Adsorption of Hexavalent Chromium by Chitosan-Based Polymeric Surfactants

Moo-Yeal Lee, Kyung-Jin Hong, Yoshitsune Shin-Ya, Toshio Kajiuchi

Department of International Development Engineering, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

ABSTRACT: Chitosan-based polymeric surfactants (CBPSs) were prepared by the partial *N*-acylation of amine groups on chitosan with acid anhydrides. To apply the CBPSs for the removal of Cr(VI) commonly found in wastewater, a batch test was conducted to evaluate the adsorption capacity. The removal efficiency of Cr(VI) by the CBPS depended on several factors, including the solution pH, CBPS dose, and ionic strength. Our results show that the CBPSs exhibited a greater adsorption capacity for Cr(VI) than have other modified chitosans reported in the literature. The maximum adsorption capacity of Cr(VI) was 180 mg/g of CBPS at a final pH of 5.3. From the results of dynamic light scattering, we propose that the removal mechanism of Cr(VI) by the CBPSs was mainly through the adsorption of negatively charged chromium ions by positively charged amine groups on the CBPSs followed by colloidal precipitation because of its lower solubility. Conclusively, we found that the CBPS was significantly effective for the removal of Cr(VI). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 44–50, 2005

Key words: chitosan; surfactants; adsorption

INTRODUCTION

Hexavalent chromium is widely used in electroplating, leather tanning, and metallurgy and as a corrosion control agent. In general, Cr(VI) exists in aqueous solution as oxyanions such as $Cr_2O_7^{2-}$, $HCr_2O_7^-$, $HCrO_4^-$, and CrO_4^{2-}.[1] Because these ions are toxic, carcinogenic, mutagenic, and teratogenic through dermal and oral exposure,[2–5] they can be major pollutants in the waste streams from these industries. Thus, the removal of Cr(VI) in wastewater is of significant importance from an environmental viewpoint. Conventional methods for the removal of Cr(VI) include chemical precipitation, redox reaction, mechanical filtration, membrane separation, ion exchange, and adsorption.[6–9] In recent years, biosorption has received increasing attention as an effective and environmentally friendly treatment method for the reduction of Cr(VI) pollution in industrial effluents.[10,11]

Chitosan, poly(1-4)-D-glucosamine, is a deacetylated material of chitin that can be obtained in large quantities from the shells of shrimp and crabs. In practice, chitosan is the second most abundant polysaccharide in the world and has not been fully used as yet. The advantages of this polymer include low cost, availability, biodegradability, low toxicity, and high biocompatibility. It has been documented that chitosan exhibits a high adsorption capacity for heavy metal in wastewater because its amine and acetamido groups are nonspecific binding sites.[12,13] It has again been reported that chitosan needs further modification to facilitate mass transfer and to expose the active binding sites for the improvement of adsorption capacity.[11,14] In consequence, several researchers have attempted to modify chitosan and have produced functionalized chitosan sorbents, such as porous chitosan beads,[15] crosslinked chitosan beads,[16] chitosan azacrown ether,[17,18] grafted chitosan,[19] chitosan resin,[20] and chitosan coated onto ceramic alumina,[21] which have showed a remarkable increase in adsorption capacity compared to untreated chitosan.

Hence, in this study, we attempted to prepare chitosan-based polymeric surfactants (CBPSs) as a new modified chitosan sorbent. The CBPSs, possessing both hydrophilic groups (—NH₂ and —OH) and hydrophobic groups (substituted alkyl chains), was expected to behave as a polymeric surfactant. The objective of this study was to evaluate the feasibility of the CBPSs for the removal of Cr(VI) in synthetic wastewater. The ability of the CBPSs to remove Cr(VI) was investigated under various reaction conditions, including solution pH, chromium concentration, CBPS dose, and ionic strength.

EXPERIMENTAL

Materials

Chitosan 10 (molecular weight = 60×10^3; 80% deacetylated) was purchased from Wako Chemical

Correspondence to: M. Y. Lee, Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180 (leem2@rpi.edu)
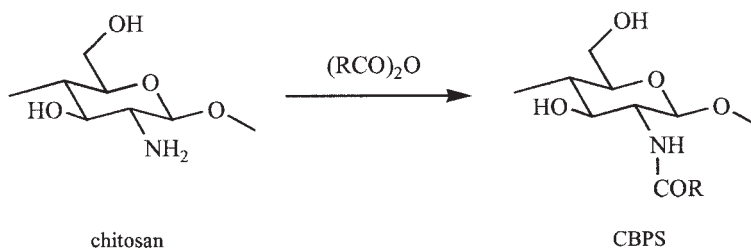
Scheme 1 Synthesis of the CBPS through the *N*-acylation of chitosan with an acid anhydride.

Industries (Osaka, Japan) and was used without further purification. Acid anhydrides, such as hexanoic (C_6), lauric (C_{12}), and palmitic anhydrides (C_{16}) (Aldrich, Milwaukee, WI), were chosen as alkyl groups for the synthesis of the CBPSs. The Cr(VI) stock solution was prepared in distilled water with potassium dichromate ($K_2Cr_2O_7$) and was used as a synthetic wastewater. All of the other chemicals were of the highest purity available.

Synthesis of the CBPSs

Scheme 1 illustrates the selective *N*-acylation proposed for the synthesis of the CBPSs with acid anhydrides. Chitosan 10 (4 g) was dissolved in 60 mL of 20% (v/v) aqueous acetic acid solution, and the mixture was mechanically stirred and then diluted with 400 mL of methanol. Each molar equivalent (0.1 and 0.2) of acid anhydride to one glucosamine residue was dissolved in 200 mL of methanol and then added to the chitosan solution. The mixture was agitated overnight at room temperature and then mixed vigorously with 1000 mL of acetone. Afterward, the CBPS was precipitated by centrifugation and sequentially washed three times with acetone and diethyl ether to remove water and unreacted reagent. The CBPS was freeze-dried before it was used for the subsequent experiment.

Solubility and surface tension of the CBPSs

To determine the solubility of the CBPSs, the pH of the CBPS solution (1 g/L) was adjusted with HCl, CH_3COOH, and NaOH to various pH values. The change in optical density by the flocculation of the CBPS was analyzed at 660 nm with an ultraviolet spectrophotometer (U-3210, Hitachi High-Technologies Co., Tokyo).

Surface tension was determined by the plate method with a tensiometer (CBVP-A3, Kyowa Kaimenkagaku, Tokyo). Each 50 mL of the CBPS solution (0.25–4 g/L) was agitated for 72 h at pH 5.0 and centrifuged at 15,000 rpm for 10 min to remove impurities. Each supernatant was added in a dish, and suction of the equilibrated surface was done before the

measurements were performed. The surface tension was obtained at a constant temperature (25°C) after the reequilibration of the surface for at least 1 h. The measurements were repeated three times, and the respective mean value was taken.

Adsorption of Cr(VI) by the CBPSs

Batch tests were conducted to investigate the effectiveness of the CBPSs in the removal of Cr(VI). For the study of pH effect, 15 mL of the CBPS (10 g/L) were added to vials containing 15 mL of the Cr(VI) solution (100 mg/L). The pH values of the solutions were adjusted with HNO_3 or NaOH in pH ranges from 2.0 to 12.0, and the vials were placed on a stirrer for 24 h. Thereafter, the mixtures were transferred into a dialysis membrane (molecular weight cutoff = 6000–8000, Spectrum Laboratories, Inc., Rancho Dominguez, CA), and the outer membrane was filled with 120 mL of chromium-free distilled water. The samples were placed on a stirrer for 48 h, and then, the solutions retained in outer membrane were collected for the analysis of the residual content of chromium. The concentration of chromium was determined by inductively coupled plasma spectrometry (SPS 7000, Seiko Instruments, Inc., Chiba, Japan). In addition, chitosan was prepared in the same way and compared with the result of Cr(VI) removal by the CBPSs.

The equilibrium adsorption isotherm of the CBPSs (10 g/L) was determined by contact with various concentrations of Cr(VI) solution (100–4000 mg/L) at pH 5.0. After they were stirred for 24 h, the samples were transferred into the dialysis membrane. Afterward, the previous procedure was followed. The removal efficiency of Cr(VI) was also evaluated with different CBPS doses (1–30 g/L). The CBPS was added to the Cr(VI) solution (3000 mg/L) at pH 5.0, and then, the solution was shaken for 24 h. Thereafter, the samples were transferred into the dialysis membrane. A similar experiment was also carried out to study the effect of ionic strength on the Cr(VI) removal by CBPS (10 g/L). The ionic strength was adjusted with NaCl at pH 5.0. Afterward, the same procedure as discussed previously was followed for each experiment. All of the

experiments were performed at room temperature, and the samples were prepared in duplicate.

Dynamic light scattering (DLS) measurements

During the adsorption of Cr(VI) by the CBPS, the change in colloid diameter was characterized with a DLS spectrophotometer (DLS-7000, Otsuka Electronics Co., Osaka, Japan). The system consisted of a 10-mW He–Ne laser operating at a wavelength of 633 nm and a detector for photon counting. Each 25 mL of the CBPS solution (10 g/L) was added to a 100-mL flask containing 25 mL of Cr(VI) solution (400 mg/L) at pH 5.0, and then, the mixture was agitated on a stirrer for 24 h. Thereafter, the solution was centrifuged at 3000 rpm for 5 min to remove large precipitates, and the supernatant was collected for DLS analysis. All of the measurements were carried out at an observation angle of 90°, and autocorrelation decay curves were analyzed by standard histogram methods (Marquadt analysis). The light-scattering data gave results for the equivalent hydrodynamic diameter (effective range = 3 nm–3 μm), obtained from the Stokes–Einstein equation. A liquid sample cell with a path length of 12 mm was used, and all of the measurements were conducted at a constant temperature (25°C).

RESULTS AND DISCUSSION

Properties of the CBPSs

To prepare a CBPS possessing hydrophilic groups (—NH$_2$ and —OH) and hydrophobic groups (—CH$_2$— and —CH$_3$), the amine groups on chitosan
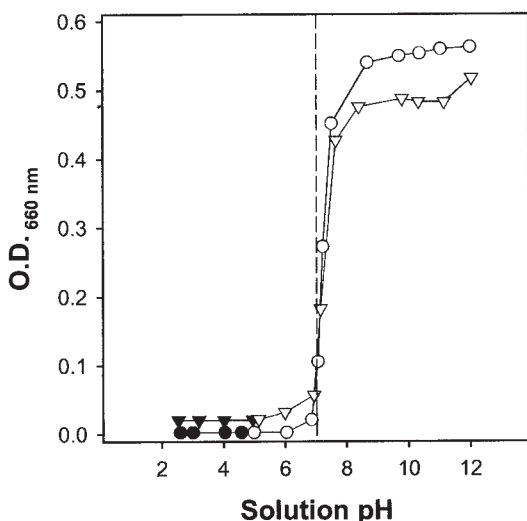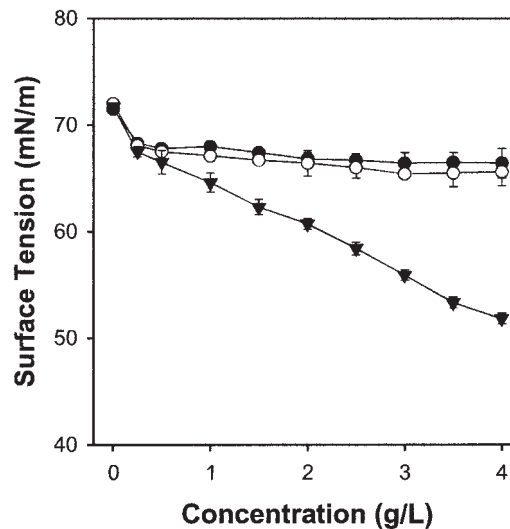

Figure 2 Surface tension of (●) chitosan, (○) CBPS$_{10}$–C$_{12,0.2}$, and (▼) CBPS$_{10}$–C$_{16,0.2}$ in aqueous solutions at pH 5.0 as a function of their concentrations.

were partially acylated with different carbon lengths of acid anhydrides. The degree of substitution on the CBPS was expressed as the initial monomolar ratio of acid anhydride to NH$_2$ on a repeating unit of chitosan. Thus, CBPS$_{10}$–C$_{16,0.2}$ was chitosan 10 modified with palmitic (C$_{16}$) anhydride at an initial monomolar ratio of 0.2. The solubility of the CBPS and chitosan was measured at different pH values (Fig. 1). CBPS and chitosan abruptly started to precipitate at pH values above 6.5 because of a lack of protonated amine groups (—NH$_3^+$), but most of those were dissolved under pH 6.0. In addition, CBPS$_{10}$–C$_{16,0.2}$ included a very small colloid-like emulsion, so it was slightly unclear even at pH 6.0.

The surface tensions of the CBPSs and chitosan are shown in Figure 2. The surface tension of CBPS$_{10}$–C$_{16,0.2}$ decreased with increasing concentration, whereas there was no significant change in the surface tensions of CBPS$_{10}$–C$_{12,0.2}$ and chitosan. Among the samples tested in this study, CBPS$_{10}$–C$_{16,0.2}$ showed the lowest surface tension. It was, therefore, reasonable to assume that CBPS$_{10}$–C$_{16,0.2}$ was concentrated at the air–water interface and presumably formed micelles in the solution like polymeric surfactants do.

Equilibrium time in the dialysis membrane operation

The permeation of free Cr(VI) ions not adsorbed to the CBPS through the dialysis membrane was investigated as a function of time at pH 6.0 (Fig. 3). The result indicated that free Cr(VI) ions were rapidly permeated through the dialysis membrane, and more than 90% of those were permeated within 24 h. During the dialysis, the color of the inner membrane solution was

Figure 1 Optical density (OD) of chitosan in (●) CH$_3$COOH and (○) NaOH solutions and of CBPS$_{10}$–C$_{16,0.2}$ in (▼) HCl and (▽) NaOH solutions.
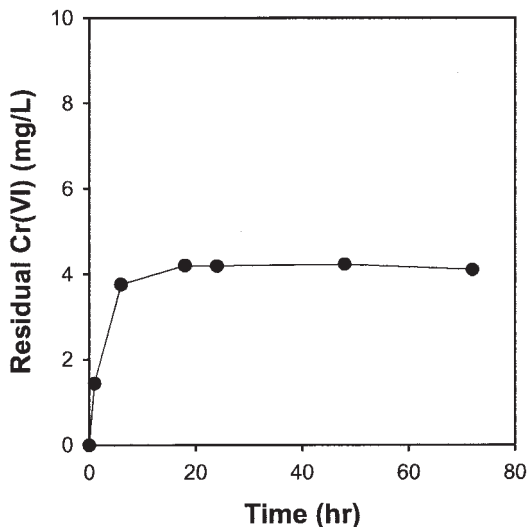
Figure 3 Permeation time of free Cr(VI) ions not adsorbed to the CBPS through the dialysis membrane (initial conditions: 100 mg of Cr(VI)/L and 5 g of $CBPS_{10}$–$C_{16,0.2}$/L at pH 6.0).

yellowish brown and that of outer membrane solution had not changed significantly. The adsorbed amount of Cr(VI) to the CBPS (Q_e) was obtained as follows:

$$Q_e = (C_i V_i - CV)/W \qquad (1)$$

where C_i is the initial Cr(VI) concentration (mg/L) in the inner membrane solution, C is the equilibrium Cr(VI) concentration (mg/L) in the outer membrane solution, V_i is the volume of inner membrane solution (L), V is the total volume of solution (L), and W is the amount of CBPS used (g). We assumed that the concentration of free Cr(VI) ions in the inner membrane solution was identical with that of the Cr(VI) ions in the outer membrane solution at equilibrium state. On the basis of the previous observations, an equilibrium permeation time of 48 h was used for further experiments.

Effect of the solution pH

Figure 4 illustrates the optimum range of pH for the maximum removal of Cr(VI) by the CBPS. It was shown that the removal efficiency of Cr(VI) by the CBPS was dependent on pH, whereas that of Cr(VI) without a CBPS (as a blank) was constant in various pH ranges. Hexavalent chromium uptake by $CBPS_{10}$–$C_{16,0.2}$ increased as the pH increased from 2.0 to 5.5, and then, a pH optimum was observed around pH 6. However, chitosan did not show a unique pH optimum (data not shown). At pH 8.0, the removal of Cr(VI) by $CBPS_{10}$–$C_{16,0.2}$ was only 12.1% compared to a 65.6% removal observed at pH 5.5. It was remarkable that there was a greater decrease in the Cr(VI) removal

by the CBPS at pH < 7 compared to the blank. These results could be attributed to the change of NH_2 on the CBPS to NH_3^+. With the amine group on chitosan monomer represented as R—NH_2, it is known that NH_2 on a CBPS may react with H^+ ions, and the dissociation equation could be represented by the following:

$$R\text{—}NH_2 + H_3O^+ \leftrightarrows R\text{—}NH_3{}^+ + H_2O \qquad (2)$$
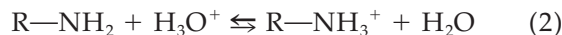
Because the protonation constant (pK_a) of the amine group is 6.3, we calculated that the extent of protonation was 9, 50, 91, and 99% at pH values of 7.3, 6.3, 5.3, and 4.3, respectively. However, Cr(VI) exists in several stable forms in aqueous solution, including $Cr_2O_7^{2-}$, $HCr_2O_7^-$, $HCrO_4^-$, and CrO_4^{2-}, and the relative abundance of any particular species is dependent on the Cr(VI) concentration and pH (Fig. 5). Because the CBPS was positively charged below pK_a, theoretically, Cr(VI) ions could have electrostatically interacted with NH_3^+ groups at pH < 6.3 and formed complexes with NH_3^+ on the CBPS. As the solution pH increased, the CBPS underwent deprotonation, and the removal efficiency decreased. Accordingly, the removal of Cr(VI) by the CBPS significantly increased at pH < pK_a. The experimentally observed steep decrease in Cr(VI) removal could be explained by rapid changes in the protonated and deprotonated forms of the amine groups on the CBPS. However, it was still unclear why the CBPS showed a pH optimum for the removal of Cr(VI). We, thus, attempted to explain this phenomenon through subsequent experiments by measuring the equilibrium adsorption isotherm and with DLS.
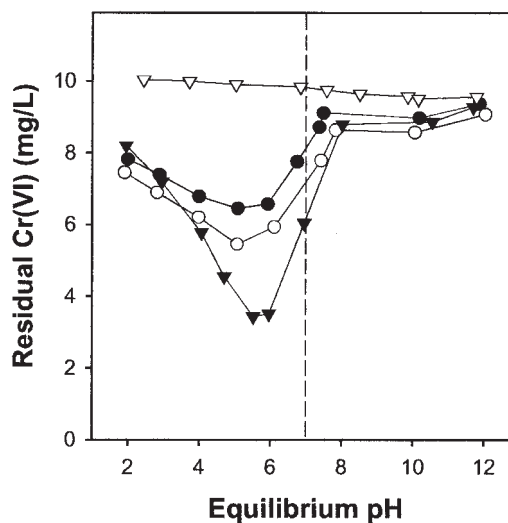

Figure 4 Effect of the solution pH on the removal of Cr(VI) by (●) $CBPS_{10}$–$C_{6,0.2}$, (○) $CBPS_{10}$–$C_{12,0.2}$, (▼) $CBPS_{10}$–$C_{16,0.2}$, and (▽) the blank (initial conditions: 100 mg of Cr(VI)/L and 5 g of each chitosan sample/L).
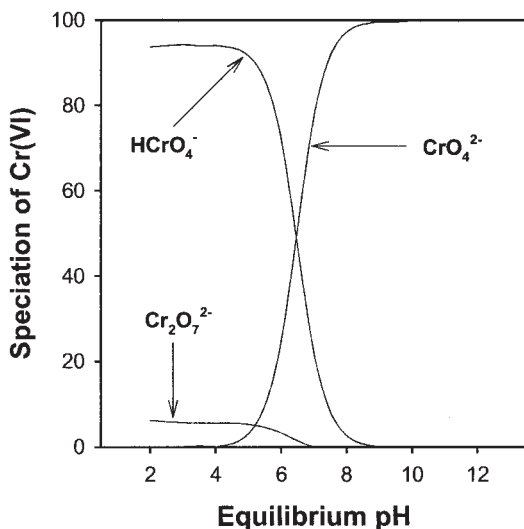
Figure 5 Chemical equilibrium speciation of Cr(VI) computed by MINTEQA2/PRODEFA2.

Effect of the Cr(VI) concentration

The equilibrium adsorption isotherm for Cr(VI) by the CBPS and chitosan is described in Figure 6. The result implied that the adsorption increased with increasing equilibrium concentration of Cr(VI). In comparison with chitosan, the CBPS was considered to be more suitable to adsorb Cr(VI) in aqueous solution, espe-
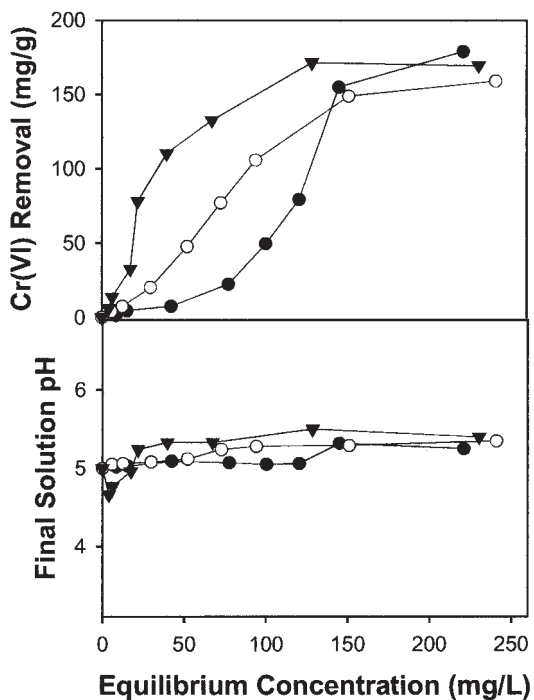

Figure 6 Maximum adsorption of Cr(VI) by (●) chitosan, (○) $CBPS_{10}-C_{12,0.2}$, and (▼) $CBPS_{10}-C_{16,0.2}$ (initial conditions: 100–4000 mg of Cr(VI)/L and 10 g of each chitosan sample/L at pH 5.0).
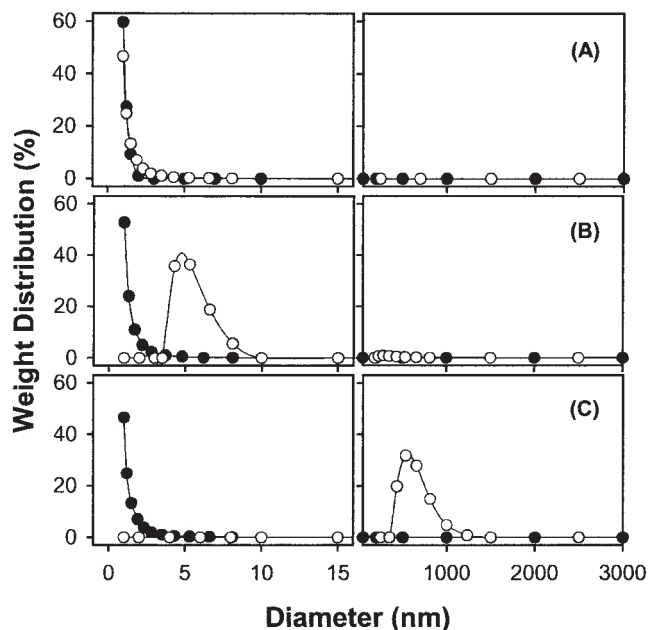

Figure 7 Hydrodynamic diameters of (A) chitosan, (B) $CBPS_{10}-C_{12,0.2}$, and (C) $CBPS_{10}-C_{16,0.2}$ found by DLS analysis: 10 g of each chitosan sample/L (●) before and (○) after contact with 400 mg of Cr(VI)/L at an initial pH of 5.0.

cially at low concentrations of Cr(VI). For examples, $CBPS_{10}-C_{16,0.2}$ (g/L) reduced the Cr(VI) concentration from 100 mg/L to below 22 mg/L, whereas chitosan (g/L) only reduce it down to 78 mg/L. As a result, the adsorption capacity of $CBPS_{10}-C_{16,0.2}$ was 180 mg of Cr(VI)/g at a final pH of 5.3. The maximum amounts of Cr(VI) adsorbed per unit mass of sorbent reported in the literature are 27 mg for chitosan;[12] 51 mg for NI(II) imprinted chitosan resin;[20] 50 and 78 mg for noncrosslinked chitosan and crosslinked chitosan, respectively;[22] and 153.8 mg for ceramic aluminum coated chitosan.[21] The value reported here for the CBPS was considerably greater than those reported elsewhere, indicating that the CBPS led to an enhancement in adsorption capacity for Cr(VI). In addition, the experimental data on Cr(VI) adsorption by the CBPS did not fit into the linear form of the Langmuir and Freundlich relationships (data not shown). It was, therefore, reasonable to assume that the removal mechanism of Cr(VI) by the CBPS was not a simple adsorption process.

A major removal mechanism was considered to be an electrostatic interaction between negatively charged chromium ions and positively charged amine groups on the CBPS. To investigate whether the CBPS made colloidal precipitates in the solution after complexing with Cr(VI), DLS analysis was performed (Fig. 7). The results show that the CBPS was easily precipitated and formed colloids after complexing with Cr(VI) at pH 5.0, presumably because of its increased hydrophobicity by modification, whereas chitosan

TABLE I
Hydrodynamic Diameters (nm) of Chitosan, $CBPS_{10}-C_{12,0.2}$, and $CBPS_{10}-C_{16,0.2}$
During the Adsorption of Cr(VI) (200 mg/L)

	pH			
Sample	3.0	4.0	5.0	6.0
Chitosan	1.4 ± 0.6	1.4 ± 0.7	1.4 ± 0.6	157 ± 98
$CBPS_{10}-C_{12,0.2}$	1.4 ± 0.6	1.3 ± 0.6	5.4 ± 1.1	1165 ± 298
$CBPS_{10}-C_{16,0.2}$	567 ± 167	602 ± 152	618 ± 159	7485 ± 1203

With chitosan, no precipitation occurred. With $CBPS_{10}-C_{12,0.2}$ and $CBPS_{10}-C_{16,0.2}$, precipitation occurred at pH values above 5.0.

was not precipitated. $CBPS_{10}-C_{16,0.2}$, a partially modified chitosan with a palmitic anhydride, was the most hydrophobic among the tested samples. Interestingly, $CBPS_{10}-C_{16,0.2}$, with a longer alkyl chain, was precipitated more easily and made bigger colloids. In addition, the CBPS and chitosan were more easily precipitated at higher pH values (Table I). We, therefore, propose that the removal of Cr(VI) by CBPS was mainly due to the adsorption of $HCrO_4^-$ by NH_3^+ on the CBPS followed by its colloidal precipitation due to its lower solubility through a deficiency of protonated amine groups, which can be described as follows:

$$CBPS—NH_3^+ + HCrO_4^-$$

$$\rightarrow CBPS—NH_3^+ —HCrO_4^- \downarrow \ (pH\ 5–6) \quad (3)$$
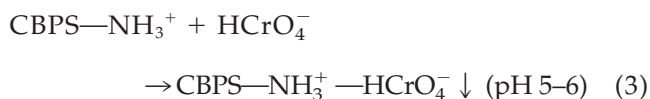
It is clear that this is the reason the CBPS with a longer alkyl chain showed a higher removal efficiency of Cr(VI) at the pH optimum. In addition, the reason the CBPS showed a lower removal efficiency at pH 2–4 is presumably because of too many H^+ ions, which eventually hindered the complexation between CBPS–NH_3^+ and $HCrO_4^-$.

Effect of the CBPS dose and ionic strength

When liquid waste is treated in a waste treatment plant, the amounts of adsorbent, which have to be added to remove metal ions, seem to be important from an economical aspect. Thus, the effect of the CBPS concentration on Cr(VI) removal was investigated (Fig. 8). It was observed that the residual concentration of Cr(VI) dramatically decreased with increasing initial concentration of CBPS. This was due to an increase in NH_3^+ groups, which led to a complexation between CBPS–NH_3^+ and Cr(VI), and subsequently, precipitated in the solutions.

Because wastewaters contain various kinds of ions, the influence of ionic strength on Cr(VI) removal by the CBPS was studied. The result indicate that when the ionic strength was increased up to 0.5M, there was a decrease in the removal efficiency, whereas there were negligible changes at over 0.5M (Fig. 9). If the dominant mechanism of Cr(VI) removal was adsorp-

tion between negatively charged chromium ions and positively charged amine groups on the CBPS, the ionic strength had a large effect on the adsorption capacity because electrostatic attraction is very important.[23,24] In principle, variations in background electrolyte concentrations remarkably influence the sorbate–sorbent interactions involving the electrostatic attraction. The fact implies that an increase in the ionic strength not only decreased the ion activity of chromium ions but also increased the concentration of competitive chloride anions. If the change in ionic strength does not have any appreciable effect on Cr(VI) removal, this indicates that Cr(VI) removal by the sorbent is mainly through covalent binding or precipitation. Our results imply that the CBPS became less effective in removing Cr(VI) in the presence of very high sodium chloride concentrations. However, the CBPS still had a marked tendency to form complexes with Cr(VI), leading to the formation of colloids, which caused the CBPS to have a greater adsorption capacity in higher salt solutions.
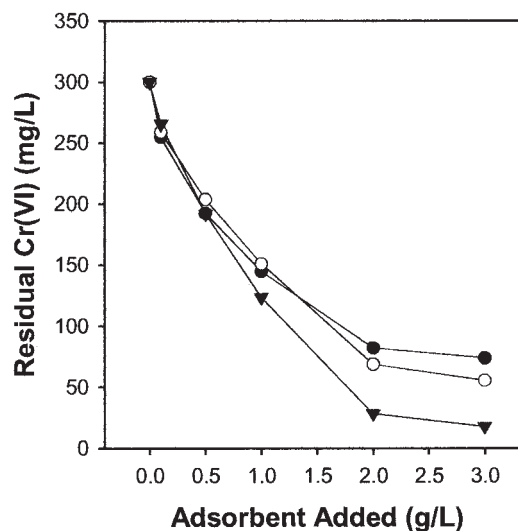

Figure 8 Effect of (●) chitosan, (○) $CBPS_{10}-C_{12,0.2}$, and (▼) $CBPS_{10}-C_{16,0.2}$ doses on the removal of Cr(VI) (initial conditions: 3000 mg of Cr(VI)/L and 1–30 g of each chitosan sample/L at pH 5.0).
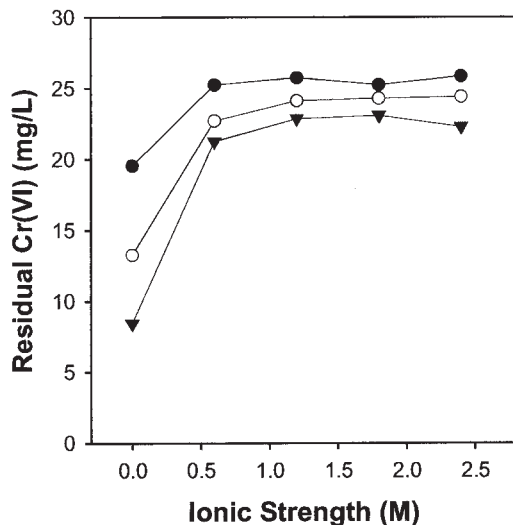
Figure 9 Effect of ionic strength on the removal of Cr(VI) by (●) chitosan, (○) $CBPS_{10}$–$C_{12,0.2}$, and (▼) $CBPS_{10}$–$C_{16,0.2}$ (initial conditions: 400 mg of Cr(VI)/L and 10 g of each chitosan sample/L with 0.6–2.4M NaCl/L at pH 5.0).

CONCLUSIONS

CBPSs were synthesized by partial *N*-acylation of amine groups on chitosan. Because of their hydrophobic characteristics, the CBPSs had a tendency to form intrapolymer aggregations like a polymeric surfactant. In this study, an adsorption process with the CBPS was considered as an alternative to conventional methods to treat wastewater contaminated with Cr(VI). The removal efficiency of Cr(VI) by the CBPSs significantly depended on pH and changed remarkably at a pH optimum around 6. Moreover, the CBPS exhibited a distinctly higher removal efficiency of Cr(VI) than chitosan. The dominant removal mechanism of Cr(VI) by CBPS appeared to be adsorption by electrostatic attraction followed by colloidal precipitation. Among the CBPS samples, $CBPS_{10}$–$C_{16,0.2}$ was the most effective in the removal of Cr(VI) because of its higher hydrophobicity, which led to increased colloidal precipitation. Our results indicate that CBPSs are applicable as novel sorbents for the removal of Cr(VI) in wastewater.

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