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Removal of heavy metal ions from water by cross-linked carboxymethyl corn starch

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Abstract

Corn starch after cross-linking with $POCl_3$ (1%, v/w, starch db) was carboxymethylated with sodium chloroacetate (5–20%, v/w, starch db) to examine the metal removal activity of the starch from water. The cross-linked carboxymethyl starch [degree of substitution (DS) 0.02–0.08] was dispersed (0.5–3.0%) in aqueous solutions of divalent metal ions (Cu, Pb, Cd and Hg, ∽200 ppm), and the starch–metal complex was filtered. Removal efficiency of the metal ions from their aqueous solutions increased proportionally with the DS of the carboxymethyl group and the starch content in the solution. Ionization of the carboxymethyl groups in starch was necessary for the effective metal removal. When the starch pH was adjusted below 4.0 after carboxymethylation, the starch was no longer an effective metal binder. The metal ions interacted with starch, 10 min after the starch was added. Lead, cadmium, and mercury ions in water were almost completely removed when 1% starch (DS 0.081, pH 6.0) was used. Under the same conditions, copper concentration was reduced from 203 to 71 ppm. Starch could be recovered by washing the metal ions from the complex with weak acid (pH 2.0) although the metal-binding activity of the starch was slightly reduced by this process.

Keywords: Starch–metal complex ; Carboxymethyl groups; Metal removal; Corn starch

1. Introduction

Various removal methods of heavy metals from waste water have been developed (Wing, 1974; Wing, Rayford & Doane, 1978; Cavaseno, 1980). Chemical precipitation is one of the most common methods for removing the heavy metal ions from waste water. In this method, lime (CaO), hydrated lime ($Ca(OH)_2$), caustic soda (50% NaOH), soda ash (Na_2CO_3), and sodium sulfide (Na_2S) are commonly used as precipitants (Lanouette and Paulson, 1976). Activated carbon can also remove hexavalent chromium, mercury, and various metals complexed with organic materials such as dyes or colorants.

Reverse osmosis is one of the methods frequently used in plating industries to recover or reuse the metals, but this is basically a process for concentrating ions, and is effective only when the concentration is sufficiently high. Cementation is another process to remove metals, by which metal ions form deposits with more readily oxidized metals (Manahan, 1990).

One of the effective methods for heavy metal removal from waste water is ion exchange by specific resins. It is often used when the removal of heavy metals by other methods is not successful, or when the recovery of the metals is necessary. However, the recovery cost of the resins is quite high and the activity of the recovered resin is generally not satisfactory.

In many cases, these removal or recovery methods for heavy metal ions are not sufficiently effective alone, and thus combinations of two or more methods are frequently required (Wing, 1974).

A starch derivative has been developed as an effective metal scavenger at USDA in Peoria, Illinois, USA (Wing, 1974; Wing and Doane, 1976). The starch was substituted with xanthate esters, which can form chelates with various heavy metal ions in the aqueous medium. As xanthation is a relatively simple process and starch itself is a cheap biopolymer, the derivative can be produced at an economical cost. However, xanthate degrades slowly and generates a sulfide off-flavor during the storage and application (Wing and Doane, 1976).

In this study, cornstarch was cross-linked and carboxymethylated at a relatively low degree of substitution (DS), and its removal capacity for various divalent metal ions from their aqueous solutions was investigated.

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Table 1
DS and reaction yield for carboxymethylation[a] of cross-linked[b] corn starch with various amounts of sodium chloroacetate

$ClCH_2COONa$ content (%)[c]	DS	Reaction yield (%)
5	0.022	16
10	0.045	16
15	0.068	17
20	0.081	15

[a] 2 h at 45°C.
[b] 1 h at room temperature with 1.0% $POCl_3$.
[c] w/w, starch db.

2. Materials and methods

2.1. Materials

Normal corn starch (∽ 25% amylose) was provided by Samyang Genex (Seoul, Korea). Phosphorus oxychloride ($POCl_3$) and sodium chloroacetate ($ClCH_2COONa$) were purchased from Fluka Chemie AG (Buchs, Switzerland) and Kanto Chemical Co., Inc. (Tokyo, Japan), respectively. Standard solutions (1000 ppm) of sodium (NaCl), lead ($Pb(NO_3)_2$), cadmium ($CdSO_4$), and mercury ions ($HgCl_2$) used for the analysis with an inductively coupled plasma-atomic emission spectrophotometer (ICP-AES) were purchased from Showa Chemical Inc. (Tokyo, Japan).

2.2. Preparation of cross-linked carboxymethyl starches

Corn starch (100 g, db) was dispersed in distilled water (300 ml) and the slurry was adjusted to pH 11.0 with 1 N NaOH solution. The cross-linking agent, $POCl_3$ (1 ml) was added dropwise over 10 min, while maintaining the pH at 11.0 with the NaOH solution. The starch dispersion was stirred for 1 h at room temperature, and then filtered through Whatman No. 41 filter paper (Felton and Schopmeyer, 1940; Wurzburg, 1958, 1986; Chiu and Rutenberg, 1980).

The filtered starch cake was dispersed in absolute ethanol (300 ml), and a 50% NaOH solution (20 g) was slowly added. Sodium chloroacetate (5, 10, 15, and 20% v/w, based on starch db) was added in the starch–ethanol dispersion, and the mixture was stirred for 2 h at 45°C in a sealed container (Filbert and Woodbury, 1950; Hjermstad, Kesler & Rapids, 1956; Caldwell and Martin, 1957; Gotlieb, 1973). After the reaction, the starch slurry was filtered, washed three times with distilled water (3 × 400 ml), and then dried at 40°C overnight in a convection oven. To examine the pH effect, starch was adjusted to pH 2–8 with 1 N HCl before drying.

2.3. Degree of substitution of carboxymethyl group

Carboxymethylated starch (3 g, db) dispersed in deionized water (20 ml) was adjusted to pH 2.0 with 1 N HCl, and the dispersion was stirred for 10 min to convert the ionized carboxyl groups to free acid form. The starch was filtered (Whatman No. 41 filter article), washed three times with deionized water (3 × 40 ml), and gelatinized in water (40 ml) by boiling for 30 min in a water bath. Carboxymethyl groups were titrated with standardized 0.1 N NaOH solution (Mitchell and Wijinberg, 1995). The cross-linked starch prior to carboxymethylation was used as a blank. DS was calculated by following the equation given by Rutenberg and Solarek (1984), and the reaction yield was calculated as the percent molar ratio of substituted carboxymethyl groups to added chloroacetate.

2.4. Removal of metal ions from water

An aqueous solution of copper ions (Cu 203 ppm) was prepared by dissolving cupric sulfate ($CuSO_4 \cdot 5H_2O$, 0.8 g) in distilled water (1 l). Cross-linked carboxymethyl starch (0.5–3.0 g, db) was added in the copper solution (100 ml), and the dispersion was stirred for 10–30 min for the starch to form a complex with the metal ions. The starch–metal complex was removed by filtration (Whatman No. 41), and the filtrate was used for the residual metal analysis.

To compare the removal effect of other metal ions, Pb (203 ppm), Hg (208 ppm), and Cd (194 ppm) solutions were prepared by dissolving lead acetate ($Pb(CH_3CO_2)_2 \cdot 3H_2O$, 0.19 g), mercuric acetate ($Hg(CH_3CO_2)_2$, 0.33 g) and cadmium sulfate ($CdSO_4$, 0.25 g) in distilled water (1 l), respectively.

2.5. Analysis of metal ions

After the metal solution was treated with the cross-linked carboxymethyl starch, residual metal ion content in the filtrate was measured either by a colorimetric method (Helrich, 1990) for Cu, or by using an ICP-AES (Plasma 40, Perkin Elmer, Norwalk, CT, USA) for Na, Pb, Cd, and Hg ions.

2.6. Recovery of starch

Cross-linked carboxymethyl starch (pH 8.0, 1 g) used to remove the copper ions was redispersed in deionized water (40 ml), and the dispersion was adjusted to pH 2.0 by adding 1 N HNO_3 solution. After stirring for 5 min, the dispersion was filtered. The starch residue was washed with water (2 × 40 ml), readjusted to pH 8.0 with 1 N NaOH, and dried at 40°C overnight. Degree of Cu removal with the recovered starch was measured, and the recovery yield (percent ratio of the removed metal content by recovered starch to that by fresh starch) was calculated.

2.7. Starch loss

The amount of soluble starch in metal solution while dispersing the starch for metal removal was measured with the filtrate by using phenol–sulfuric acid method (Dubois, Gilles, Hamilton, Rebers & Smith, 1956).

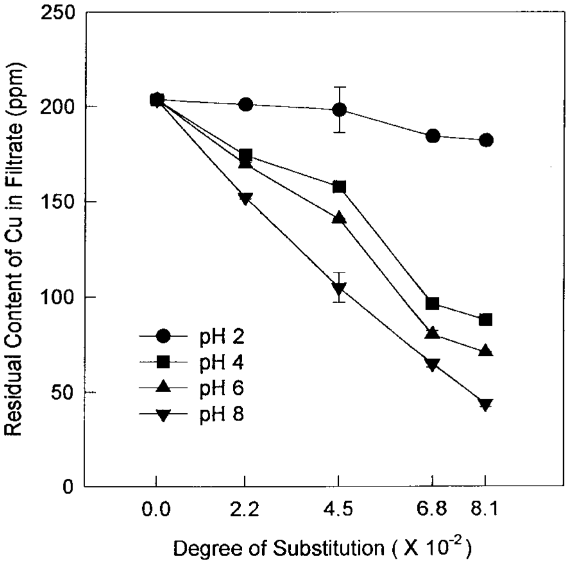

Fig. 1. Removal of copper ions from an aqueous cupric sulfate solution (Cu^{2+} 203 ppm) with cross-linked carboxymethyl starches (1%, w/v, based on the solution) of different DS and pH values.

3. Results and discussion

3.1. Degree of substitution and reaction yields

The DS of carboxymethyl groups in starch increased from 0.022 to 0.081 in proportion to the amount of sodium chloroacetate in the reaction mixture (5–20% based on starch) (Table 1). The corresponding reaction yields were relatively low (15–17%), but did not vary significantly with the reagent content. It is assumed that the reaction yield can be raised by increasing reaction temperature or time.

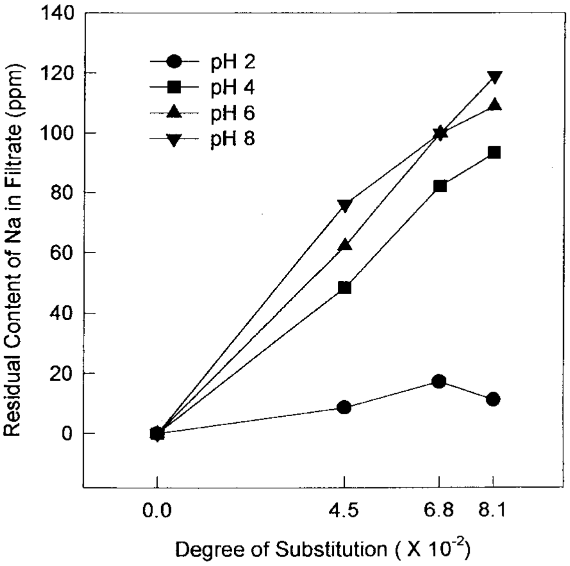

Fig. 2. Residual content of sodium ions in copper solution, released from cross-linked carboxymethyl starches during the removal of copper ions.

3.2. Effects of degree of substitution and pH on metal removal

For Cu removal, residual metal concentration in the solution decreased when DS of the carboxymethyl groups in starch increased (Fig. 1). This indicates that the metal ions in the solution interact with the carboxymethyl groups of starch. Beside the DS, starch pH, which was adjusted after carboxymethylation, positively affected the removal efficiency of copper ions from the solution. Carboxymethylated starch at DS 0.081 which was adjusted to pH 8 reduced the residual copper concentration from 203 to 44 ppm with 1% addition of the starch in the copper solution. Based on this concentration decrease in the solution, the bound Cu ions were calculated to be approximately 80% of the initial Cu amount.

When the starch pH was 6 or 4, the residual Cu content in the filtrate decreased to 71 or 80 ppm, respectively. At pH 2, however, the starch was no longer effective in removing Cu from the solution (Fig. 1). This pH effect on the metal removal efficiency revealed that the carboxymethyl groups behaved as ion exchangers for Cu ions in the solution. This was also proved by the simultaneous increase in sodium content in the solution (Fig. 2).

The cupric sulfate solution tested had weak acidity (pH $\backsim$ 5.0). When 1% (w/v) of pH 2 starch was added to the solution, the pH of the solution became 3.3. With the starches of pH 4, 6, and 8, the pH values of the solution became 4.5, 5.0, and 5.4, respectively. As the pK_a value of the carboxymethyl group was approximately 4.3 (Anonymous, 1996), the carboxymethyl groups existed in the free acid form when starch at pH 2 was added. However, when starch pH was 4 or higher, the carboxymethyl groups theoretically existed as sodium salts. For effective ion exchange activity, the ionization of the carboxymethyl groups was needed, and this explained why at pH 2 the starch did not show Cu binding activity.

When copper content was decreased from 203 to 44 ppm, with 1% starch of DS 0.081 and pH 8, the simultaneous release of sodium into the filtrate increased from 0 to 122 ppm (Fig. 2). These changes in both ion contents were not significantly different (159 vs 122 ppm). From the calculations with the atomic mass of Cu and Na (40 vs 23, respectively), the molar ratio corresponding to these changes was 4.0:5.3. Therefore, the exchanges between both cations did not occur in the theoretical ratio of 1:2 for di- and monovalent ions. Considering the porous structure of the starch granule, some of the free metal ions still remained inside the granule, possibly intracting electrostatically with the starch chains. Therefore the physical entrapments of metal ions could be an additional mechanism for metal removal by starch.

3.3. Starch dissolution during metal removal

Starch solubilization into the metal solution during

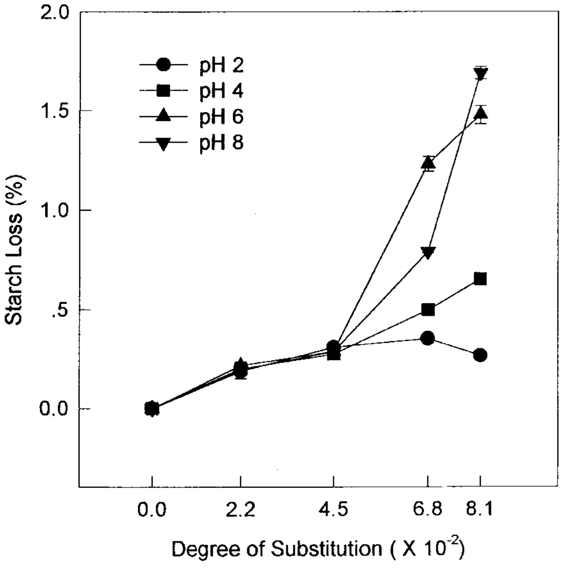

Fig. 3. Loss of cross-linked carboxymethyl starches of different DS and pH values into the copper solution during the removal of copper ions.

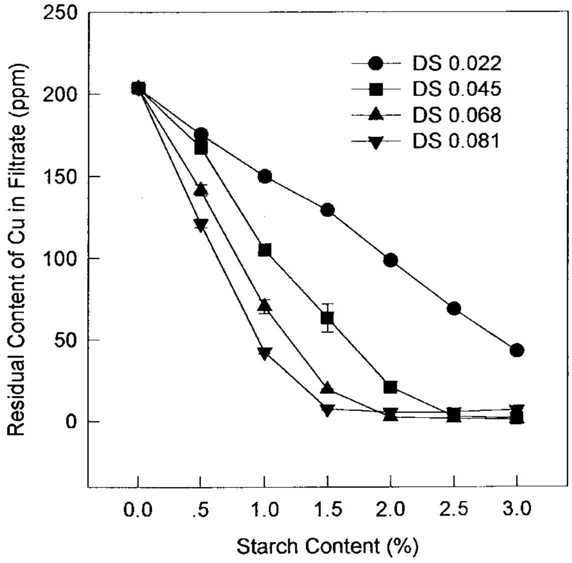

Fig. 5. Effect of starch content on the removal of copper ions with cross-linked carboxymethyl starches (pH 8.0) of different DS values.

starch–metal chelate formation is not desirable because this causes an increase in the organic content of the water. Loss of starch by dissolution during the removal of copper ions increased up to 1.69% as the DS increased to 0.081 (Fig. 3). Carboxymethylation makes starch more hydrophilic, and thus starch of high DS of carboxymethyl group is more water-soluble. By cross-linking the starch prior to carboxymethylation, water solubility was reduced, and the starch–metal complex could be readily removed by filtration. At a DS below 0.045, however, no significant starch loss was observed, and starch pH did not affect the starch solubility (Fig. 3). When DS became higher, starch became more soluble, and this trend was further facilitated by raising the pH. As the ionization of carboxymethyl groups was determined by pH, the solubility of the starch varies with the starch pH. Comparing starch losses at pH 4 and 6, 0.6% of the added starch (DS 0.081) was solubilized at pH 4, which was equivalent to approximately half of the loss occurred at pH 6 (Fig. 3). At pH 8.0, starch loss reached the maximum (1.69%). Starch can be more insoluble with a higher degree of cross-linking. Alternatively, more water-resistant polysaccharides compared to starch can be used as raw materials for carboxymethylation.

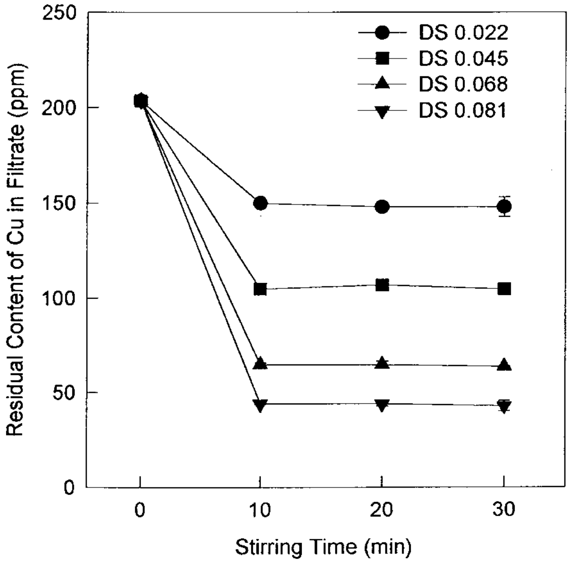

Fig. 4. Effect of stirring time on the removal of copper ions with cross-linked carboxymethyl starches (pH 8.0) of different DS values.

3.4. *Effect of mixing time on metal removal*

When a cross-linked carboxymethyl starch (DS 0.081, pH 8) was dispersed in cupric sulfate solution (203 ppm Cu), the Cu removal was completed in 10 min (Fig. 4). This result indicates that the copper ions rapidly form chelates with the carboxymethyl groups of starch. The rapid interaction of metal ions with the starch will be beneficial for practical use. For example, the starch could be used as a filtering resin for a short period of treatment of waste water during filtration. Other metal ions showed similar reactivity with the starch (data not shown).

3.5. *Effect of starch amount*

When the starch addition into the copper solution (203 ppm Cu) was increased to 3.0%, the residual Cu content in the filtrate decreased gradually (Fig. 5). At DS 0.081, the copper ions in the solution were almost completely removed with 1.5% starch addition based on the solution volume. If the carboxymethyl groups in the starch (DS 0.081) at 1.5% addition interacted with all the Cu ions in the solution (203 ppm), the molar ratio between the carboxymethyl groups and Cu ions for the interaction became approximately 3:2 by calculation. This value showed that

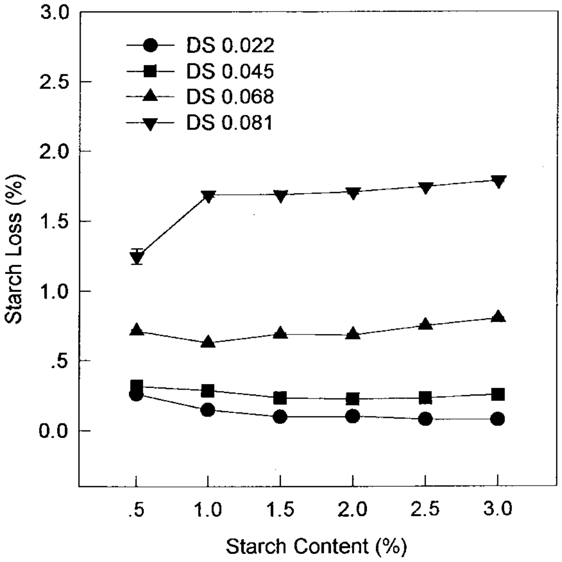

Fig. 6. Effect of starch content on starch loss during the removal of copper ions with cross-linked carboxymethyl starches (pH 8.0) of different DS values.

the number of removed Cu cations per carboxyl group was more than the stoichiometric value of 0.5. It was assumed that some of the Cu ions might be physically entrapped inside the starch granules and these ions were not measured in the filtrate.

The starch of the least DS (0.022) continuously reduced the copper content as the starch addition increased up to 3%. Therefore, using a small quantity of a high DS starch or a large quantity of a low DS starch might be equally applicable. The use of more than 1% starch to remove 200 ppm of Cu is significantly higher than the concentration of metal-binding biopolymers or starch xanthate normally used (Wing, 1974). To be of practical value as a metal scavenger, the DS for carboxymethylation should be significantly higher than the values tested in these experiments.

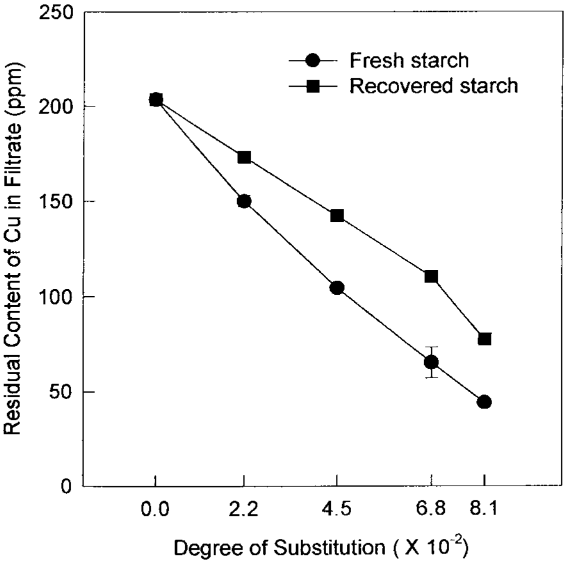

Fig. 7. Comparison of fresh and recovered cross-linked carboxymethyl starches (pH 8.0) on copper removal.

Starch loss appeared relatively constant regardless of the starch content in metal solution (Fig. 6). Starch loss at DS 0.081 was approximately twice than that at DS 0.068 when 1% of starch was used, whereas the metal removal efficiencies at both the DS values were not significantly different (Fig. 5). In cases where starch loss is required to be reduced, starch at DS 0.068 would be more desirable than DS 0.081.

3.6. Recovery of starch

The starch which had been used for copper removal was recovered by adjusting the pH to 2.0 by acid addition (1 N HNO_3), and subsequent waiting of the released Cu ions. The Cu-free starch was then reactivated by adjusting the pH to a value greater than 6 for ionization of carboxymethyl groups.

The removal efficiency of the recovered starch (pH 8.0) appeared slightly less than that of fresh starch (Fig. 7). The recovered starch retained a relatively good portion of the original activity for metal removal. In the case of Cu removal, the recovered starch of DS 0.081 (pH 8) reduced the Cu ion content to 77 ppm. This result was equivalent to 79% recovery of the removal activity of fresh starch. The reduced activity of the recovered starch possibly resulted from starch loss during the starch recovery process.

3.7. Removal of lead and other heavy metal ions

For lead removal from a lead acetate solution (437 ppm Pb), the DS of the carboxymethyl group showed a positive correlation with the removal efficiency, as was the case of Cu (Fig. 8). Starch loss during lead removal increased significantly when the DS was above 0.045 (Fig. 9). The starch loss data almost coincided with those measured for Cu removal (Fig. 2).

Comparing pH values of starch, the starch adjusted to pH 6 showed slightly less metal removal activity than starch at pH 8 (Fig. 8). However, at DS 0.068 and pH 6, starch (1%) could almost completely remove the lead ions (437 ppm). During the removal process, approximately 0.9% of the starch was lost by solubilization (Fig. 9). This result showed that the degree of Pb removal was more than twice of that of copper ions. This difference could be explained by the significantly higher molecular weight of lead ion compared to the copper ion (207.2 vs 63.5). The molar concentrations of lead (437 ppm) and copper (203 ppm) in the solutions were 2.11×10^{-3} and 3.20×10^{-3}, respectively. Therefore, the reduced concentration of both the metal ions were similar in molar concentration ($\backsim$ 2 mmol/l). This result may indicate that the carboxymethyl groups in starch display relatively equal binding affinity to both divalent metal ions.

Table 2 shows the removal of four divalent ions at a similar concentration ($\backsim$ 200 ppm) by four starches different in DS and pH. By using 1% (w/v) of the starch, cadmium and mercury ions (194 and 208 ppm, respectively) could be

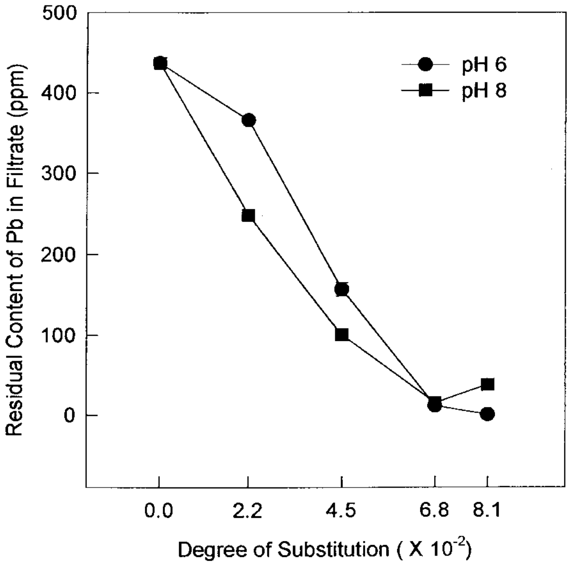

Fig. 8. Removal of lead ions from an aqueous lead acetate solution (Pb^{2+} 437 ppm) with cross-linked carboxymethyl starches (1%, w/v, based on the solution) of different DS and pH values.

almost completely removed (over 99%), in the tested range of DS and pH. In some cases, the starch at pH 8 showed slightly lower efficiencies than that at pH 6. This possibly resulted from the higher solubility of the starch at pH 8.0.

4. Conclusions

By cross-linking and carboxymethylation, corn starch could become an active and relatively insoluble metal scavenger for toxic divalent cations such as Cu, Pb, Cd, and Hg ions contaminated in water. At a low DS (0.08) of carboxymethyl groups, several hundred ppm of these metal ions could be effectively removed from water by dispersing 1% of the starch for several minutes and subsequent filtering the starch–metal complex. The starch could be regenerated by a weak acidic washing. For effective metal removal, the metal solution should not be too acidic. By raising the levels of carboxymethylation and cross-linking, metal scavenging activity of the starch could be increased up to the level required for industrial applications.

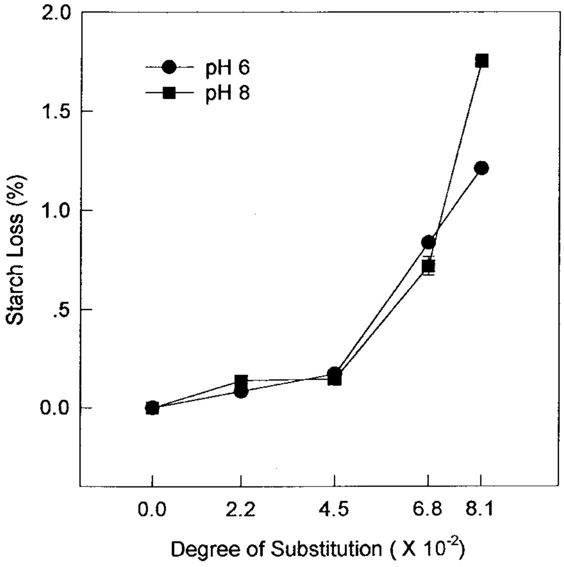

Fig. 9. Loss of cross-linked carboxymethyl starches of different DS and pH values into the lead solution during the removal of lead ions.

Table 2
Changes in various metal concentrations (ppm) in water by treatment with cross-linked carboxymethyl corn starches[a]

Starch		Copper		Lead		Cadmium		Mercury	
DS[b]	pH[c]	Initial	Final	Initial	Final	Initial	Final	Initial	Final
0.068	6	203	76	203	0.7	194	0.7	208	0.3
0.068	8	203	65	203	0.5	194	0.3	208	0.4
0.081	6	203	71	203	1.2	194	0.7	208	0.2
0.081	8	203	44	203	11.8	194	1.9	208	1.1

[a] Starch was dispersed (1%, w/v) in metal solution for 10 min at room temperature and starch–metal comples was filtered.

[b] DS of carboxymethyl group.

[c] Starch pH was adjusted after carboxymethylation.

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