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Adsorption of divalent metal ions by succinylated and oxidized corn starches

D.-K. Kweon[a], J.-K. Choi[b], E.-K. Kim[c], S.-T. Lim[c,*]

[a]Department of Chemical Engineering, Cambridge University, Cambridge CB2 3RA, UK
[b]Samyang Genex Corporation, Inchon 404-250, South Korea
[c]Graduate School of Biotechnology, Korea University, Seoul 136-701, South Korea

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Abstract

Corn starch was succinylated (degree of substitution, DS 0.03–0.07) with succinic anhydride in an aqueous alkaline medium (pH 10), or oxidized (DS 0.13–0.29) with sodium hypochlorite in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and sodium bromide, and the adsorption properties of the starches for Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} in their aqueous salt solutions were investigated under various conditions. Regardless of the metal type, the adsorption capacity of both ionic starches reached a state of equilibrium within 5–10 min for starch dispersion in metal solutions. The succinylated starch was most effective in binding Pb^{2+}, whereas the oxidized starch was effective for Cu^{2+} among the tested metal ions. Cd^{2+} was least effective in binding either to the succinylated or to the oxidized starch. However, the oxidized starch was partially soluble in aqueous solutions, and thus the starch dissolution resulted in reduced metal-adsorption efficiency. The metal-adsorption of both ionic starches followed the Langmuir adsorption isotherm. The maximum adsorption capacity (Q) and Langmuir constant (b) for a succinylated starch (DS 0.07) for Pb^{2+} were 0.534 mmol g^{-1} and 2.276×10^{-3} ppm^{-1}, respectively. These values were higher than those of Cu^{2+}, Zn^{2+}, and Cd^{2+}. The Q and b values for an oxidized starch (DS 0.29) for Cu^{2+} were significantly higher (1.245 mmol g^{-1} and 14.98×10^{-3} ppm^{-1}, respectively) than those of Pb^{2+}, Zn^{2+}, and Cd^{2+}. Therefore, among the tested ions, Pb^{2+} was adsorbed most effectively by the succinylated starch, and Cu^{2+} by the oxidized starch. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Succinylated starch; Oxidized starch; Metal-adsorption; Langumir constant

1. Introduction

Environmental pollution caused by toxic heavy metals in industrial effluents is one of the most pressing problems in many densely populated cities worldwide. Under the current regulations in most countries, industries are obligated to treat wastewater and to reduce toxic metal concentration to less than certain designated values (Shany & Reedijk, 1984).

The use of synthetic resins for chelating toxic metal ions in wastewater is a possible approach for preventing environmental pollution and recycling metals. These resins are mostly composed of petroleum-based synthetic polymers (Egawas, Nonaka, Abe & Nakayama, 1992; Kern & Schulz, 1957; Kise & Sato, 1985; Lee & Hong, 1995; Lezzi & Cobianco, 1994; Liu, Chang & Hu, 1990; Liu, Chen, Lee, Hwang, Jou & Hsu, 1992; Saito, Uezu, Hori, Furusaki, Suge & Okamoto, 1988). In general, after the adsorption process for metal ions, the chelating resins are discarded in landfills or treated by incineration. However, these processes often result in secondary environmental pollution by contaminating the soil or air. In addition, these synthetic polymers are usually non-renewable and non-biodegradable.

Starch, an agricultural biopolymer, is more attractive for industrial use because of its renewability, biodegradability, and low unit cost. However, starch by itself could not be satisfactorily applied in chelating or adsorbing heavy metal ions to replace the synthetic chelate resins, because it has inherently no chelating or metal-interaction capacity. Hence, several approaches have been made to utilize starch as a metal scavenger, by introducing the substituents of chelating activity, such as carboxylate, xanthate, acrylamide, and tertiary amine phosphate groups (Chan, 1995; Khali & Frarag, 1998; Khali, Frarag & Fattah, 1996; Khali, Frarag & Hebeish, 1991; Kim & Lim, 1999; Wing, Doanc & Russel, 1975).

Among the various starch derivatives, starch substituted with a carboxyl group such as succinic or maleic acid has been used as a thickening or stabilizing agent in soup, snack,

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* Corresponding author. Tel.: +82-2-3290-3435; fax: +82-2-927-5201.
E-mail address: limst@mail.korea.ac.kr (S.-T. Lim).

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and frozen food products (Trubiano, 1987). Oxidized starch is widely used in papermaking, where its specific properties are used to close the pores of paper to lay fuzz on the surface, to increase the tensile fold and bursting strength of the paper (Kirby, 1987). However, no research has been undertaken to investigate the metal-binding properties of these anionic starches. In this study, the adsorption characteristics for Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} of succinylated or oxidized corn starches having different degrees of substitution or oxidation were examined under various conditions.

2. Materials and methods

2.1. Materials

Corn starch, sodium bromide (NaBr), and free radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were purchased from Aldrich Chemical Company (Milwaukee, USA). Sodium hypochlorite solution (12% NaOCl) and succinic anhydride were purchased from Yukuri Pure Chemical Co., Ltd (Osaka, Japan) and Kanto Chemical Co., Ltd (Tokyo, Japan), respectively. All other commercial chemicals were reagent grade and used without further purification.

2.2. Succinylation and degree of substitution (DS) measurement

Succinylated starch was prepared in an aqueous dispersion of starch with an alkaline catalyst (Caldwell, 1949). Succinic anhydride (1 or 5 g) was slowly added to an aqueous dispersion of starch (10 g/400 ml) while the mixture was being mechanically stirred. The stirring was continued for 1 h at 25°C while maintaining the pH of the dispersion at 10 with 1 N NaOH solution. The reaction mixture was filtered and washed three times with 50% aqueous ethanol (100 ml × 3). The filtered residue was re-dispersed in water (400 ml) and the mixture was adjusted to pH 6.0 by adding 1 N HCl. The starch was re-washed with 50% aqueous ethanol (100 ml), and dried in a vacuum oven at 40°C overnight.

The DS for succinylation was measured by alkaline titration for the carboxyl group (Rutenberg & Solarek, 1984). The succinylated starch (1 g) was dispersed in a 2.5 N HCl/isopropyl alcohol solution (25 ml) by stirring for 30 min. The dispersion was filtered through a glass-filter and the residue was washed with isopropyl alcohol (100 ml). The starch was re-dispersed in deionized water (300 ml), and then the dispersion was heated in a boiling water-bath for 10 min. The starch solution was titrated with 0.1 N NaOH. The DS was calculated by the following equation:

$$\mathrm{DS} = \frac{0.162 \times (A \times N)/W}{1 - [0.101 \times (A \times N)/W]} \tag{1}$$

In the equation, A, N, and W represent the titration volume (ml) of the NaOH solution, normality of the NaOH solution, and dry weight (g) of the succinylated starch, respectively.

2.3. Oxidation and DS measurement

Corn starch was oxidized in the presence of TEMPO by the method of Nooy, Besemer and Bekkum (1995). Corn starch (10 g) (dry basis) was reacted with 12% NaOCl solution (200 ml) containing TEMPO (0.05 g) and NaBr (0.1 or 0.5 g) at −4°C for 30 min. The starch was precipitated by adding anhydrous ethanol (500 ml), washed with 50% aqueous ethanol (100 ml × 3), and dried in a vacuum oven at 40°C overnight.

The DS for oxidation was theoretically calculated by alkaline titration (Mattisson & Legendre, 1952) under an assumption that oxidization occurred only at the primary alcohol group in anhydroglucose units (AGUs) of starch, resulting in carboxylate groups. The oxidized starch (1 g) was dispersed in acidic solution (0.1 N HCl, 25 ml) by stirring for 30 min, and then the dispersion was glass-filtered and washed with distilled water (100 ml). The starch residue was re-dispersed in deionized water (300 ml), and gelatinized by heating in a boiling water-bath for 10 min. The starch solution was titrated at room temperature with 0.1 N NaOH, and the carboxyl content was calculated by the following equation:

$$\mathrm{DS} = \frac{0.162 \times (A \times N)/W}{1 - [0.015 \times (A \times N)/W]} \tag{2}$$

In the equation, A, N, and W represent the titration volumes (ml) of the NaOH solution normality of the NaOH solution, and the dry weight (g) of the oxidized starch, respectively.

2.4. Structural characterization

Fourier transform-infrared (FT-IR) spectra were obtained from KBr pellets of native, succinylated, and oxidized starches with an FT-IR spectrometer (Perkin–Elmer Spectrum GX, Beaconsfield, UK).

2.5. Metal-adsorption capacity

The metal-adsorption capacity of the succinylated or oxidized starch was determined by a batch method. Aqueous metal salt solution (100 ppm, 50 ml) of $CuSO_4{\cdot}5H_2O$, $ZnSO_4{\cdot}7H_2O$, $Pb(NO_3)_2$ or $CdSO_4{\cdot}2H_2O$ was mixed with the anionic starches (0.1 g) by shaking at room temperature for 1–30 min. The solution was glass-filtered, and the metal ion content remaining in the filtrate was determined by atomic absorption spectroscopy (Shimadzu AA-6701, Chiba, Japan).

2.6. Adsorption isotherm

The adsorption isotherm of the succinylated or oxidized starch for divalent metal ions was fitted to a Langmuir adsorption expressed by the following equation (Huang &

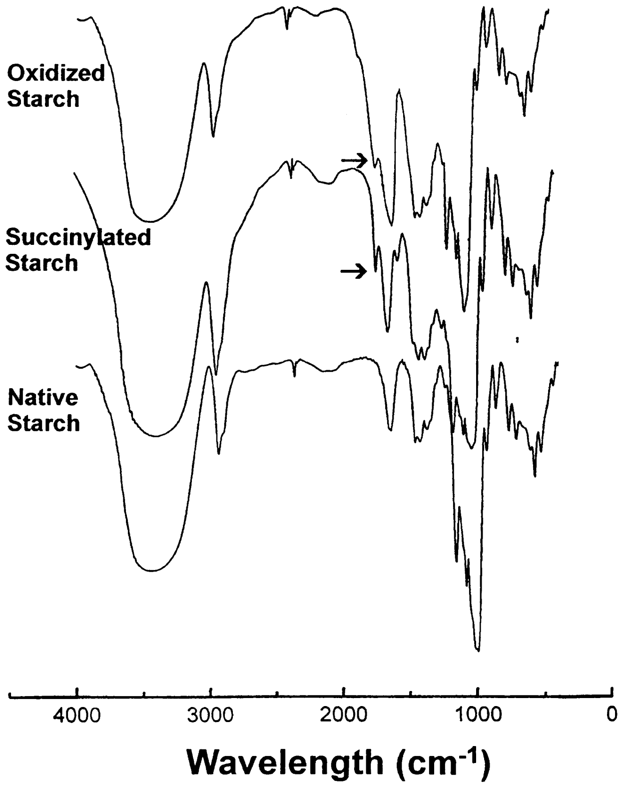


Fig. 1. FT-IR spectra of native, succinylated, and oxidized corn starches.

Ostovic, 1978):

$$(C/Q_e) = [1/(Qb)] + (C/Q) \quad (3)$$

where C represents the concentration of metal ion (mol/l) in the solution, and Q_e, Q and b were measured amounts of the adsorbed metal ions to starch (mol/g), the maximum amount of the adsorbed metal ion (mol/g) and the Langmuir constant, respectively. Thus, a plot of C/Q_e vs. C should yield a straight line with a slope $1/Q$ and intercept of $1/(Qb)$, from which Q and b can be measured. The higher the Langmuir constant (b) the more metal ions bound to the surface of the adsorbent.

Table 1
Degree of substitution (DS) for succinylation (reaction for 1 h at 25°C) and oxidation (reaction for 30 min at −4°C) with different amounts of succinic anhydride (SA) and NaBr in reaction mixtures

Carboxyl starch	Reactants (g)			DS
	Starch	SA	NaBr	
Succinylated starch	10	1		0.03
		5		0.07
Oxidized starch	10		0.1	0.13
			0.5	0.29

3. Results and discussion

3.1. Degree of succinylation and oxidation

The FT-IR spectra of native, succinylated and oxidized corn starches are shown in Fig. 1. The native corn starch showed a typical broad hydroxyl peak around 3400 cm^{-1}. On succinylation or oxidation, the FT-IR spectrum showed a new peak around 1730 cm^{-1} for the carboxylic acids of succinate or gluconate groups (marked by arrows).

In this experiment, the degree of succinylation and oxidation could be controlled by the addition of succinic anhydride (1 or 5 g) and NaBr (0.1 or 0.5 g), respectively. The DS value for succinylation under the experimental conditions used in this study was 0.03 or 0.07, whereas that for oxidation was much higher, 0.13 or 0.29 (Table 1).

3.2. Metal-adsorption capacity

3.2.1. Effect of DS

The metal-adsorption capacity of the anionic starches prepared at different degrees of succinylation and oxidation was measured by dispersing the starch in aqueous metal solutions for 10 min at room temperature.

As shown in Fig. 2, a succinylated starch having DS 0.07 showed the adsorption capacities of 0.178 (mmol/g) for Pb^{2+} and 0.133 (mmol/g) for Cu^{2+}, when 0.1 g starch was dispersed in 100 ppm metal solution (50 ml) for 10 min. Based on the molar weight of each AGU having DS 0.07, these values were equivalent to 30.08 and 22.47 mmol/AGU, respectively. Zn^{2+} and Cd^{2+} were adsorbed much less compared to Pb^{2+} and Cu^{2+} under the same conditions.

Native starch itself appeared to adsorb minor amounts of metal ions. Physical entrapment of the metal ions as well as minor electrostatic properties of the starch would be the characteristics for the metal-adsorption of native starch.

The oxidized starch displayed metal-adsorption characteristics that were different from those of succinylated starch. Cu^{2+} and Zn^{2+} adsorptions were largely increased with DS increase, from 0.043 to 0.235 mmol g^{-1} (7.14 to 39.02 mmol/AGU) for Cu^{2+}, and from 0.015 to 0.185 mmol g^{-1} (2.49 to 30.72 mmol/AGU) for Zn^{2+}, whereas Pb^{2+} and Cd^{2+} adsorptions remained almost constant. Despite the higher DS values, the oxidized starch displayed metal scavenging activity, which was not significantly higher than that of succinylated starch.

It is not clear why the metal ion and anionic starch displayed different adsorption characteristics. Perhaps the geometry and electric density of both substituents were the two major factors for their interactions. Succinate groups were attached on the AGUs with ester linkage, whereas the carboxyl groups in oxidized starch were fixed on the C-6 of the glucose unit. The different behaviors of the two ionic starches may be attributed to the difference in stereospecificity of the ionic groups. More research should be done for clear understanding.

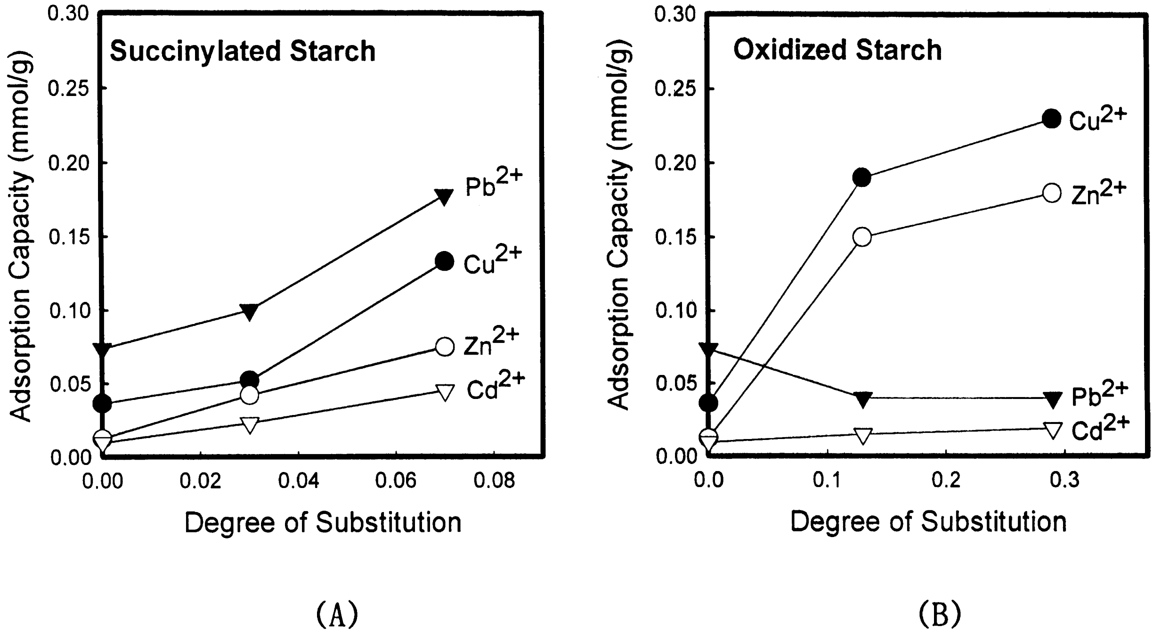


Fig. 2. Metal-adsorption capacity of succinylated and oxidized starches for Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} at different degrees of substitution.

The metal-adsorption capacity of the ionic starches tested in this experiment was, to some extent, less than that of synthetic resins although the adsorption capacity of the succinylated corn starch for Pb^{2+} and that of the oxidized corn starch for Cu^{2+} or Zn^{2+} approaches that of the synthetic resin used for metal removal. Furthermore, these ionic starches have an advantage over the resins because of biodegradability and economic feasibility.

3.2.2. *Effect of adsorption time*

The adsorption time of starch in the metal solution was changed from 1 to 30 min, and the adsorbed metal contents during this period were examined. As shown in Fig. 3, the succinylated starch (DS 0.07) reached the maximum adsorption capacity within 10 min for all metal ions tested. However, the oxidized starch (DS 0.29) reached the maximum at 5 min, and the adsorption capacity decreased as the adsorption time increased. Substitution with the ionic group or oxidation increased the water solubility or swellability of the starch. The reduced metal-adsorption shown by the oxidized starch was caused by the increased amount of dissolved starch when the adsorption time was over 10 min. To prevent the loss by soluble starch, cross-linking has been suggested (Kim & Lim, 1999).

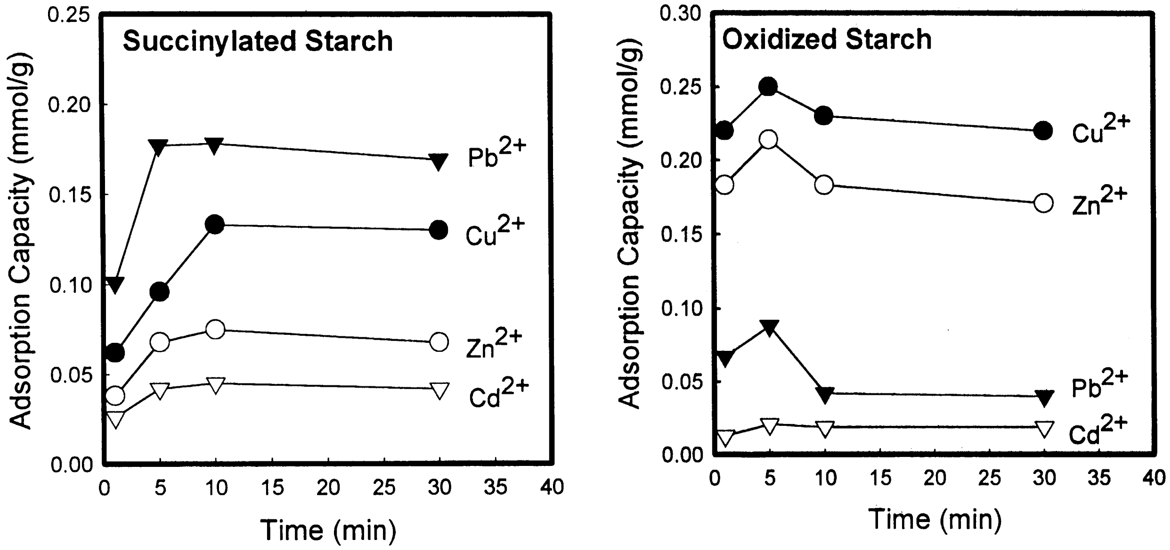
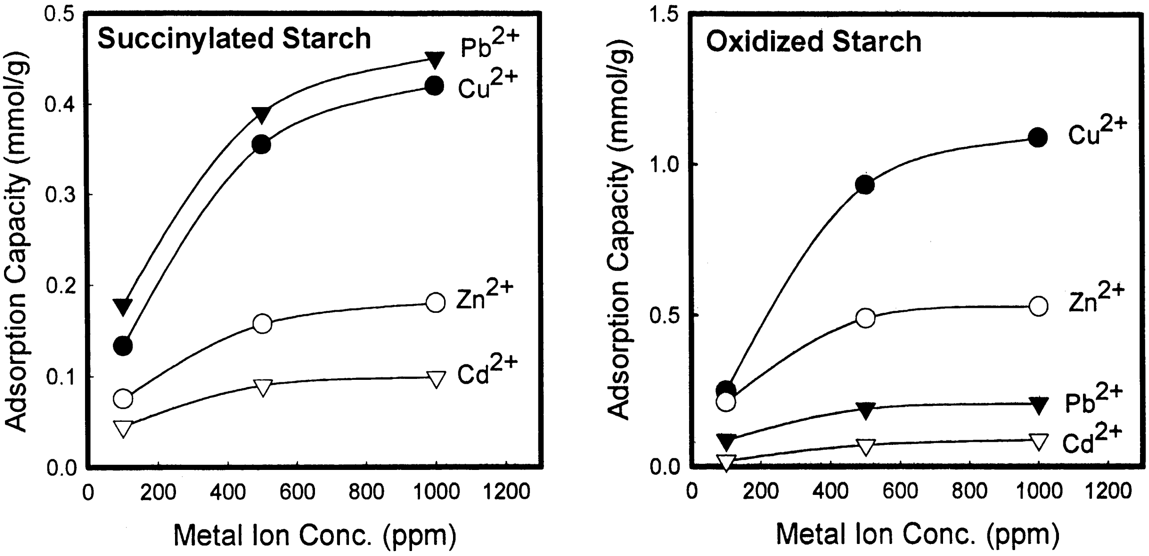


Fig. 3. Metal-adsorption capacity of succinylated and oxidized starches for Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} at different times.

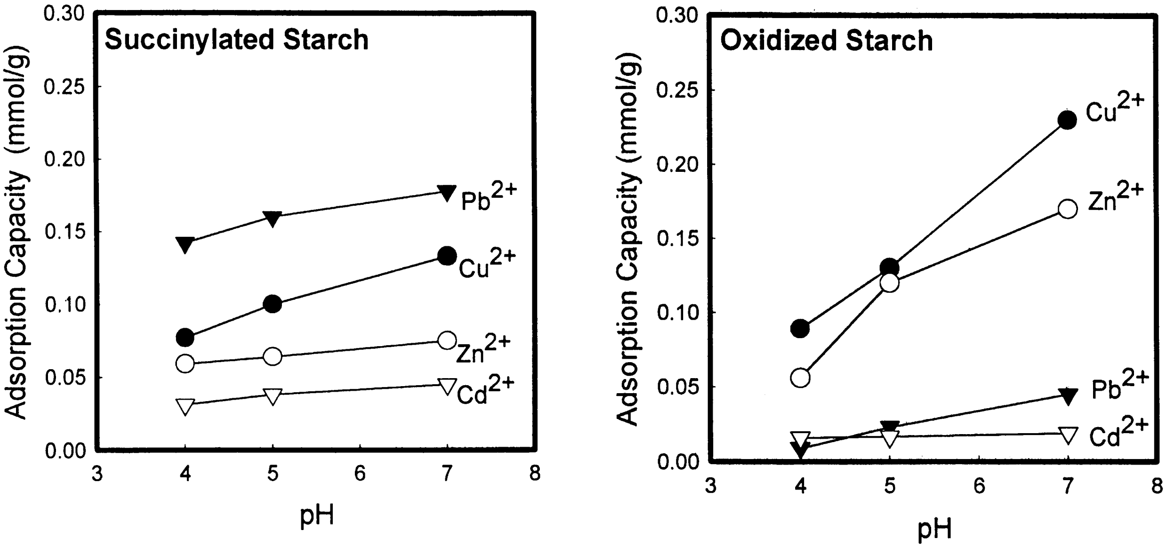


(A) (B)

Fig. 4. Metal-adsorption capacity of succinylated or oxidized starch for Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} at different metal ion concentrations.

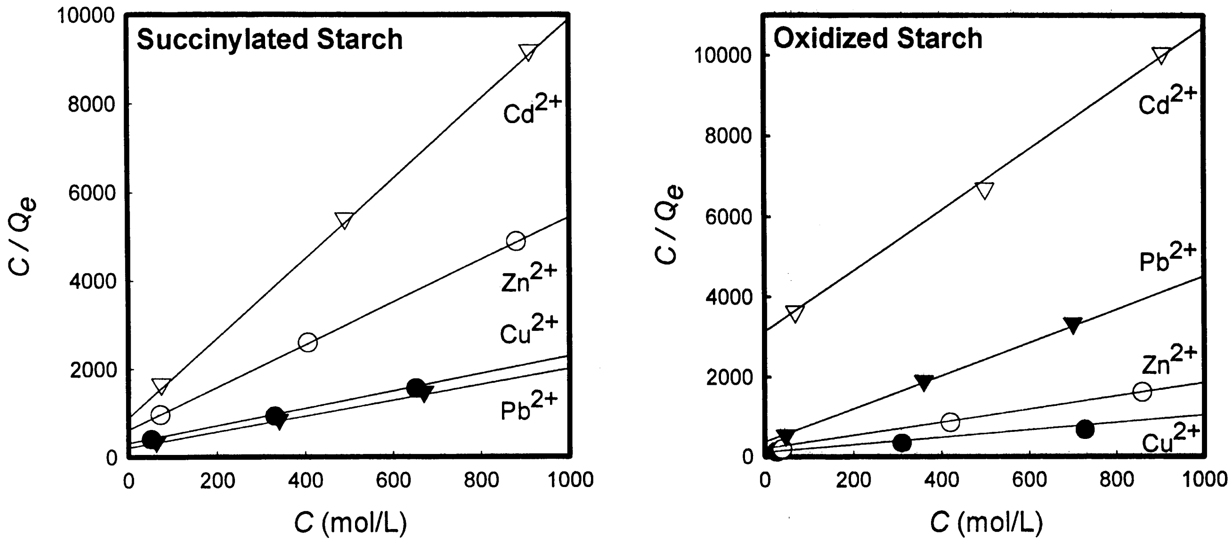
3.2.3. Effect of metal ion concentration

As shown in Fig. 4, the adsorbed amount of metal ions by the ionic starches was dependent on the initial metal ion concentration in the solution. When Pb^{2+} and Cu^{2+} concentrations were 100 ppm, the adsorption capacities of the succinylated starch (DS 0.07) for the ions were 0.125 and 0.175 mmol g^{-1}, which were equivalent to 21.12 and 29.57 mmol/AGU, respectively. However, at 500 ppm, the adsorption capacity was raised to 0.355 and 0.395 mmol g^{-1} (59.99 and 66.76 mmol/AGU), respectively for Pb^{2+} and Cu^{2+}. The increase in the adsorption capacity was more significant for Pb^{2+} and Cu^{2+} than for Zn^{2+} or Cd^{2+}, resulting in significant adsorption differences at high metal concentrations. The oxidized starch (DS 0.29) displayed an increasing trend similar to the succinylated starch. Among the tested ions, however, Cu^{2+} displayed the highest adsorption capacity by the oxidized starch (1.235 mmol g^{-1},



(A) (B)

Fig. 5. Metal-adsorption capacity of succinylated or oxidized starch for Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} at different metal solution pHs.



(A) (B)

Fig. 6. Langmuir plots for the adsorption capacity of succinylated or oxidized starch for Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}.

205.1 mmol/AGU). This value was approximately two times that obtained from Zn^{2+}. Both ionic starches showed a plateau at approximately 1000 ppm with 0.1 g of starch content in 50 ml solution.

The DS values for succinylated and oxidized starches (0.07 and 0.29, respectively) indicate that the starches theoretically have 70 mmol of succinate groups and 290 mmol of carboxylate groups per AGU. If a divalent metal ion interacts with two carboxylate groups on the starch a DS of 0.07 and 0.29 will bind 35 and 145 mmol of the divalent cations, respectively. However, in the range of metal ion concentration up to 500 ppm, the adsorption capacity of Pb^{2+}, Cu^{2+}, and Zn^{2+} appeared higher than these values for the ionic starches. This result might indicate that the adsorption between the ionic starches and metal ions was not only from the ionic interactions but also from physical entrapments. The metal ions found in native starch also display this trend.

3.2.4. Effect of pH

The metal-adsorption capacity of the anionic starches was compared at different pHs of the metal solutions. In Fig. 5, it can be seen that both anionic starches became more reactive with metal ions as the pH of the metal solution increased. The absorbent surface will be highly protonated in an acid medium. The protonated adsorbent cannot effectively interact with the metal ions because of the loss of negative charge (Huang & Ostovic, 1978). Thus, the increased proton concentration in the medium inhibited the metal–chelate complex of the adsorbent. In particular, it was found that the oxidized starch was more susceptible to pH than the succinylated starch (Fig. 5). The ester linkages between the succinylate group and AGU might also contribute to the metal-binding activity.

3.3. Adsorption isotherm

The Langmuir plots for the metal-adsorption by the

Table 2
Maximum adsorption capacity (Q) and Langmuir constant (b) of native, succinylated, and oxidized corn starches for the adsorption of divalent metal ions

Metal ions	Native starch		Succinylated starch[a]		Oxidized starch[b]	
	Q (mol/g)	$b \times 10^3$ (ppm^{-1})	Q (mol/g)	$b \times 10^3$ (ppm^{-1})	Q (mol/g)	$b \times 10^3$ (ppm^{-1})
Cu^{2+}	0.135	0.091	0.516	1.011	1.245	14.98
Zn^{2+}	0.105	0.017	0.206	0.345	0.570	5.084
Pb^{2+}	0.139	0.042	0.534	2.276	0.233	0.705
Cd^{2+}	0.079	0.011	0.110	0.113	0.130	0.042

[a] DS: 0.07.
[b] DS: 0.29.

anionic starches are shown in Fig. 6. The relationship between C/Q_e and C was linear, indicating that the metal-adsorption behavior of the anionic starches followed the Langmuir adsorption isotherm. Consequently, this suggests that the metal ions form a monolayer coverage on the adsorbent surface. The values of Q and b obtained from these plots are listed in Table 2. Native corn starch itself showed positive values of the maximum adsorption capacity (Q), 0.079–0.135 mmol g^{-1}. As indicated with previous data, the native starch has some entrapment inside the swollen starch granules for metal ions, and the Langmuir constant (b) for this was in the range between 0.011×10^{-3} and 0.091×10^{-3} ppm^{-1}.

On succinylation or oxidation, Q and b for the starch increased prominently. Among the four metal ions treated with the succinylated starch, Pb^{2+} displayed the highest values (0.534 mmol g^{-1} and 2.276×10^{-3} ppm^{-1}), and Cu^{2+} showed the second highest values (0.516 mmol g^{-1} and 1.011×10^{-3} ppm^{-1}). However, Q and b for Zn^{2+} and Cd^{2+} showed only minor increases. For oxidized starch, Cu^{2+} showed the most prominent increases in Q and b (0.135–1.245 mmol g^{-1} and 0.0911×10^{-3} to 4.98×10^{-3} ppm^{-1}, respectively). Furthermore, Zn^{2+} showed the second highest values (0.570 mmol g^{-1} and 5.084×10^{-3} ppm^{-1}) whereas Q and b for Pb^{2+} and Cd^{2+} showed only minor increases.

These results agree with the previous data from the metal adsorption in aqueous dispersions. Therefore, the succinylated corn starch will be a better choice for the removal of Pb^{2+} from water, whereas the oxidized starch works more efficiently with Cu^{2+}.

Acknowledgements

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