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Adsorption Behavior of Dithiocarbamate β-Chitosan Gels for Cadmium(II)

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Research Article

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ABSTRACT

Adsorption gels were prepared by means of chemical modification of β-chitosan by immobilizing functional groups of dithiocarbamate to investigate its adsorption behavior for cadmium(II) such as effect of cross-linking, adsorption rate, pH dependency, loading capacity by batch-wise experimental work and mutual adsorptive separation of cadmium(II) from zinc(II) using a packed column. Thus prepared adsorption gel exhibited high selectivity towards cadmium(II) over zinc(II) and high loading capacity for cadmium(II) regardless of cross-linking. Satisfactory separation of cadmium(II) from zinc(II) was achieved using a packed column.

INTRODUCTION

Cadmium occurs together with zinc in the majority of zinc ores. Consequently, serious environmental pollutions by cadmium such as Itai-itai disease have been brought by unsuitable control of mining wastes of zinc ores and mining effluents [1]. Although the demand for cadmium has been decreased year by year due to the adverse effect caused by its toxicity [2], cadmium compounds have been still employed for versatile applications such as pigments, batteries and solar panels. Therefore, the effective and selective removal of cadmium from spent materials has been strongly required.

Adsorptive removal of toxic metals including cadmium using various adsorbents has been reported as review articles [3-7] and general articles [8,9]. Chitosan is a polysaccharide rich in primary amino groups produced by alkaline hydrolysis of shells of crustacean. It can be easily chemically modified via these amino groups. This modified chitosan has been investigated as adsorption gels for some metal ions as well as original chitosan [10-18]. Adsorptive removal of Cd(II) ion using gels of original unmodified chitosan has been also reported, in which primary amino groups were reported to be effective for adsorption of Cd(II) ion [19-22]. Muzzarelli et al. [23,24] reported the chemical modification of α-chitosan produced from krill (*Euphausia superba*) with functional groups of dithiocarbamate, which is abbreviated as DTC hereafter, and also briefly reported its adsorption behavior for some metal ions including Cd(II). In the previous paper [25], we also prepared lyophilic chitosan containing DTC functional groups for a solvent extraction reagent and found its high selectivity to Cu(II) and Ni(II). The chitosan compounds chemically modified with DTC functional groups are abbreviated as DTC-chitosan, hereafter. In the present paper, the detailed adsorption behavior of DTC-chitosan for Cd(II) was investigated from viewpoint of its separation from Zn(II) ion, in particular.

According to the Pearson's HSAB theory [26], Cd(II) is classified as a typical soft Lewis acid. Although nitrogen atoms of the primary amino group are classified as a slightly soft Lewis base exhibiting some affinity to some kinds of metal ions classified as soft Lewis acids, the affinity to Cd(II) ion is expected to be much more increased in case some functional groups containing sulfur atoms, classified as a strong soft Lewis base, such as the DTC group are immobilized onto polymer matrices of chitosan by means

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of some chemical modification. Additionally, since Zn(II) is classified as a border line Lewis acid, the selectivity to Cd(II) over Zn(II) is expected to be much enhanced by such modification of chitosan.

Because, due to many primary amine functional groups, chitosan and its derivatives are totally or partly soluble in acidic aqueous solutions depending on the kinds of acids, they should be crosslinked to avoid the dissolution to be employed as adsorption gels in aqueous solutions. In the present work, the effect of crosslinking was investigated by carrying out the adsorption tests using the gels crosslinked using ethylene glycol diglycidyl ether and those which were not crosslinked for comparison.

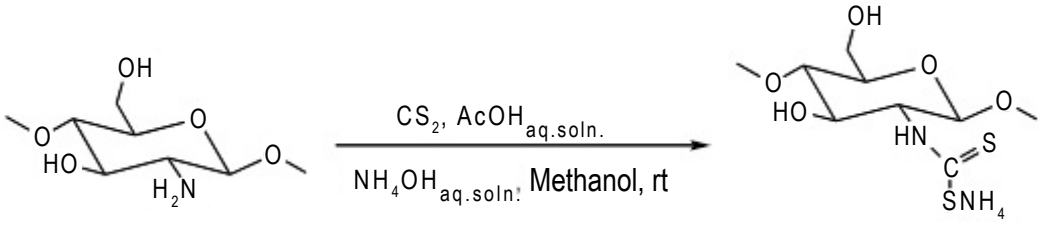
It is well known that there are 2 types of chitosan, *α* and *β*-chitosan. The former is produced from the shells of Crustacea such as prawns and crabs and characterized by highly crystalline nature, which impedes the smooth penetration of reagents for chemical modification, resulting in the only unsatisfactory degree of modification. On the other hand, *β*-chitosan produced from squid gristle contains parallel molecular chain arrangement and is characterized by more amorphous property, due to which higher degree of introduction of functional groups is achievable onto nitrogen atoms of primary amino groups.

From these viewpoints, in the present work, we prepared DTC-chitosan from *β*-chitosan to investigate its adsorption behavior for Cd(II) and Zn(II) ions and their mutual separation.

EXPERIMENTAL SECTION

Materials

β-chitosan (deacetylation degree 84 %) was purchased from Yaegaki Bio-industry, Inc., Hime ji, Japan, and used without further purification. On the other hand, α-chitosan (deacetylation degree 95 %) was purchased from Funakoshi Co. Ltd., Tokyo, Japan, and also used without further purification. As mentioned earlier, in order to investigate the effect of crosslinking, 2 types of adsorption gels, the crosslinked gels using ethylene glycol diglycidyl ether and those were not crosslinked prepared. These are abbreviated as crosslinked and uncrosslinked or non-crosslinked gels, respectively, hereafter. The uncrosslinked and crosslinked DTC *β*-chitosan gels were prepared by a single and four step reactions according to the synthetic routes shown in **Schemes 1 and 2**, respectively. Analytical grade reagents for the chemical modification, metal salts, and other chemicals were purchased from Wako Pure Chemical Industries, Ltd. and were used without further purification. The immobilizing reactions of the functional groups of dithiocarbamate onto *β*-chitosan is shown in **Schemes 1 and 2** were carried out in a similar manner to the preparation of lipophilic DTC chitosan gel from *O*,*O*' dodecanoyl chitosan [25].



Scheme 1. Synthetic route of uncrosslinked DTC *β*-chitosan.

Preparation of Uncrosslinked DTC β-Chitosan

Three grams of *β*-chitosan (15.6 mmol (counted by the number of primary amino groups) was dissolved into 300 cm^3 of 10 vol% aqueous acetic acid solution. Methanol (200 cm^3) and carbon disulfide (8.00 cm^3, d=1.26 g cm^{-3}, 13.2 mmol) were added into this viscous solution. After shaking for half an hour, 28 wt% ammonia solution (90.0 cm^3, d=0.904 g cm^{-3}, 1.24 mol) was slowly added. After shaking for further 24 h at room temperature, the mixture was filtered. The crude gel of the filter cake was washed with methanol until the filtrate became clear. After the gel was further washed with distilled water and dried *in vacuo*, pale yellow solid was obtained. It was ground and sieved by 300 μm sieve. The yield was 2.10 g. Sulfur contents measured using combustion ion chromatography was found to be 2.68 mol kg^{-1}-gel. For the purpose of stable protecting of DTC groups, this prepared sample was converted to ammonium salt by neutralizing using dilute ammonia solution followed by washing with distilled water and drying *in vacuo*.

Preparation of Crosslinked DTC β-Chitosan

Ten grams of *β*-chitosan (55.8 mmol (counted by the number of primary amino groups)) was dispersed into 200 cm^3 ethanol. Benzaldehyde (40 cm^3, d=1.04 g cm^{-3}, 392 mmol) was added to this suspension, then the mixture was stirred for 24 h at room temperature. After filtration, the crude gel was washed with ethanol to remove excess amounts of benzaldehyde and distilled water, followed by drying *in vacuo*.

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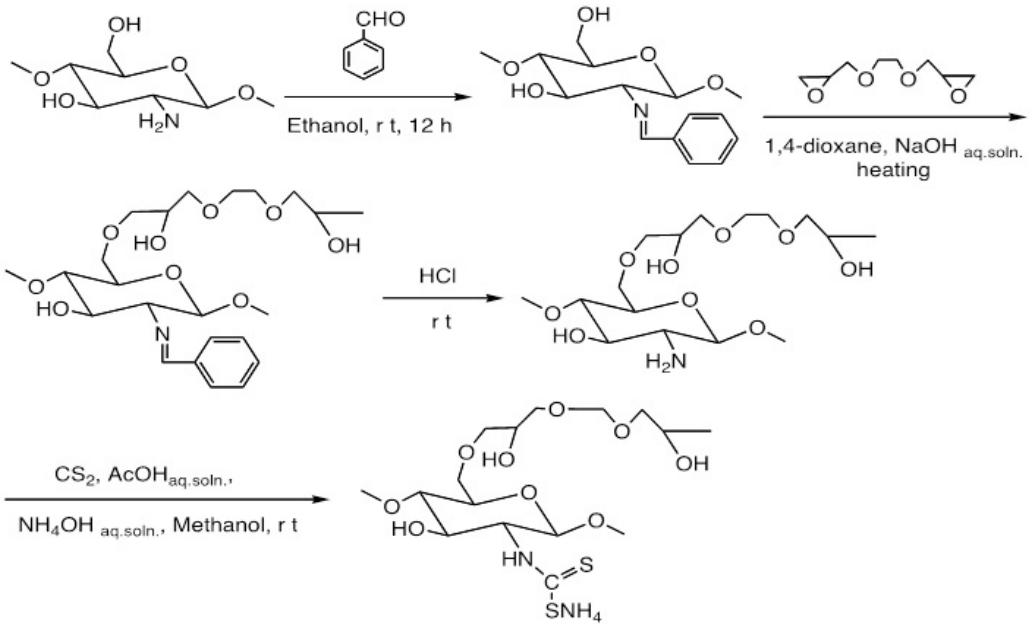

Scheme 2. Synthetic route of crosslinked DTC *β*-chitosan.

The obtained dry gel was added together with ethylene glycol diglycidyl ether (16.0 g, 91.9 mmol) as a crosslinking reagent to the mixture of 1,4-dioxane (150 cm^3) and 1 M (M=mol dm^{-3}) sodium hydroxide solution (20.0 cm^3) to undergo the reaction at 50-60°C for 3 h, after which the suspension was filtered and the crude gel was washed with ethanol and distilled water each three times, and then dried *in vacuo*.

Thus obtained dry gel was added to 0.5 M hydrochloric acid solution (500 cm^3) and the mixture was stirred for 18 h at room temperature. After decantation, the gel was washed with ethanol and distilled water each three times, then dried at 65°C for 10 h.

Thus produced dry gel (5.00 g) was dissolved into 10 vol% aqueous acetic acid solution (300 cm^3). Methanol (200 cm^3) and carbon disulfide (10.0 cm^3, d=1.26 g cm^{-3}, 16.5 mmol) were added to this viscous solution. After shaking for 5 min, 28 wt% ammonia solution (100 cm^3, d=0.904 g cm^{-3}, 1.38 mol) was slowly added. After further shaking for 24 h at room temperature, the mixture was filtered. The crude gel of the filter cake was washed with ethanol and distilled water each three times, and then further stirred with ethanol (500 cm^3) to wash for 32 h at room temperature. The gel was dried at 65°C for 12 h to obtain pale yellow solid, which was ground and sieved by 300 μm sieve. The yield of thus prepared final product gel was 5.10 g. Sulfur contents in the prepared gels were measured by means of combustion ion chromatography (ion chromatography (Dionex ICS-1500) equipped with automatic combustion equipment (MITSUBISHI AQF-100), by which solid sample is completely pyrolyzed into gases, including SO_2, which are nebulized in absorbing solution, where SO_2 is further oxidized by the aid of H_2O_2 into SO_4^{2-} ion to be quantitatively analyzed by the ion chromatography.

For the purpose of stably stocking thus prepared sample as ammonia salt, the gel was neutralized using dilute ammonia solution followed by washing using distilled water and dried *in vacuo*.

Solubility Test in Acidic Solutions

For comparison of the feed material, the solubility of *β*-chitosan and *α*-chitosan was measured at varying pH in dilute hydrochloric acid solution. Further, similar dissolution tests were carried out for both products, crosslinked and non-crosslinked DTC *β*-chitosan, to investigate the effect of crosslinking. Here, 20 mg of the solid sample was added into the 15 cm^3 of dilute hydrochloric acid solution and shaken at 30°C for 24 h. After the filtration, total organic carbon (TOC) concentrations in the filtrates were measured using a TOC meter (Shimadzu TOC-V) and % dissolution was calculated according to equation (1).

$$\% \text{ dissolution} = (C_{dissolved}/C_i) \times 100 \quad (1)$$

Where, $C_{dissolved}$ is total carbon amount dissolved into the aqueous dilute hydrochloric acid solution, the filtrate, measured by the TOC meter while C_i is total carbon content in the gel employed, which was measured by totally dissolving the gel in aqua regia followed by dilution with water also using the TOC meter.

Batch Adsorption Tests

Batch adsorption tests were carried out in the similar manner reported in the previous work [27,28]. Batch adsorption tests were carried out by shaking 25 mg of the gel together with 15 cm^3 aqueous solution containing 1 mM metal nitrate at 30°C using thermostat shaker. The pH of the solution was adjusted by using 0.1 M nitric acid and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer solution and measured using Beckman *φ*-45 pH meter. After filtration, metal concentrations in the filtrates were measured using atomic absorption spectrophotometer (AAS, Shimadzu AA-6650).

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% adsorption was calculated as follows.

$$\% \text{ Adsorption} = \{(C_i - C_{eq})/C_i\} \times 100 \quad (2)$$

Amount of adsorption on the gel, q (mol kg^{-1}-gel), was calculated as follows.

$$q = \{(C_i - C_{eq})/w\} \times V \quad (3)$$

Where, C_i (mol dm^{-3}) and C_{eq} (mol dm^{-3}) are initial and equilibrium metal concentrations, respectively, while V (dm^3) and w (kg) represent the volume of aqueous solution and weight of the gel, respectively.

Column Adsorption Test

The test of breakthrough followed by elution for the separation of low concentration of Cd(II) from the large excess concentration of Zn(II) was carried out at 30°C using a glass column (diameter=8 mm) packed with crosslinked or non-crosslinked DTC *β*-chitosan gel as shown in **Figure 1**. In this column, 0.150 g of the tested gel was packed after mixed together with 0.1 g of glass beads (average diameter 1.3 mm) to form the adsorption bed, which is further put between layers of the same size of glass beads to uniform the flow rate distribution. The pH was adjusted at 3.0 and the concentrations of Zn(II) and Cd(II) in the feed solution were 1 and 0.1 mM, respectively. The feed solution was percolated into the column at a constant flow rate of 4.9 cm^3/h using a peristaltic pump (IWAKI PST-100N, Japan). Before initiation of the feeding, the column was conditioned by passing the aqueous solution of the same pH containing no metal ion overnight in advance. After the breakthrough, the column was washed using distilled water so as to expel unbounded metal ions, and then the metal ions loaded on the adsorption bed was eluted using 0.1 M nitric acid. The effluent samples were collected by fraction collector (Bio-Rad, model 2110) at each 1 h to measure the metal concentrations using AAS.

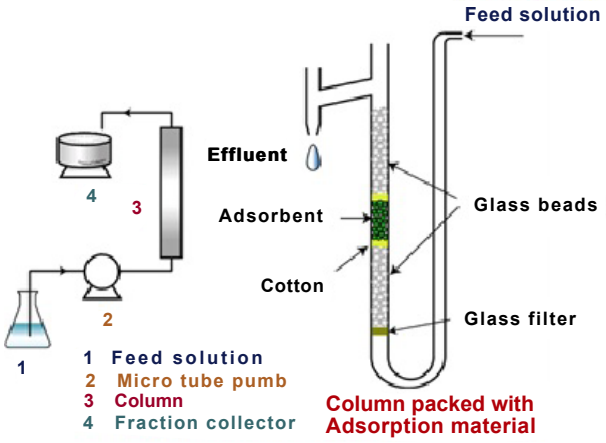

Figure 1. Schematic setup of the column packed with crosslinked or non-crosslinked DTC *β*-chitosan gel for the separation of Cd(II) from Zn(II).

RESULTS AND DISCUSSION

Characterization of the DTC β-Chitosan Gels

Figure 2 shows the FTIR spectra of *β*-chitosan, the feed material, and crosslinked DTC *β*-chitosan gel, the final product, as well as crosslinked *β*-chitosan for comparison. From the observation of the peaks at around 1,500 cm^{-1} assigned to *C-N* single bond adjacent to a sulfur atom and at around 1,000 cm^{-1} assigned to *C*=S double bond adjacent to the sulfur atom, the introduction of DTC groups onto the polymer matrices of chitosan was confirmed. Although the peaks derived from DTC groups were not significant, it is in agreement with the observation by Muzzarelli *et al.*, who reported that the peaks assigned to *N-C*=S appeared at 1480 cm^{-1} and 940 cm^{-1} in the case of DTC *α*-chitosan gel [23].

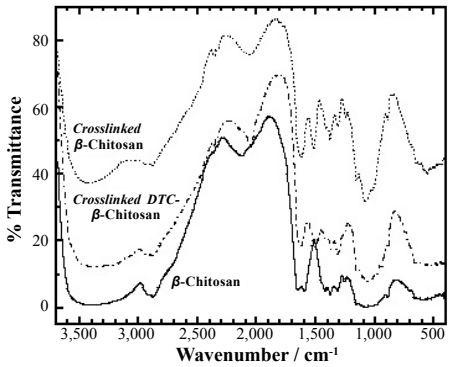

Figure 2. FTIR spectra of original *β*-chitosan, crosslinked unmodified *β*-chitosan gel and crosslinked DTC *β*-chitosan gel.

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The sulfur contents in the uncrosslinked and crosslinked DTC β-chitosan gels measured as mentioned earlier were 2.68 and 2.22 mol kg^{-1}-gel, respectively, suggesting that the amounts of the immobilized DTC functional groups are 1.34 and 1.11 mol kg^{-1}-gel, respectively, because DTC functional groups contain two sulfur atoms. The higher amount of the immobilized DTC functional groups onto the uncrosslinked gel than the crosslinked gel might be attributed to unsuccessful protection of primary amino groups from the attack of the crosslinking reagent, i.e., the number of primary amino groups effective for the reaction with CS_2 might be decreased by the crosslinking reaction.

Solubility Test into Acidic Solutions

Figure 3 shows the effect of pH on % dissolution of the gels of crosslinked and uncrosslinked DTC β-chitosan in dilute hydrochloric acid solutions at varying pH together with those of original β- and β-chitosans, for comparison. As mentioned earlier, α-chitosan has crystalline nature while β-chitosan is amorphous. However, both original chitosans exhibited high aqueous solubility at pH=1 - 2 regardless of the degree of their crystallinity. On the other hand, both crosslinked and uncrosslinked DTC β-chitosan gels are hardly dissolved in the whole pH 1-6 tested. Similar behavior was observed also in dilute nitric acid solutions. Consequently, it appears that the immobilization of DTC functional groups enhanced the hydrophobicity of the prepared gels, suppressing their aqueous solubility.

From this result, it is reasonable to consider that the crosslinking is not always necessary for DTC β-chitosan gel in case adsorption is carried out in the pH range 1-6 due to its insolubility nature.

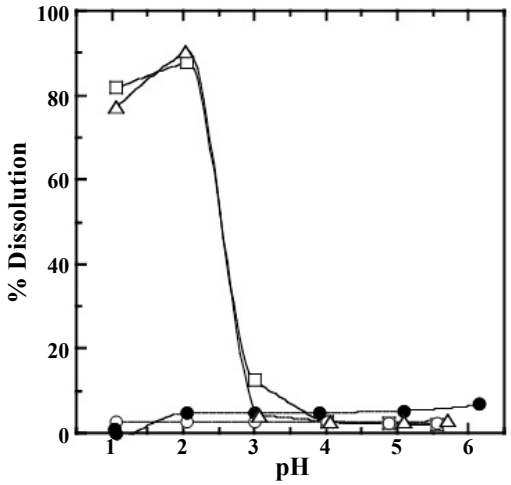

Figure 3. Effect of pH on % dissolution in dilute hydrochloric acid solutions of the prepared chitosan gels and feed material chitosan, for comparison. □: original β-chitosan, ○: uncrosslinked DTC β-chitosan gel, ●: crosslinked DTC β-chitosan gel, Δ: original α-chitosan.

Batch-wise Adsorption Test

Figure 4 shows the effect of shaking time on % adsorption of Cd(II) ion on the uncrosslinked and crosslinked DTC β-chitosan gels. Although it takes 20 h for non-crosslinked DTC β-chitosan gel to reach equilibrium, it takes only 4 h for crosslinked one; that is, the latter gel exhibits fast adsorption compared with the former gel, which is inferred to be attributable to the high polarity or high electro-negativity of the crosslinked moiety containing many ethereal oxygen atoms, exhibiting high affinity for cationic species such as Cd(II) ions.

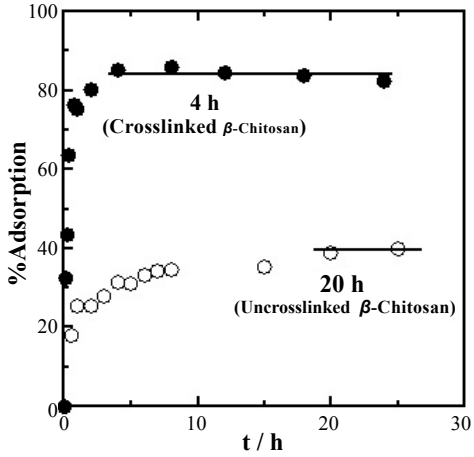

Figure 4. Effect of shaking time on % adsorption of Cd(II) on uncrosslinked and crosslinked DTC β- chitosan gels.

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Figure 5a shows the effect of pH on % adsorption of Cd(II) and Zn(II) on the uncrosslinked DTC β-chitosan gel and on the original β-chitosan while **Figure 5b** shows the similar plots on the crosslinked DTC β-chitosan gel and crosslinked unmodified β-chitosan gel for comparison.

It can be seen from **Figure 5a** that although the adsorption of both Cd(II) and Zn(II) takes place at nearly the same pH on original β-chitosan, suggesting only poor selectivity to Cd(II) over Zn(II), the modification with DTC functional groups greatly enhances the adsorption of these metal ions where the enhancement for Cd(II) is much greater than for Zn(II), resulting in the big improvement of the selectivity to Cd(II) over Zn(II). Although the adsorption behavior of Cd(II) on uncrosslinked DTC β-chitosan gel appears complicated at pH 3-6, the adsorption of both metal ions increases with increasing pH, suggesting that it takes place according to the cation exchange mechanism between hydrogen atoms of DTC functional groups of the modified chitosan and cationic metal species.

From the comparison of **Figure 5a** with **5b**, the adsorption of Cd(II) on DTC β-chitosan gel is lowered by crosslinking at pH higher than 4 while that of Zn(II) is also a little bit lowered by crosslinking, suggesting the crosslinking impedes the adsorption in the case of DTC β-chitosan gel. However, in the case of unmodified β-chitosan, the adsorption of Cd(II) was increased by the crosslinking while that of Zn(II) appeared nearly the same. It might be considered that polyether oxygen atoms used for the crosslinking preferentially coordinate Cd(II), improving its adsorption.

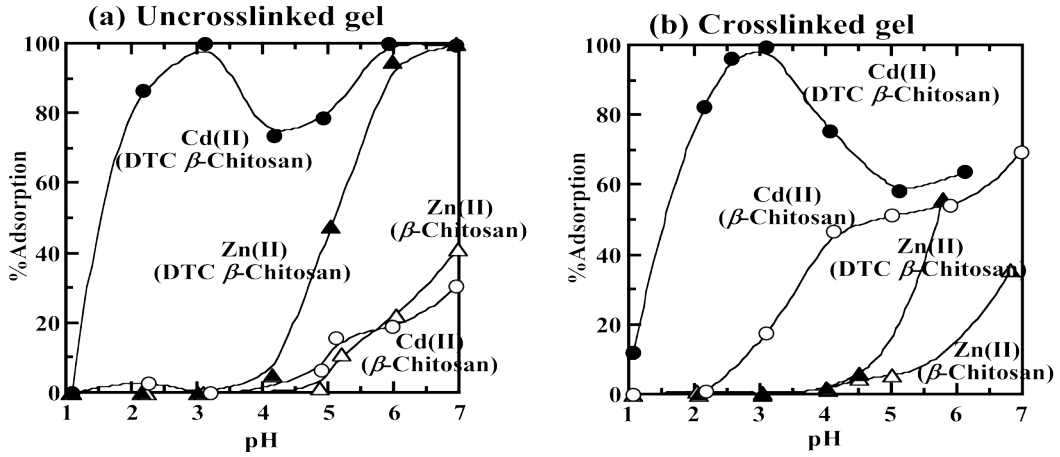

Figure 5. Effect of pH on % adsorption of Cd(II) and Zn(II) on (a) uncrosslinked DTC β-chitosan gel and original β-chitosan, and on (b) crosslinked DTC β-chitosan and crosslinked unmodified β-chitosan gel.

Figure 6 shows adsorption isotherms of Cd(II) on the uncrosslinked and the crosslinked DTC β-chitosan gels. Both plots exhibit the typical Langmuir type isotherms, because the gels have ion-exchangeable DTC groups. From the values at plateau region, the maximum adsorption capacities of uncrosslinked and crosslinked DTC β-chitosan gels were evaluated as 0.60 and 0.67 mol kg^{-1}-gel, respectively. From the comparison between the maximum adsorption capacities and the amounts of the immobilized DTC functional groups on each gel, the stoichiometric relationship between Cd(II) ion and DTC group can be roughly estimated as 1:2. In case a single DTC group functions as a bidentate group, it is reasonable to consider that divalent positive charge of Cd(II) ion is neutralized by 2 DTC functional groups of modified chitosan; i.e., Cd(II) is adsorbed by forming 1:2 Cd(II):DTC polymeric complexes.

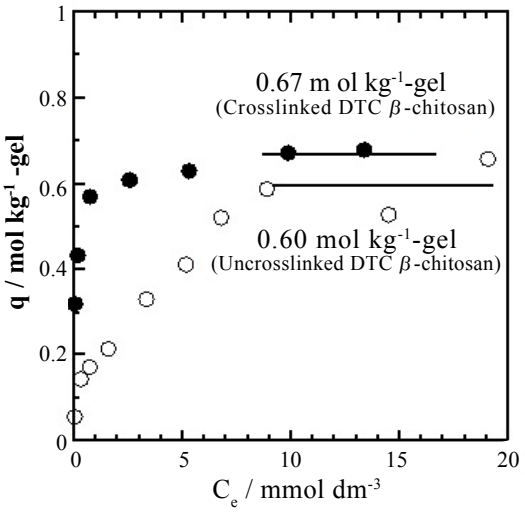

Figure 6. Adsorption isotherms of Cd(II) on uncrosslinked and crosslinked DTC β-chitosan gels at 30 °C.

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Separation of Cd(II) from Zn(II) Using a Packed Column

The selective removal of low concentration of Cd(II) from the large excess concentration of Zn(II) was investigated using a column packed with the uncrosslinked or crosslinked DTC β-chitosan gels as mentioned earlier.

Figure 7a and 7b show breakthrough and elution profiles of Cd(II) and Zn(II) using a column packed with uncrosslinked DTC β-chitosan gel. Different from the result of the batch-wise adsorption test shown in **Figure 5a**, the breakthrough curves for Cd(II) and Zn(II) shown in **Figure 7a** are close each other, suggesting that the mutual separation of Cd(II) from Zn(II) is unsatisfactory by using packed column and it is difficult to recover pure Zn(II) ion free from Cd(II) ion by the breakthrough process. In **Figure 7b**, only Cd(II) ion was eluted while Zn(II) ion was hardly detected. However, the outlet concentration of Cd(II) was low compared to that in the feed solution; i.e., the maximum value of the elution profile of Cd(II) ion was only around 0.85. Additionally, it takes a long time for Cd(II) ion to be totally eluted from this column. These results may be affected by the slow adsorption on the uncrosslinked gel shown in **Figure 4**.

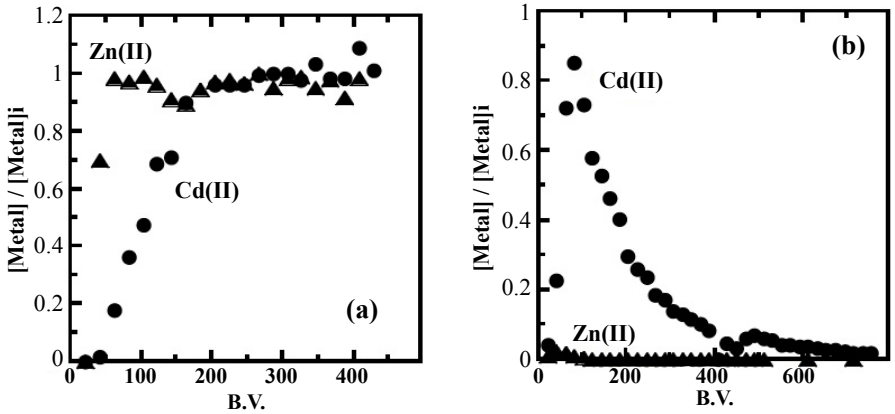

Figure 7. Breakthrough (a) and elution (b) profiles of Cd(II) and Zn(II) from the column packed with uncrosslinked DTC β-chitosan gel.

Figure 8a and 8b show breakthrough and elution profiles of Cd(II) and Zn(II) from the column packed with the crosslinked DTC β-chitosan gel. Different from the result using the uncrosslinked gel shown in **Figure 7a**, Zn(II) was immediately broke through just after the initiation of the feed, while the breakthrough of Cd(II) took place after as late as about 140 B.V. This result clearly suggests that pure Zn(II) solution can be recovered before the breakthrough of Cd(II) and that the complete removal of trace concentration of Cd(II) from large excess concentration of Zn(II) ion was achieved by using this packed column. On the other hand, as shown in **Figure 8b**, the sharp elution profile of Cd(II) was observed using 0.1 M nitric acid solution. In this case, outlet Cd(II) concentration was four times higher than the feed concentration and the eluted solution was free from the contamination of Zn(II). It is evident from the results that the performance of crosslinked DTC β-chitosan gel is much better than that uncrosslinked DTC β-chitosan gel in the column operation.

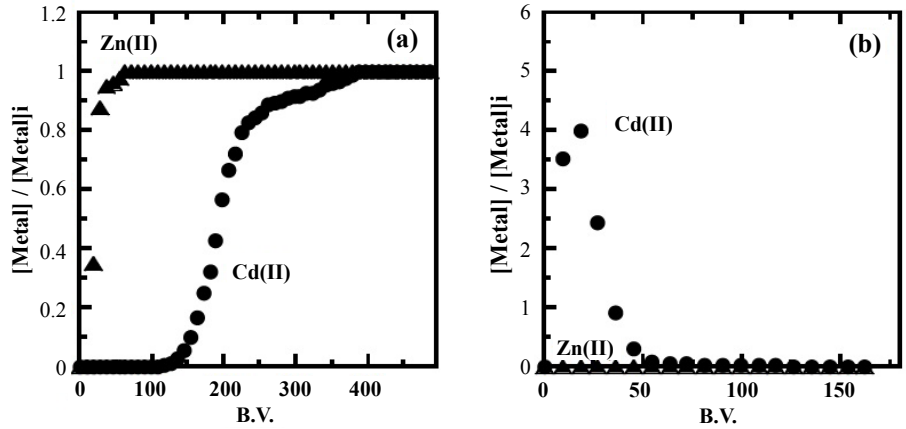

Figure 8. Breakthrough (a) and elution (b) profiles of Cd(II) and Zn(II) from the column packed with crosslinked DTC β-chitosan gel.

CONCLUSIONS

Crosslinked and uncrosslinked adsorption gels containing the functional groups of dithiocarbamate were prepared from β-chitosan by a chemical modification to investigate their adsorption behaviors for Cd(II). The contents of the immobilized dithiocarbamate groups onto the gels were evaluated for the sulfur content measured by combustion ion chromatography were 1.34 and 1.11 mol kg^{-1}-gel in the case of uncrosslinked and crosslinked gels, respectively. Both gels were hardly soluble in aqueous solutions regardless of pH over the pH 1-6 and exhibited rapid adsorption rate and high selectivity to Cd(II). Maximum

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adsorption capacities of Cd(II) on the crosslinked and uncrosslinked gels were 0.67 and 0.60 mol kg^{-1}-gel, respectively. Successful mutual separation of Cd(II) from Zn(II) was achieved using a column packed with crosslinked gel.

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