

# DURABILITY OF CHITOSAN/CELLULOSE HYDROGEL BEADS REGENERATED FROM AN IONIC LIQUID IN ACIDIC AND BASIC MEDIA AND THEIR METAL ADSORPTIVE CHARACTERISTICS

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## Abstract

*Chitosan–cellulose gel beads were regenerated from an ionic liquid, and their application to a metal adsorbent was examined. The chitosan–cellulose gel beads, which were prepared from 1-ethyl-3-methylimidazolium acetate, were more stable in the acidic and basic aqueous solutions than cellulose or chitosan. The adsorption of copper on chitosan–cellulose gel beads was examined, and the adsorption amount of copper ion increased with pH, suggesting that amino groups on chitosan were related to adsorption. The adsorption isotherm of copper, zinc, and nickel ions was well described by the Langmuir model, and the adsorption ability of these metal ions obeyed the Irving-Williams series.  $Fe^{3+}$ ,  $Mn^{2+}$ , and  $Co^{2+}$  from a buffer solution and  $Pt^{4+}$ ,  $Au^{3+}$ , and  $Pd^{2+}$  from a hydrochloric acid solution were not adsorbed on the chitosan–cellulose gel beads.*

**Keywords:** *Chitin, cellulose, ionic liquid, Emim, adsorption, copper, zinc, nickel*

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## 1. Introduction

Chitosan, which consists of D-glucosamine with  $\beta$ -(1,4) bonds, is a superior metal adsorbent and is expected to be used in the removal of metallic ions in wastewater. Its adsorption capacity and selectivity can be enhanced by chemical modification [1]. However, chitosan is easily soluble in dilute acidic solutions because of the protonation of the amino group. In most cases, crosslinking among amino groups of chitosan is carried out for insolubilization. The metal adsorption capacity generally decreases with an increase in the extent of crosslinking because amino groups on chitosan bind the metal ions. Recently, the preparation of chitosan–cellulose hydrogel beads enhanced the mechanical and chemical strength. Li and Bai mechanically prepared chitosan–cellulose hydrogel beads [2]. The prepared gel beads were also soluble in the acidic solution, and crosslinking of the gels was needed as an adsorbent. Because an ionic liquid can dissolve polysaccharides such as cellulose and chitosan, Sun *et al.* prepared chitosan–cellulose beads by regeneration from the ionic liquid 1-butyl-3-methyl imidazolium chloride ([Bmim][Cl]) [3]. Their gel beads were stable in a 0.1 mol/dm<sup>3</sup> HCl solution and were applied to Ni adsorption. Chitosan–cellulose gel beads, regenerated from [Bmim][Cl], were also applied to microcystin adsorption [4]. Moreover, to easily recover the gel beads, magnetic cellulose–chitosan hydrogels were prepared as a metal adsorbent [5,6]. Chitosan–cellulose gel beads that were regenerated from 1-ethyl-3-methyl imidazolium acetate ([Emim][Ac]) were prepared and applied to dye adsorption [7]. The preparation condition of the chitosan–cellulose gel beads regenerated from [Emim][Ac] was milder than those of [Bmim][Cl].

In this study, we prepared chitosan–cellulose gel beads regenerated from [Emim][Ac] and examined their durability in acidic and basic solutions and the adsorptive characteristics of the metal ions.

## 2. Materials and Methods

### 2.1. Chemicals

Cellulose powder (type C; Advantec, Japan) and chitosan (low molecular weight, 75–85% deacetylated, Sigma-Aldrich, USA) were used. The ionic liquid used in this study was 1-ethyl-3-methyl imidazolium acetate ([Emim][Ac]) (IOLITEC Ionic Liquid Technology, Germany). All the remaining reagents were of analytical grade and were used without further purification.

### 2.2. Preparation of Chitosan–Cellulose Hydrogel Beads

Chitosan–cellulose hydrogel beads were prepared by modifying a previously reported procedure [7]. Cellulose and chitosan were added to [Emim][Ac] and stirred at 80°C to form a homogeneous solution with a total concentration of 5–10% (w/w). Using a Terumo 1-mL syringe, the obtained solution was extruded dropwise into water and left to stand for 1 h for the beads to harden. Then, the hydrogel beads were collected and thoroughly rinsed with deionized water. The obtained hydrogel beads were stored in the deionized water and filtered just before use. Although cellulose hydrogel beads were prepared in a similar procedure, chitosan gel beads could not be prepared.

### 2.3. Characteristic of Chitosan–Cellulose Hydrogel Beads

Both the specific surface area and the pore size of the hydrogel beads were measured by micromeritics automatic surface area and a porosimetry analyser (Tristar 3000, Shimadzu, Japan). The surface of the adsorbent was observed by electron microscopy (JSM7500 FD, JEOL, Japan). The hydration rates of the hydrogel beads were measured by a moisture analyser (MOC63u, Shimadzu, Japan). The durability tests of the

hydrogel beads were conducted in 0.1 mol/dm<sup>3</sup> acetic acid, 0.1 mol/dm<sup>3</sup> HCl, 0.1 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>, and 0.1 mol/dm<sup>3</sup> NaOH solutions.

## 2.4. Adsorption of Metals on Hydrogel Beads

The adsorption tests of various metal ions, including Fe(III), Cu(II), Co(II), Ni(II), Zn(II), Mn(II), Pt(IV), Au(III), and Pd(II), on hydrogel beads were measured to evaluate the adsorption ability by shaking 250 mg of gel beads in 20 mL of the test solution that contained 1.0 mmol/dm<sup>3</sup> of the individual metal ions at 100 rpm for 24 h at 30°C. It was confirmed that an adsorption equilibrium was attained within 12 h. The pH values and acidities were adjusted using the following solution: 0.1 mol/dm<sup>3</sup> HCl/CH<sub>3</sub>COOH/CH<sub>3</sub>COONa for Fe(III), Cu(II), Co(II), Ni(II), Zn(II), and Mn(II) and 1–5 mol/dm<sup>3</sup> HC for Pt(IV), Au(III), and Pd(II). After attaining equilibrium, the mixtures were filtered to separate the gel beads.

The adsorption isotherms were measured to evaluate the maximum adsorption capacity of both adsorbents by shaking 250 mg of the adsorbents with 10 mL of the test solutions containing individual metals that ranged from 0.5 to 40 mmol/dm<sup>3</sup>. The initial and residual concentrations of the metal ions in the filtrate were measured by inductively coupled plasma atomic emission spectrometry (ICPS-8100, Shimadzu, Japan). The pH values of the solution were measured with a pH meter (F-52, Horiba, Japan) before and after the adsorption experiment. The amount of adsorbed metal ions was calculated from the difference in metal concentration between the initial solution and the filtrate. The amount of the metal adsorbed on the adsorbent [ $q$  (mmol/g-adsorbent)] was calculated using the following equation:

$$q = \frac{C_i - C_f}{M} \times V \quad (1)$$

where  $C_i$  and  $C_f$  are the metal concentrations (mmol/dm<sup>3</sup>) before and after adsorption,  $V$  is the volume of the test solution (L), and  $M$  is the dry mass of the adsorbent (g).

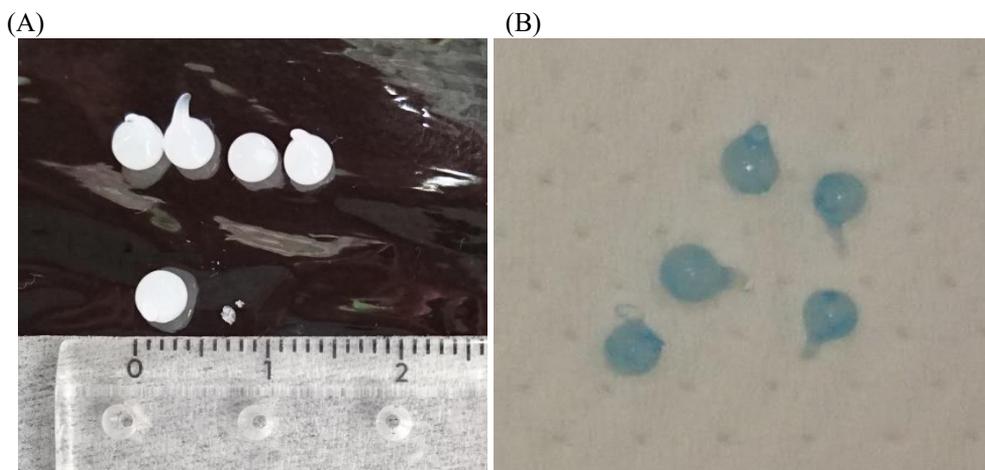
## 3. Results and Discussion

### 3.1 Characteristics of Chitosan–Cellulose Hydrogel Beads

Figure 1 shows photo images of the chitosan–cellulose gel beads before and after copper adsorption. The shapes were almost spherical, and the mean diameter of the beads was ca 4 mm. After Cu adsorption, the colour of the beads uniformly changed to blue, suggesting that copper was adsorbed on the chitosan–cellulose hydrogel beads. The average pore sizes and the specific surface areas of the cellulose beads and the chitosan–cellulose beads are listed in Table 1 with the hydration rates of the beads. The hydration rate of the chitosan–cellulose hydrogel beads exceeded that of cellulose. This result corresponds to a previous work, where adding cellulose in the chitosan reduced the water content [2].

**Table 1.** Characteristics of gel beads

	Specific surface area (m <sup>2</sup> /g)	Pore size (nm)	Hydration rate (%)
Cellulose 4 wt%	44.77	17.23	86.3
Cellulose 4 wt% + Chitosan 2 wt%	7.05	26.34	90.1



**Figure 1.** Images of chitosan–cellulose gel beads before (A) and after (B) copper adsorption.

### 3.2 Durability of Chitosan–Cellulose Hydrogel Beads

The chitosan–cellulose hydrogel beads, the cellulose beads, and the chitosan flakes were tested for durability in the acidic and basic solutions. Table 2 lists the ratio of the weights of the beads or flakes after being placed in water, 0.1 mol/dm<sup>3</sup> acetic acid, 0.1 mol/dm<sup>3</sup> hydrochloric acid, 0.1 mol/dm<sup>3</sup> sulfuric acid, and 0.1 mol/dm<sup>3</sup> sodium hydroxide solutions for 24 h to the initial weights of the beads. After 24 h, chitosan was completely dissolved in the acetic acid and hydrochloric acid solutions and the shapes of the cellulose–chitosan gel beads were maintained in all the tested solutions. The cellulose–chitosan gel beads that were formed by blending chitosan and cellulose were dissolved in an acetic acid solution [2], and the gels that were regenerated from [Bmim][Cl] were stable in the HCl aqueous solution with pH=1 [3]. The present gels regenerated from [Emim][Ac] were stable even in the acidic acid and basic solutions. This suggests that the interaction of cellulose and chitosan in the gel beads regenerated from the ionic liquid solution was critical for the durability.

**Table 2.** Durability of gel beads and flakes

	Water	Acetic acid	HCl	H <sub>2</sub> SO <sub>4</sub>	NaOH
Cellulose gel beads	1.00	0.98	1.00	1.00	0.68
Chitosan flakes	1.00	0.00	0.00	0.32	0.99
Cellulose–chitosan beads	1.00	1.00	0.99	0.94	0.93

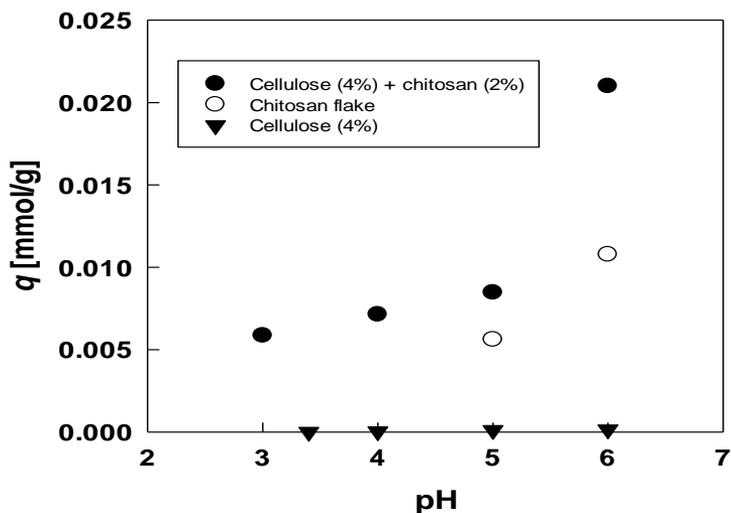
### 3.3 Adsorption of Metallic Ions on Chitosan-Cellulose Hydrogel Beads

Figure 2 shows the effect of pH on Cu adsorption on the chitosan–cellulose and cellulose gel beads, as well as chitosan flakes. As described above, chitosan flakes were dissolved in the acidic solution (pH=3 and 4). The Cu adsorption was attributed to chitosan [1]. The adsorption capacities of the chitosan–cellulose gel beads and the chitosan flakes increased with pH because of the protonation of the amino groups on chitosan at a lower pH [2,3].

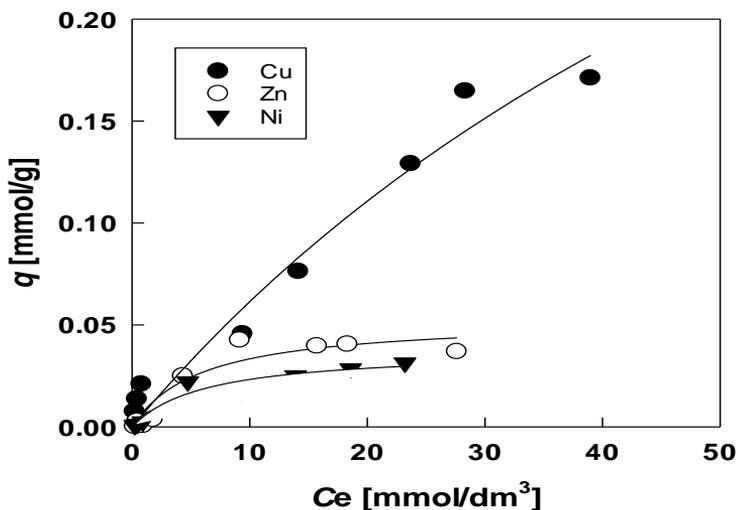
The adsorption ability of the chitosan–cellulose hydrogels for metals from the aqueous solution were examined. We observed no appreciable adsorption of Fe<sup>3+</sup>, Mn<sup>2+</sup>, and Co<sup>2+</sup>

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from the buffer solution and  $\text{Pt}^{4+}$ ,  $\text{Au}^{3+}$ , and  $\text{Pd}^{2+}$  from the hydrochloric acid solution. However, an adsorption affinity to  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  was exhibited. **Figure 3** shows the adsorption isotherms of these metals. The data were analysed by the Langmuir isotherm. The parameters, the maximum amount of adsorption ( $q_{\text{max}}$ ), and a constant of the Langmuir model ( $K$ ) were determined by a non-linear regression program included in the Sigmaplot 14 software. Solid lines in **Figure 3** were calculated by these parameters. The calculated lines agree well with the experimental results. The obtained parameters are listed in **Table 3**. The order of the  $q_{\text{max}}$  values was  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$  and obeyed the Irving-Williams series, which refers to the stabilities between metal cations and ligands.



**Figure 2.** Effect of pH on adsorption of  $\text{Cu}^{2+}$  on cellulose, cellulose (4%)–chitosan (2%) hydrogel beads, and chitosan flakes (initial  $\text{Cu}^{2+}$  concentration of  $1.0 \text{ mmol/dm}^3$ )



**Figure 3.** Adsorption isotherm of metallic ions on cellulose (4%)–chitosan (2%) hydrogel beads

**Table 3.** Langmuir parameters

	$10^2 q_{\max}$ (mmol/g)	$10^2 K$ (dm <sup>3</sup> /mmol)
<b>Cu</b>	56.7±3.2	1.21±0.92
<b>Zn</b>	5.28±0.92	17.1±9.1
<b>Ni</b>	3.76±0.65	16.2±8.5

#### 4. Conclusion

Chitosan–cellulose gel beads were regenerated from an ionic liquid ([Emim][Ac]) and used as an adsorbent for metal removal. The prepared cellulose–chitosan gel beads had higher stability in the acidic and basic aqueous solutions than cellulose or chitosan. The adsorption of Cu on the chitosan–cellulose gel beads increased with pH, suggesting that the amino groups on chitosan were concerned with adsorption. The adsorption isotherm of the metal ions was well described by the Langmuir model, and the adsorption ability of the metal ions obeyed the Irving-Williams series. The chitosan–cellulose gel regenerated from [Emim][Ac] had high chemical stability and excellent metal adsorption ability.

#### 5. Acknowledgments

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