

# Preparation, Characterization, and Behavior of Cellulose–Titanium(IV) Oxide Modified with Organosilicone

LING-ZHI MENG, CHUAN-QING DU, YUAN-YIN CHEN, YONG-BING HE

Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

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**ABSTRACT:** Cellulose–titanium(IV) oxide modified with organosilicone (CTSN) was prepared by a reaction of cellulose powder with titanate chloride, followed by a reaction with 4-aza-6-aminohexyl triethoxysilane, and was characterized by infrared spectroscopy, scanning electron microscopy (SEM), and thermogravimetric analysis. An SEM image of titanium(IV) oxide-coated cellulose and a Ti mapping image showed that titanium oxide was well dispersed on the cellulose surface. Titanium and silicon mapping images of CTSN, obtained with SEM, indicated that both oxides were uniformly dispersed on the cellulose surface. The atomic ratio of Ti to Si was obtained with X-ray energy spectral composition analysis. The adsorption behavior of CTSN toward Hg(II), Cu(II), Pb(II), Fe(III), and Cr(III) ions in aqueous solutions was determined. The adsorption behavior of CTSN toward human serum protein was preliminarily examined. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 61–66, 2002; DOI 10.1002/app.10188

**Key words:** composites; cellulose; adsorption; TiO<sub>2</sub>; human serum protein; organosilicone; modification

## INTRODUCTION

Cellulose is the most abundant naturally occurring polymer in the world. The replaceable, renewable, and biodegrading properties of cellulose have made it one of the most widely studied polymers.<sup>1–3</sup> The properties of cellulose may be improved with changes in its chemical structure. Cellulose derivatives have been used for the enrichment and separation of metal ions,<sup>4–6</sup> proteins,<sup>7</sup> and dyes.<sup>8</sup> These derivatives are obtained by the grafting, etherification, and esterification of cellulose. However, cellulose has not yet reached its potential in many areas of application. Although this high molecular weight polymer has plenty of hydroxyl groups (three reactive hydroxyl

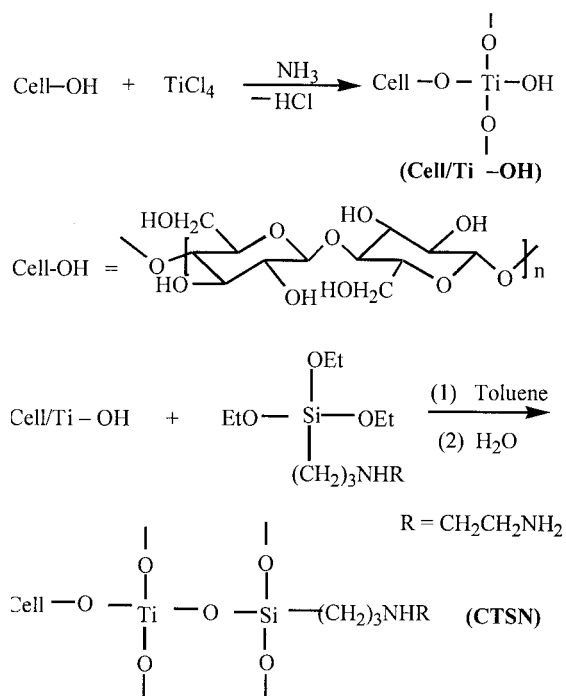
groups per anhydroglucose unit), these hydroxyl groups are involved in intermolecular and intramolecular hydrogen bonding.<sup>9,10</sup> For improvements in the activity of cellulose and enlarge its application scope, the breaking of cellulose hydrogen bonds is helpful. In recent years, the preparation and characterization of cellulose–metal oxide hybrid materials have been reported. Silva and coworkers<sup>5,11</sup> prepared cellulose coated with titanium(IV) oxide (Cell/Ti–OH), which has good adsorption behavior for metal ions. Alfaya and Gushikem<sup>12</sup> and Meng et al.<sup>13</sup> reported the preparation, characterization, and adsorption properties of cellulose–aluminum oxide modified with organosilicone, which can be immobilized efficiently on the surface of cellulose–aluminum oxide; these cellulose derivatives have better adsorption properties for metal ions.

In this article, we report on the preparation, characterization, and adsorption properties of cellulose–titanium(IV) oxide modified with 4-aza-6-aminohexyl triethoxysilane (CTSN), which has a

Correspondence to: Y.-B. He (ybhe@whu.edu.cn).

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Scheme 1

high adsorption capacity for heavy metal ions and transition-metal ions in aqueous solutions. With respect to Hg(II) and Cu(II) ions, the influence of the temperature of the aqueous solution and the concentration of CTSN on the adsorption capability is discussed. The adsorption ability of CTSN for human serum protein is also explored. The preparation route of CTSN is shown in Scheme 1.

## EXPERIMENTAL

### Materials

Cellulose powder was supplied by the Shanghai Chemical Reagents Factory (Shanghai, China). Titanic chloride was supplied by the Peking Zhong-Lian Chemical Reagents Factory (Peking, China). 4-Aza-6-aminoethyl triethoxysilane was supplied by the Wuhan University Chemical Plant (Wuhan, China). Other chemicals were supplied by the Shanghai Chemical Reagents Co. (Shanghai, China); they were analytical-reagent-grade and were used without further purification, unless stated otherwise.

### Measurements

Elemental analyses were carried out with a 1106 elemental autoanalysis apparatus (Carlo-Erba,

Italy). The infrared spectra were recorded on a Nicolet 170SX Fourier transform infrared spectrometer (Hitachi, Tokyo, Japan). Scanning electron microscopy (SEM) was performed with an X-650 scanning electron microscope (Hitachi). Thermogravimetric analyses (TGA) were carried out on a TGS-2 thermal analyzer (Perkin-Elmer, USA). The runs were performed at a heating rate of 10°C/min from 30 to 750°C in static air. The concentrations of metal ions were determined by titration or by a 180-80 atomic absorption spectrometer (Hitachi). The concentrations of human serum protein were determined with a 1061 ultraviolet absorption spectrometer (Hitachi).

### Preparation of Cell/Ti-OH<sup>5,11</sup>

Cellulose powder (20 g) was immersed in 200 mL of purified carbon tetrachloride, and the mixture was stirred for about 30 min at room temperature; then, 5 mL of titanac chloride was added. The mixture was stirred and refluxed for 5 h under a nitrogen atmosphere. After cooling, the mixture was filtered under reduced pressure and washed with carbon tetrachloride. Then, the residue was immersed in ethanol, and the current of ammonia gas was passed through it for the elimination of hydrochloride. The residue was filtered under reduced pressure, exhaustively washed with a mixed solvent of ethanol and water (50 vol %), and finally washed two times with doubly distilled water. The solid was dried at 80°C under reduced pressure to a constant weight. Cell/Ti-OH was obtained as a white powder.

The quantity of titanium(IV) oxide was determined by the calcination of 0.2 g of Cell/Ti-OH at 700°C in air for 2 h; the residue was weighed, and the titanium(IV) oxide content was 8.0% (w/w). Per gram of Cell/Ti-OH, there was about 1.0 mmol of titanium(IV) oxide coating.

### Modification of the Cell/Ti-OH Surface with Organosilicone

Cell/Ti-OH (4 g) was suspended in 40 mL of dry toluene and stirred for 30 min at room temperature. 4-Aza-6-aminoethyl triethoxysilane (4.2 g) was added and stirred at 90°C for 6 h under a nitrogen atmosphere. After the addition of a little distilled water, the reactant was stirred continuously at 90°C for 1 h under a nitrogen atmosphere. The residue was filtered and extracted with alcohol in a Soxhlet apparatus for 4 h and then dried at 80°C under reduced pressure to a constant weight. CTSN was obtained as a light-

yellow powder, with elemental analysis showing a nitrogen percentage of 4.49; per gram of CTSN, 1.60 mmol of the Si—(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> residue group was immobilized. The total content of TiO<sub>2</sub> and SiO<sub>2</sub> (%) was 16.1, as obtained by calcination in air at 700°C for 2 h and weighing.

For a contrast experiment, cell/Ti—OH modified by tetraethoxysilane (CTS) was similarly prepared with tetraethoxysilane instead of 4-aza-6-aminohexyl triethoxysilane. The total content of TiO<sub>2</sub> and SiO<sub>2</sub> (%) was 15.7, as obtained by calcination in air at 700°C for 2 h and weighing.

### Adsorption of CTSN for Metal Ions<sup>13</sup>

The adsorption behavior of CTSN toward metal ions was examined. CTSN ( $W = 0.02$  g) and a metal-ion aqueous solution ( $V = 10$  mL) of a known concentration ( $C_i = 2$  mmol/L) were placed in a 25-mL closed flask. A series of such flasks were shaken at a constant speed (100 times/min) and a specified constant temperature for 2 h. The metal-ion concentration ( $C_e$ ) of the liquid phase was determined by titration with EDTA for Hg(II), Cu(II), and Pb(II) or by atomic absorption spectrometry for Fe(III) and Cr(III). The adsorption capacity ( $Q$ ) and the adsorption percentage ( $E$ ) were calculated as follows:

$$Q = (C_i - C_e)V/W \text{ (mmol/g)}$$

$$E(\%) = (C_i - C_e)/C_i \times 100$$

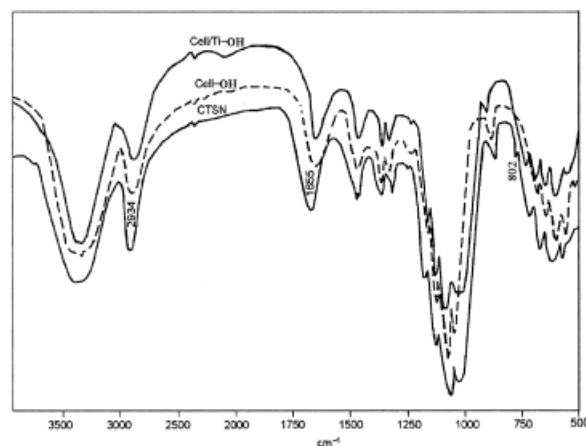
### Adsorption of CTSN for Human Serum Protein

The adsorption ability of CTSN for human serum protein was examined with an adsorption experiment. CTSN ( $W = 0.02$  g) and a human serum protein solution of a known concentration ( $C_i = 2.0$  mg/mL) were placed in a closed flask. The flask was shaken at a constant temperature (30°C) and speed (100 times/min) for 2 h. The protein concentration ( $C_e$ ) that remained in the solution was determined with ultraviolet absorption spectrometry.<sup>14,15</sup> The adsorption capacity ( $Q$ ) was calculated by the aforementioned equation.

## RESULTS AND DISCUSSION

### Infrared Spectra Characterization

The infrared spectra of cellulose (Cell—OH), Cell/Ti—OH, and CTSN were determined and are shown in Figure 1. Figure 1 indicates that the



**Figure 1** Infrared spectra of Cell—OH, Cell/Ti—OH, and CTSN.

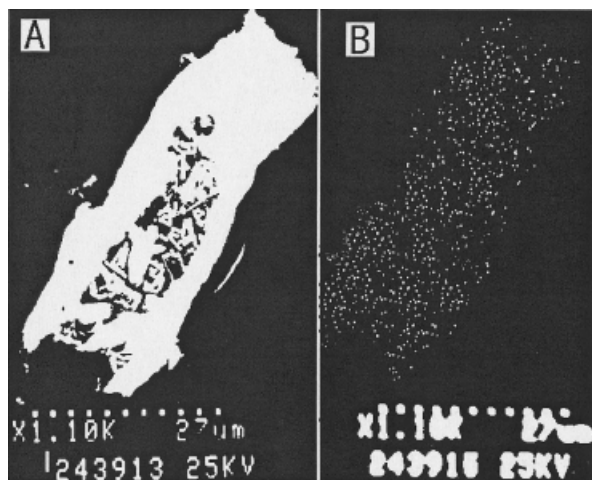
spectral bands of Cell/Ti—OH and CTSN are wider than the band of Cell—OH within 1200–800 cm<sup>-1</sup>. This is due to the contribution of the stretching vibration of Ti—O, Si—O and Ti—O—Si (950–900 cm<sup>-1</sup>); these bands are overlapping the C—O stretching vibration spectral band. The N—H bending vibration of CTSN is overlapping the O—H bending vibration and results in a small increase in the wave number and strength within 1660–1600 cm<sup>-1</sup>. The Si—C strength vibration of CTSN is at 802 cm<sup>-1</sup>.

### SEM

To obtain the morphology of the Cell/Ti—OH and CTSN surfaces, we coated a sample with carbon under a high vacuum. The scanning electron microscope was connected to a secondary electron image, and X-ray energy-dispersive detectors were used. An SEM image of Cell/Ti—OH and its Ti mapping image are shown in Figure 2(a,b), respectively. Figure 2 indicates that titanium oxide is well dispersed on the cellulose surface.

Titanium and silicon mapping images of the CTSN surface are presented in Figure 3. The mapping image of titanium [Fig. 3(a)] shows that the titanium oxide is uniformly dispersed on the cellulose surface. The emission line of Ti ( $K\alpha$ ), observable as white points, is at 4.51 keV. The emission line of Si ( $K\alpha$ ), observable as white points [Fig. 3(b)], is at 1.74 keV. This shows that the organosilicone immobilized on the surface of cellulose-titanium(IV) oxide is also uniformly dispersed.

The atomic ratio of Ti to Si for CTSN is 1.0:2.62 (27.6:72.4), as determined by X-ray energy spec-

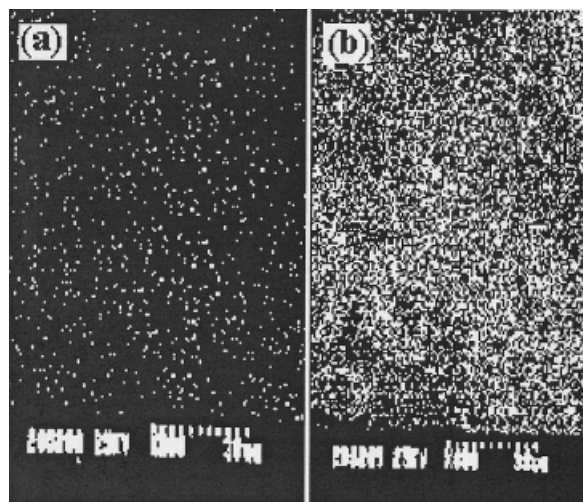


**Figure 2** (a) SEM image and (b) Ti mapping image of Cell/Ti—OH. The Ti ( $K\alpha$ ) emission line at 4.51 keV appears as white points.

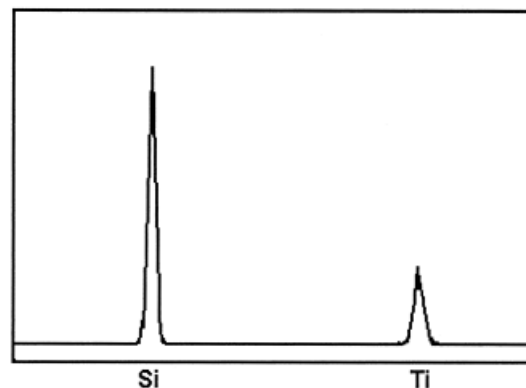
tral composition analysis (Fig. 4). The atomic ratio of Ti to Si of CTSN is 1.0:2.55 (28.2:71.8).

#### TGA

The thermogravimetry of Cell—OH, Cell/Ti—OH, and CTSN was determined, and the TG curves are presented in Figure 5. Differential thermogravimetry (DTG) curves of Cell—OH, Cell/Ti—OH, and CTSN show that the temperatures of the fastest decomposition rates are 326, 338, and 351°C for Cell—OH, Cell/Ti—OH, and CTSN, respectively. The temperature of the fastest decomposition rate for Cell/Ti—OH is somewhat higher than that of



**Figure 3** SEM mapping images of CTSN. The (a) Ti ( $K\alpha$ ) emission line at 4.51 keV and (b) Si ( $K\alpha$ ) emission line at 1.74 keV appear as white points.



**Figure 4** X-ray energy spectral composition analysis of CTSN.

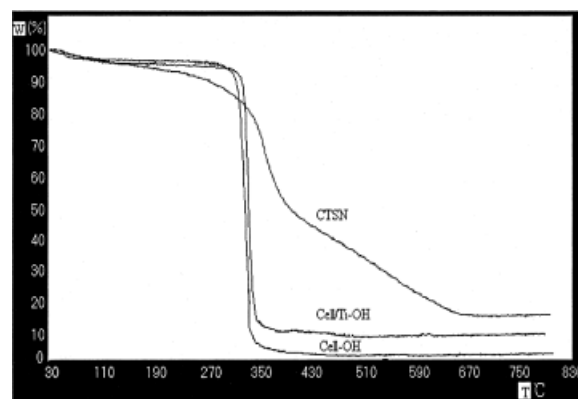
Cell—OH, and the temperature of the fastest decomposition rate for CTSN is somewhat higher than that of Cell/Ti—OH. This implies that the thermal stability of the coated cellulose is slightly increased with an increased amount of oxide coating.

#### Adsorption Behavior of CTSN toward Metal Ions

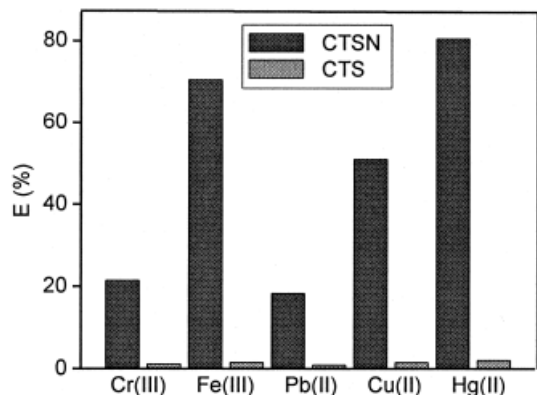
The adsorption percentages of CTSN and CTS for divalent mercury, copper, and lead ions, trivalent iron ions, and chrome ions were determined. The experimental results are plotted in Figure 6. Figure 6 shows that CTSN exhibited good adsorption for these metal ions in aqueous solution. The adsorption percentage of CTSN for trivalent iron and divalent mercury is the highest among all these metal ions. CTSN has a higher adsorption percentage than CTS for all these metal ions. This is related to the coordination ability of the nitrogen atom on the CTSN surface.

#### Effect of the Temperature on the Adsorption Percentage

From 25 to 55°C, the adsorption percentage of CTSN for divalent mercury and copper ions was



**Figure 5** TG curves of Cell—OH, Cell/Ti—OH, and CTSN.

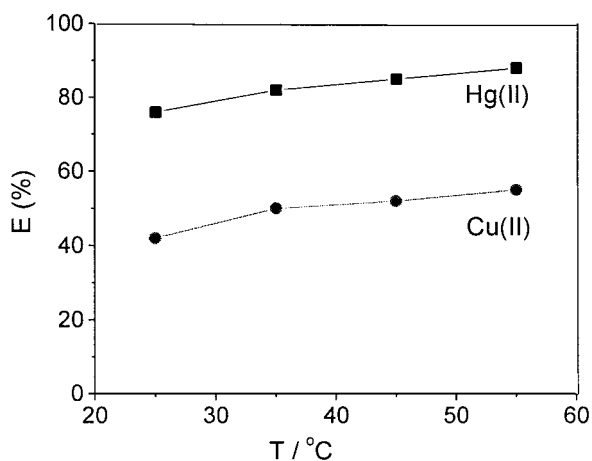


**Figure 6** Adsorption percentage of CTSN for metal ions (35°C, 2 h).

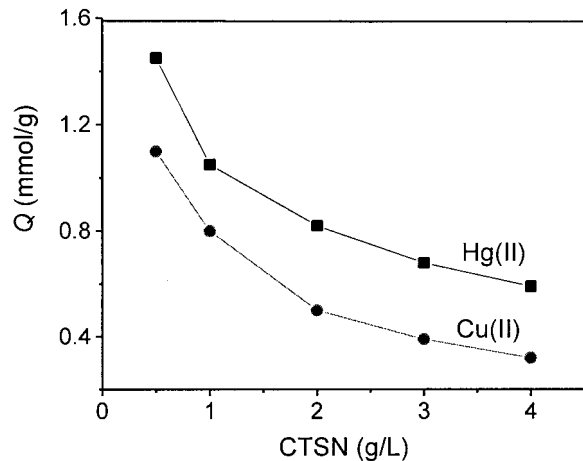
determined. The experimental results are plotted in Figure 7. Figure 7 shows that the adsorption percentage of CTSN for the two metal ions increases with an increase in the aqueous solution temperature. However, the rate of increased adsorption percentage is very slow compared with that in the literature.<sup>14,15</sup> This is related to the nitrogen coordinate atom of the CTSN surface and the ligand adsorption for metal ions in aqueous solutions.

#### Adsorption Isotherms

With a constant concentration of divalent metal ions ( $C_i = 2.0$  mmol/L) and a changing concentration of CTSN (0.5–4.0 g/L), the concentration of the mercury or copper ion that remained in the solution was determined at the equilibrium adsorption. The experimental results are presented in Figure 8. The figure shows that a lower concen-



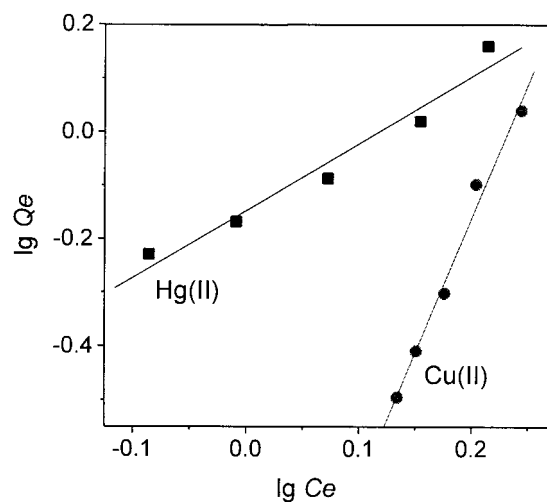
**Figure 7** Effect of the temperature on the adsorption percentage of CTSN.



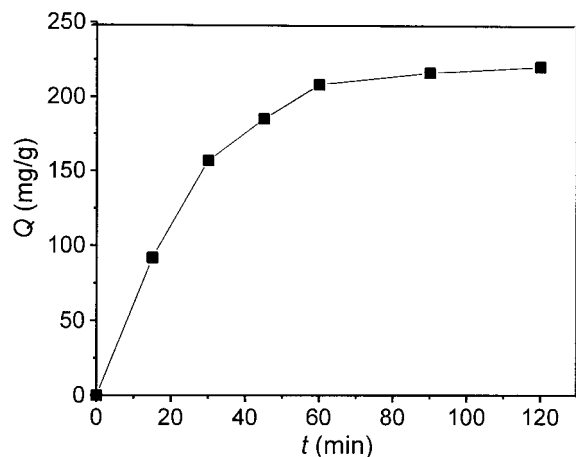
**Figure 8** Effect of the CTSN concentration on the adsorption capacity.

tration of CTSN has a higher adsorption capacity. When the concentration of CTSN is 0.5 g/L, the adsorption capacity of CTSN for Hg(II) and Cu(II) is 1.45 and 1.10 mmol/g, respectively.

A plot of  $\lg C_e$  versus  $\lg Q_e$  is presented in Figure 9. Figure 9 indicates that the adsorption isotherm lines of CTSN for divalent mercury and copper ions are the adsorptions of the Freundlich model under the experimental conditions. In the Freundlich isothermal equation,  $Q_e = K_F C_e^{1/n}$ , and its rearrangement model  $\lg Q_e = 1/n \lg C_e + \lg K_F$ , the Freundlich constants  $K_F$  and  $1/n$ , and the corresponding correlation coefficient  $r$  can be obtained with Figure 9. The empirical Freundlich equations for Hg(II) and Cu(II) are as follows:  $Q_e = 0.79 C_e^{1.26}$  for Hg(II),  $r = 0.980$ , and  $Q_e = 0.068 C_e^{5.40}$  for Cu(II),  $r = 0.993$ . Combining with Fig-



**Figure 9** Linearized Freundlich isotherms.



**Figure 10** Adsorption capacity of CTSN for human serum protein.

ures 6 and 7, this showed that the adsorption of CTSN for divalent mercury and copper ions was mainly the coordinate adsorption.

#### Adsorption Rate of CTSN for Human Serum Protein

With a constant concentration of human serum protein and CTSN, the concentration of the human serum protein that remained in the aqueous solution was determined at various adsorption times. The experimental data obtained are presented in Figure 10. CTSN has a high initial adsorption rate for the human serum protein, and the adsorption equilibrium is almost reached at 1 h. Each gram of CTSN adsorbs 220 mg of human serum protein at the adsorption equilibrium. The high initial adsorption rate of CTSN for protein is related to its structure. It is favorable for the separation and purity of the protein. The adsorption capacity of CTSN for human serum protein is similar to that of silica adsorbents modified by hydrophobic groups.<sup>15,16</sup>

#### CONCLUSION

CTSN was prepared by a reaction of cellulose powder with titanate chloride, followed by a reaction with 4-aza-6-aminoethyl triethoxysilane, and was characterized with infrared spectra, SEM, and TGA. The Ti mapping image of the Cell/Ti—OH surface shows that titanium oxide is well dispersed on the cellulose surface. The Ti and Si mapping images of

CTSN indicate that both metal oxides are uniformly dispersed on the cellulose surface. The atomic ratio of Ti to Si obtained by X-ray energy spectral composition analysis is 1.0:2.62. The adsorption capacity of CTSN for Fe(III), Cu(II), and Hg(II) ions is higher than that for Cr(III) and Pb(II). The adsorption isotherm lines of CTSN for Hg(II) and Cu(II) ions are a good fit with the Freundlich model under the experimental conditions. CTSN has a high initial adsorption rate for the human serum protein similar to that of silica adsorbents modified by hydrophobic groups.

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