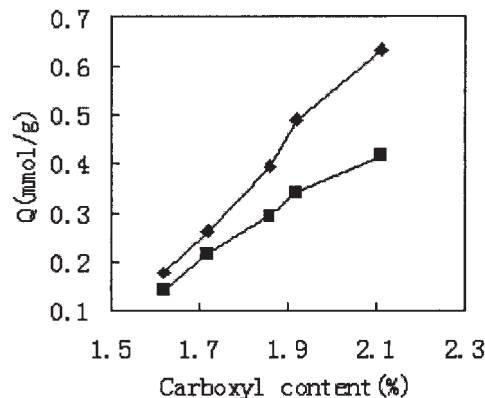
### Repeated use of recovery starch

The starch, which had been used for calcium removal, was recovered by adjusting the pH to 2.0 by acid addition (0.1M HCl), and subsequent waiting of the released calcium ion. The calcium-free starch was then reactivated by adjusting the pH to a value greater than 6.0 for ionization of carboxyl groups.

The recovered starch retained a relatively good portion of the original activity for calcium removal (Fig. 8). The removal efficiency of the recovered starch appeared slightly less than that of fresh starch. In the case of calcium removal, the recovered starch for OS2 reduced the calcium ion content to 0.707 mM. This result was equivalent to 74.18% recovery of the removal activity of fresh starch. The reduced activity of the recovered starch possibly resulted from activity sites in crosslinked oxidized starch loss during the starch recovery process.



**Figure 7** Effect of the dose of adsorbents on the removal of calcium ions, OS1 (◆); OS2 (■); OS3 (▲). (Conditions: calcium ion concentration, 0.55 mM; temperature, 30°C; pH, 8; time, 15 min.)



**Figure 8** Comparison of adsorption capacity of calcium ion on fresh starch (◆) and recovered starch (■). (Conditions: calcium ion concentration, 1.03 mM; the dose of starch, 0.1%; temperature, 30°C; pH, 8; time, 15 min.)

### CONCLUSIONS

By crosslinking and oxidation, cornstarch could become an active and relatively insoluble calcium sequestering agent. The adsorption capacity of crosslinked oxidized starch increased as the carboxyl content increased. The adsorption capacity was dependent on initial concentration, the dose of adsorbents, pH, and the adsorption temperature. The adsorption followed the Langmuir adsorption isotherm. The maximum adsorption capacity of OS1, OS2, and OS3 were 0.203, 0.768, and 1.561 mmol/g, respectively.

Because the adsorption process was exothermic, lower temperature facilitated the adsorption. Enthalpy changes ( $\Delta H^\theta$ ) for the three adsorptions under investigation were  $-12.25$ ,  $-6.65$  and  $-9.69$  kJ/mol, respectively. Moreover, the negative value of  $\Delta G^\theta$  indicated an increase in the feasibility of adsorption at lower temperature.

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