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Adsorption of Cd^{2+} and Cu^{2+} by Oxidized Cellulose from TEMPO-mediated Selective Oxidation of Alkaline Natural Cellulose Pulp

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In the present work, oxidized celluloses were prepared by the 2,2,6,6-Tetramethyl pipedine-1-oxyl radical (TEMPO)-mediated selective oxidation of the primary alcohol groups at C6 position from natural cellulose pulps treated with NaOH solution. Their adsorption properties for Cu^{2+} *and* Cd^{2+} *in aqueous salt solutions were investigated. The results showed that the greater the carboxyl content and degree of substitution, the higher the value of the adsorption capacity. However, since the oxidized cellulose prepared from cellulose treated with 25% NaOH solution, having carboxyl content 14.98%, was partially soluble in aqueous solutions, the dissolution of this sample resulted in reduced metal-adsorption efficiency. The metal-adsorption of the oxidized celluloses followed the Langmuir adsorption isotherm. Compared with the oxidized cellulose having carboxyl content 5.12% from cellulose treated with 15% NaOH solution, the oxidized cellulose having carboxyl content 5.12% from cellulose treated with 25% NaOH solution has much stronger metal-adsorption capacity.*

Keywords oxidized cellulose, natural cellulose fiber, TEMPO-mediated selective oxidation, metal-adsorption

Introduction

Polysaccharides derivatives constitute a very important part of the world market for functional polymers. Their industrial applications cover a very wide range because of their biocompatibility, biodegradation, and non-toxicity. Chemical modifications of polysaccharides are interesting routes for preparing new polymers with specific

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properties (1). After the introduction of functional groups with the ability of chelating heavy metal ions, such as the carboxyl group and sulfonic acid, the natural polymers will have ion exchange performance (2–8). The natural polymers based ion exchangers have attracted much attention and have been proposed as potential heavy metal scavengers in wastewater treatment and in the preconcentration of heavy metals from large volumes of aqueous effluents containing low levels of heavy metal ions.

By oxidation reaction, new functionalities, such as carboxyl groups, aldehyde groups and ketone groups, can be introduced to polysaccharides, such as cellulose and starch (9, 10). Since 1942 when it has been found that the oxidant NO_2 could selectively oxidize primary hydroxyl of cellulose to carboxyl groups (11), the selective oxidation of cellulose by other oxidative systems has also been extensively studied (12, 13). In the past ten years, the method of TEMPO-mediated oxidation has been applied to the selective oxidation of polysaccharides. The kinetic study (14, 15), side reactions (16–18), properties of oxidized products and selectivity (19–24) of TEMPO-mediated oxidation for polysaccharides have been investigated in detail. Kweon et al. examined the adsorption capacity of oxidized corn starches, prepared from TEMPO-mediated oxidation, for divalent metal ions; a reduced metal-adsorption efficiency by soluble oxidized starch was found (25).

It has been reported that natural cellulose can not be oxidized by the TEMPO- NaOCl-NaBr system. The oxidized products from rayon seem not to be soluble in water unless the oxidation degree at the C6 primary alcohol reaches almost 100% (24). Alkaline treatment can improve the accessibility of natural cellulose; the conditions of alkaline treatment have a great effect on the accessibility, especially the alkaline concentration (26, 27). However, there has been no report about the TEMPO-mediated oxidation of alkaline cellulose with different alkaline concentration treatment and the adsorption properties of the corresponding oxidized cellulose.

In this work, the oxidized celluloses obtained from the TEMPO-mediated selective oxidation of natural cellulose pulp treated with different NaOH solution have been characterized by FTIR and NMR, and their adsorption properties for Cu^{2+} and Cd^{2+} in aqueous salt solutions were investigated in detail.

Experimental

Materials

The natural cellulose used was a commercial pulp (DP = 1033) supplied by Gaomi Co. Ltd., China. TEMPO (2,2,6,6-Tetramethyl pipedine–1-oxyl radical) was supplied by Wako Chemicals Co., Ltd. (Japan). Sodium hypochlorite solution (ca. 10% active chlorine) was supplied by Black Penny Group (Changzhou, China). All other chemicals (analytical pure) were purchased from Shanghai Chemicals Co. Ltd., China, and were used as received.

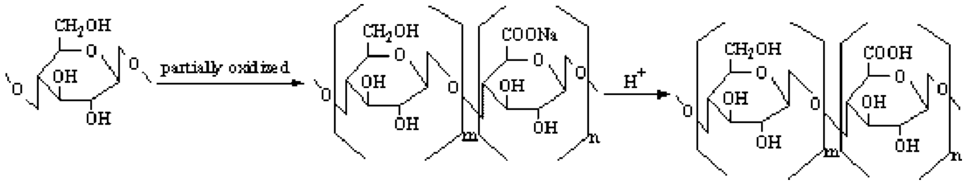
Alkaline Treatment Procedure

The alkaline treatments of natural cellulose were carried out using NaOH solutions. The samples were soaked in the solutions with stirring at 25°C for 1 h. The excess reagent was squeezed out and the sample then dipped into a large amount of eluent for washing NaOH. The samples were finally dried in air.

Preparation of Oxidized Cellulose

The alkaline natural cellulose pulp (2 g) was suspended in 150 ml of water containing TEMPO (50 mg) and sodium bromide (0.48 g). The suspension was set in a cooled water bath of 4°C, and stirred smoothly. 23 ml sodium hypochlorite (10%, adjusted to pH 10.8 using dilute HCl in advance) was put into the suspension and the pH maintained at about 10.8 with a 0.4 mol/l NaOH solution by using a pH-stat. With proceeding of the oxidation reaction, the time and its corresponding NaOH consumption were recorded.

When the desired carboxyl content was reached, the reaction solution was quickly quenched by adding excess ethanol. The white precipitates were filtered and washed thoroughly with H_2O/ethanol solution (3:7 value ratio) 5–6 times and then the obtained oxidized products were soaked in 0.1 mol/l dilute HCl solution for 15 min and washed thoroughly with H_2O. Finally, the oxidized celluloses obtained were dried at 40°C in a vacuum oven.



FTIR of Oxidized Celluloses

The Fourier transform-infrared (FTIR) spectra of oxidized celluloses were obtained using KBr pellets on a Nicolet-20sx-B FTIR spectrometer.

Solid State ^{13}C-NMR of Oxidized Celluloses

The solid state ^{13}C-NMR spectra of oxidized celluloses were recorded at 100 MHz on a Bruker AC-400 spectrometer equipped with cross-polarization magic-angle sample spinning (c.p.m.a.s) accessories.

Measurement of the Carboxyl Content

The amount of carboxylic acid produced during the oxidation process is directly proportional to the consumption of 0.4 mol/l NaOH solution, and can be evaluated by the NaOH consumption per primary hydroxyl (15) by the following equation:

$$\text{Carboxyl content } (\%) = C \times v \times 45/1000w \qquad (1)$$

where C represents the concentration of NaOH solution, mol/L; v, the volume of consumption of NaOH solution, ml; and w, the weight of cellulose materials, g.

Metal-Adsorption Capacity

The metal-adsorption capacity of the oxidized cellulose pulp was determined by a batch method. Aqueous metal salt solution (100 ppm, 50 ml) of $CuSO_4 \cdot 5H_2O$ (pH value 5.04), or $CdSO_4 \cdot 2H_2O$ (pH value 5.5), was mixed with the oxidized celluloses (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 with a Hitachi 180–80 made in Japan.

Results and Discussion

Structure and Carboxyl Acid Content of Oxidized Cellulose

The natural cellulose pulp was modified by alkaline treatment at room temperature for 40 min with 15 wt% and 25 wt% NaOH solution, respectively. The carboxyl content of the oxidized celluloses gained from their oxidation by TEMPO-NaOCl-NaBr system are shown in Table 1. The oxidation process of natural cellulose pulp treated with 15 wt% NaOH solution (2 g) consumed just 5.6 ml of 0.4 mol/l NaOH solution, whereas the cellulose treated with 25 wt% NaOH solution used 28.4 ml. The carboxyl content of the corresponding oxidized cellulose is about 5.12 wt% (sample CC5.12SHC15) and 25.6 wt% calculated by Equation (1), respectively. 28.4 ml NaOH solution (0.4 mol/l) should be consumed if the primary hydroxyl group of 2 g cellulose is completely oxidized to carboxyl groups. Thus, the 25 wt% NaOH treated sample could be almost completely selectively oxidized, whereas the 15 wt% NaOH treated sample can only be partially oxidized.

In this study the oxidized celluloses with 5.12 wt% (sample CC5.12SHC25) and 14.98 wt% carboxyl content (sample CC14.98SHC25) were obtained via partially oxidation of the 25 wt% NaOH treated sample. Their adsorption properties are examined. However, the adsorption properties of the completely oxidized product are not examined, because it is totally soluble in aqueous solution and thus the corresponding oxidized cellulose will lose its fiber shape and be at least partly soluble in aqueous solution, similar to oxidized starch (25).

The FTIR spectra of native cellulose and various oxidized celluloses from the alkaline treatment with different weight concentration of NaOH solution are shown in Figure 1. Compared with native cellulose, its corresponding oxidized cellulose and the oxidized

Table 1

Carboxyl content and degree of substitution of oxidized celluloses obtained by TEMPO-NaOCl-NaBr following the alkaline treatment with different weight concentrations of NaOH solution

Sample[a]	NaOH concentration/%	Carboxyl content[b]/%	DS[c]
Natural cellulose	/	0	0
Oxidized natural cellulose	/	1.02	0.04
CC5.12SHC15	15.0	5.12	0.20
CC5.12SHC25	25.0	5.12	0.20
CC14.98SHC25	25.0	14.98	0.59

[a] Sample CC5.12SHC15, CC5.12SHC25 and CC14.98SHC25 correspond to oxidized cellulose having carboxyl content 5.12%, 5.12% and 14.98% from cellulose pulp treated with 15.0%, 25.0% and 25.0% NaOH solution, respectively.

[b] The carboxyl content is the amount of carboxylic acid produced in the oxidation process.

[c] DS = 100 × carboxyl content/25.6.

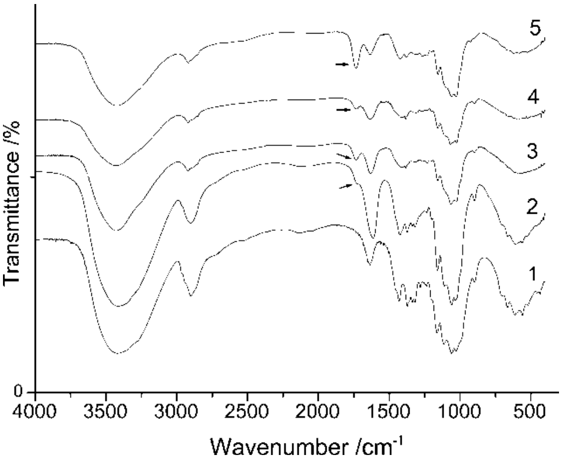


Figure 1. FTIR of native cellulose and various TEMPO oxidized celluloses prepared from the cellulose treated with different weight concentration of NaOH solution,1-natural cellulose; 2-oxidized natural cellulose; 3, 4 and 5- the oxidized cellulose having carboxyl contents 5.12%, 5.12% and 14.98% from cellulose pulp treated with 15.0%, 25.0% and 25.0% NaOH solution, respectively.

celluloses from alkaline celluloses showed a new peak at around 1730 cm^{-1} for gluconate groups (marked by arrows) that become stronger with increasing carboxyl content. The solid state ^{13}C-NMR spectrum of sample CC5.12SHC15 was examined, as shown in Figure 2. The oxidized alkaline cellulose showed a new peak at about 175 ppm belonging to C_6OOH at C_6 position and no signal from oxidation of secondary hydroxyls at C_2 and C_3 position of anhydroglucose units (AGU), compared with the native cellulose (28). This indicates that the alkaline cellulose, just like rayon, can also be selectively oxidized to a high degree by the TEMPO-NaOCl-NaBr system and the carboxyl groups of the oxidized alkaline celluloses originated from the primary hydroxyl at C_6 position. The carboxyl content will be about 25.6 wt% if the primary

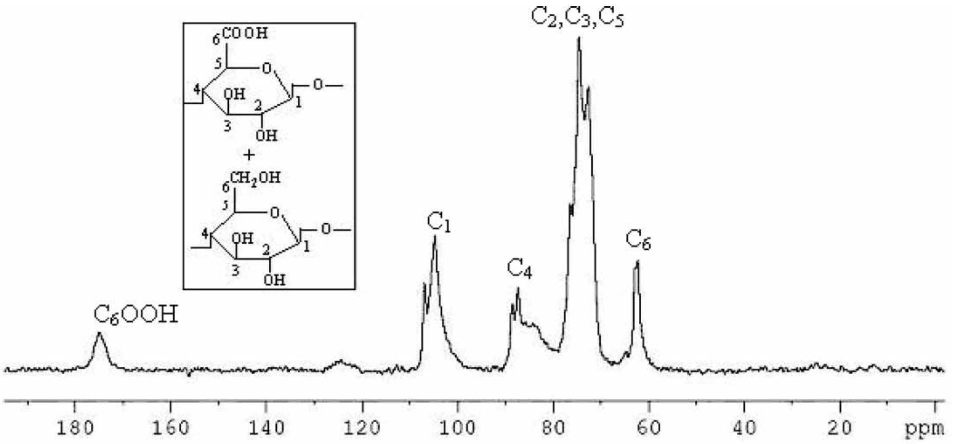


Figure 2. The solid state ^{13}C NMR spectrum of oxidized cellulose prepared from modified cellulose by 15% NaOH solution treatment (sample CC5.12SHC15).

hydroxyl of cellulose is completely oxidized to carboxyl groups. Therefore, the degree of substitution, DS, can be calculated by the equation, DS = 100 × carboxyl content/25.6. The DS values of the various oxidized celluloses are shown in Table 1.

Metal-adsorption Capacity

Effect of Carboxyl Content and DS. The metal-adsorption capacity of native cellulose and the oxidized celluloses from native cellulose and its modified products with different concentration NaOH solution was measured by dispersing the absorbent materials in Cd^{2+} and Cu^{2+} aqueous solutions for 10 min at room temperature.

As shown in Figure 3, the native cellulose, the raw material for preparation of oxidized cellulose, can adsorb Cd^{2+} and $Cu^{2+,}$ although the adsorption capacities are very small, only 0.01 mmol/g each. The metal ion binding capacity of unmodified cellulose has been attributed to the presence of functional groups such as hydroxyl and carboxyl, which provide binding sites for the metal ions. The adsorption capacity is enhanced by introducing carboxyl groups into the cellulose macromolecular chains. The greater the carboxyl content and DS, the higher the value of the adsorption capacity. The sample CC5.12SHC15 and CC5.12SHC25 show adsorption capacities of 0.36 and 0.43 mmol/g for Cu^{2+}, and 0.24 and 0.29 mmol/g for Cd^{2+}, respectively. Based on the molar weight of each AGU having DS 0.20, these values are equivalent to 58.32 and 69.66 mmol/AGU, respectively. The value of sample CC5.12SHC25 is a little higher than that of sample CC5.12SHC15. When the cellulose pulp from 25 wt% NaOH solution treatment is oxidized to carboxyl content 14.98 wt% and DS 0.59 (sample CC14.98SHC25), the adsorption capacities reach 0.75 mmol/g for Cu^{2+} and 0.58 mmol/g for Cd^{2+}, equivalent to 121.5 and 93.96 mmol/AGU, respectively.

The adsorption time of the oxidized alkaline cellulose with different carboxyl content in the metal solution was varied from 1 to 30 min, and the adsorbed metal contents during this period were examined. As shown in Figure 4, sample CC5.12SHC15 and sample CC5.12SHC25 reached their maximum absorption capacity within 10 min for Cu^{2+} and

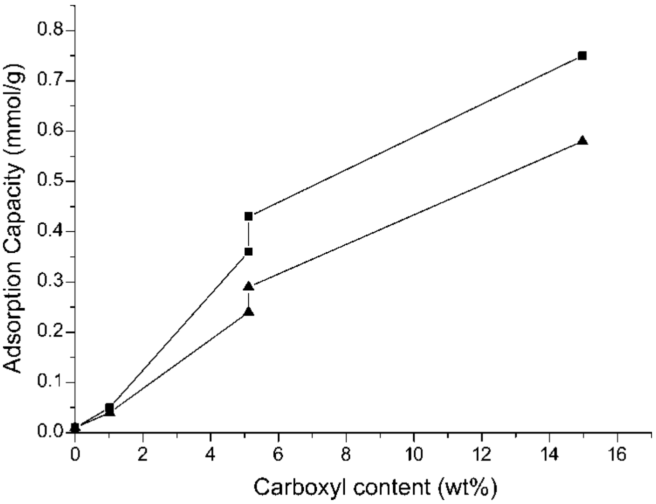


Figure 3. The adsorption capacity of native cellulose and oxidized celluloses with different carboxyl contents for Cu^{2+} and Cd^{2+}: ■-Cu^{2+}; ▲-Cd^{2+}.

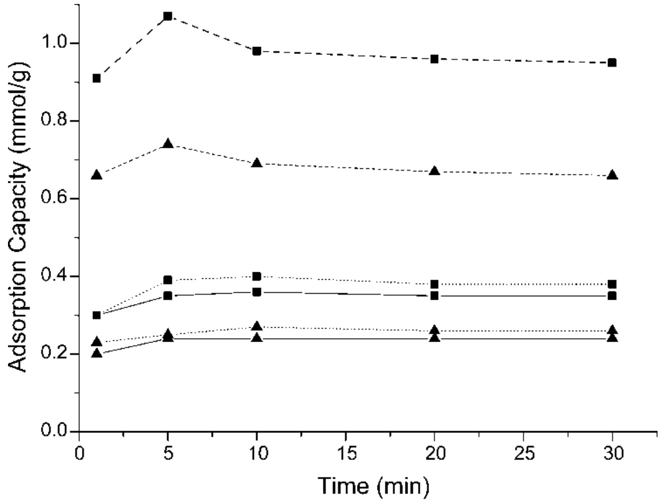


Figure 4. Metal-adsorption capacity of oxidized alkaline cellulose with different carboxyl contents at different times: ■-Cu^{2+}; ▲-Cd^{2+}; —: sample CC5.12SHC15; ...: sample CC5.12SHC25; - - -: sample CC14.98SHC25.

Cd^{2+}, and then remained almost unchanged for longer time. However, sample CC14.98SHC25 reached its maximum at about 5 min and then the adsorption capacity decreased as the adsorption time increased, especially in the range of 5–10 min. The reduced metal-adsorption shown in sample CC14.98SHC25 was mainly caused by the increased water solubility or swellability because of the introduction of excess carboxyl group and degradation of the cellulose during the oxidation process.

Effect of Alkaline Concentration. To analyze the effect of alkaline concentration on metal-adsorption capacity, the metal-adsorption capacity of sample CC5.12SHC15 and CC5.12SHC25, with the same carboxyl content of 5.12 wt% prepared from cellulose pulp treated with 15 wt% and 25 wt% NaOH solution, respectively, were examined in different metal ion concentrations. As shown in Figure 5, the amount of metal ions absorbed by the oxidized cellulose is dependent on the initial metal ion concentration in the solution and generally follow the order of $Cu^{2+} > Cd^{2+}$ (mmol/g) or $Cd^{2+} > Cu^{2+}$ (mg/g) and sample CC5.12SHC25 > sample CC5.12SHC15. Factors that may influence the relative uptake levels of metal ions from aqueous solution include ionic radius and the properties of the adsorbent. It has been reported that the smaller the ionic radius, the higher the value of hydration energy, and the lower the relative reactivity in aqueous medium (29). The ionic size of Cu^{2+} is about 1.8 nm smaller than size of Cd^{2+}. If just considering the effect of ionic radius, Cd^{2+} should have higher levels of removal from aqueous solution. But the bigger ions are more difficult to spread to the binding sites and be adsorbed than the smaller ones if the channel is not too wide. Therefore, this suggests that it is the properties of the oxidized celluloses that have a greater influence on the absorbed amount of metal ions than the ionic radius.

In Figures 6 and 7, C_e/x is plotted as function of C_e based on the data of Figure 5. Where, C_e represents the concentration of metal ion in the solution, and x represents the equilibrium sorption of the metal ion per unit mass of adsorbent material. A linear relationship is found between the C_e/x and C_e, indicating that the metal-adsorption

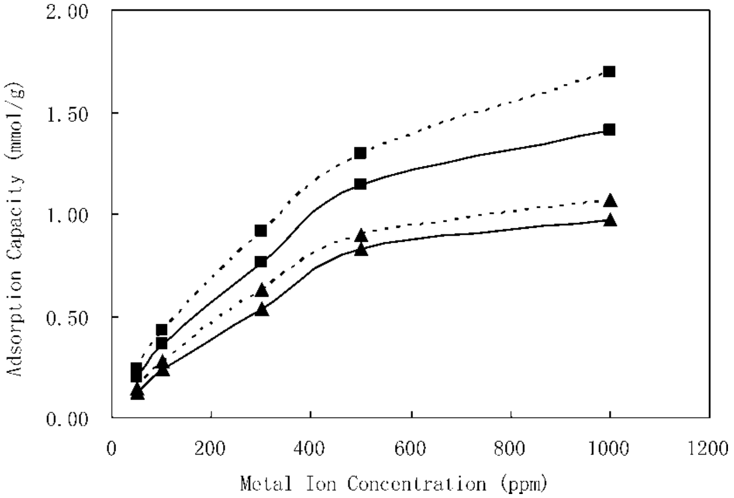


Figure 5. Metal-adsorption capacity of oxidized alkaline celluloses for Cu^{2+} and Cd^{2+} at different metal ion concentrations: ■-Cu^{2+}; ▲-Cd^{2+}; —: sample CC5.12SHC15; . . .: sample CC5.12SHC25.

behavior of the oxidized cellulose followed the Langmuir adsorption isotherm. Therefore, from the slope and intercept of the line, the maximum metal ion binding capacity of the absorbent material, Am, and the affinity constant, k, can be measured by the Langmuir isotherm equation: $C_e/x = A_m/k + Ce/A_m$, and the values are given in Table 2. Sample CC5.12SHC25 has higher metal-adsorption capacity than sample CC5.12SHC15. Under the same experimental conditions, the former has a lower equilibrium concentration of metal ions, higher maximum metal ion binding capacity and a much higher affinity constant than the latter. Maximum adsorption capacity gives an indication of the number of adsorption sites; Thus A_m of the sample CC5.12SHC25

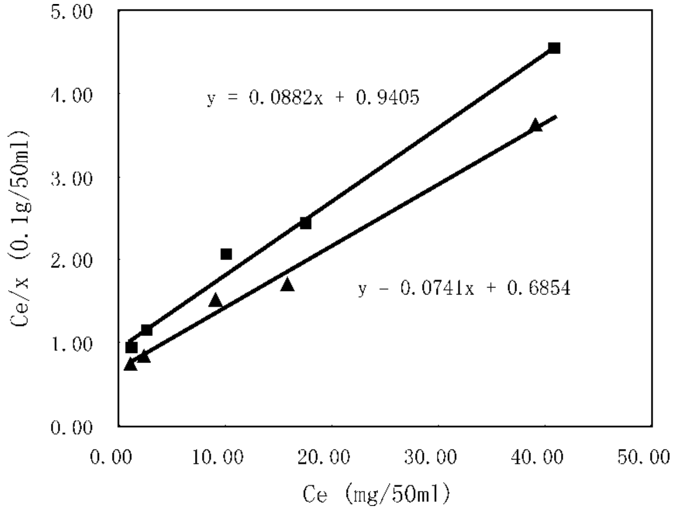


Figure 6. Langmuir plots for the adsorption capacity of oxidized cellulose prepared from the cellulose treated with 15% NaOH solution for Cu^{2+} and Cd^{2+}(sample CC5.12SHC15): ■-Cu^{2+}; ▲-Cd^{2+}.

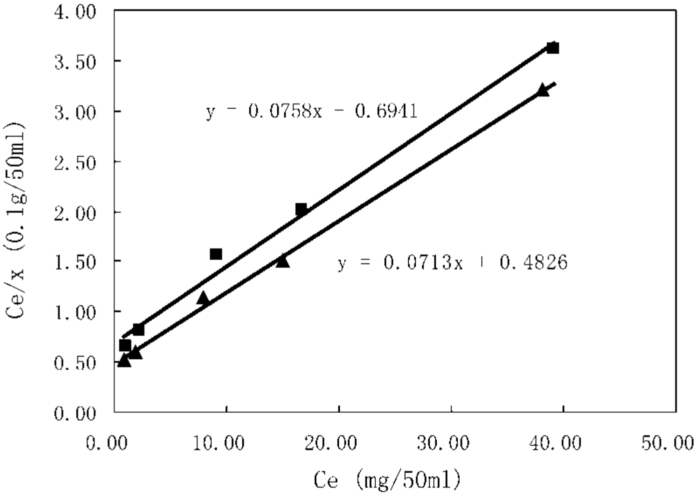


Figure 7. Langmuir plots for the adsorption capacity of oxidized cellulose prepared from the cellulose treated with 25% NaOH solution for Cu^{2+} and Cd^{2+}(sample CC5.12SHC25): ■-Cu^{2+}; ▲-Cd^{2+}.

is only a little higher than that of the sample CC5.12SHC15 because they have an almost equivalent number of carboxyl groups, the main adsorption sites. According to the Langmuir model, affinity constant k provides a measure of the binding energy or affinity of metal ion towards the adsorbent and large values of k reflect the ability of the adsorbent to bind large amounts of the metal ions.

WAXD patterns of sample CC5.12SHC15 and sample CC5.12SHC25 were obtained as shown in Figure 8. Their crystal peaks have a large difference. When the concentration of NaOH solution is above 20 wt%, the natural cellulose (cellulose I) will be changed into regenerated cellulose (cellulose II) after alkaline treatment, or the alkaline cellulose will be a mixture of cellulose I and cellulose II. The natural cellulose (cellulose I) has higher crystallinity and lower swellability and accessibility than regenerated cellulose (cellulose II). The reason for the latter effects is that the former cannot be oxidized but the latter can be completely oxidized to celluronic acid, and their mixture can only be partially oxidized. Therefore, it is suggested that it is the swellability and accessibility that causes the marked difference of affinity constant k.

3AC: the cellulose pulp treated with 15 wt% NaOH solution; 3: the oxidized cellulose from 3AC; 4AC: the cellulose pulp treated with 25 wt% NaOH solution; 4: the oxidized cellulose from 3AC.

Separation sorption process data may be expressed in terms of distribution coefficient, D, defined as the ratio of a solute in the adsorbent phase to the amount in the continuous aqueous phase. The values of D obtained from this study are given in Table 2. The results show that values of D vary markedly with changes of the equilibrium concentration of the metal ions; and that the amounts of the metal ions bound by the adsorbent materials are lower than in the continuous aqueous phase when the concentration of metal ions is above 100 ppm. These results suggest that the treatment of aqueous effluents contaminated with Cu^{2+} and Cd^{2+} ions would require several equilibrium sorption cycles to reduce the levels of the metal ions to acceptable or below intervention levels. The metal ion-saturated oxidized celluloses can be recycled by stripping with dilute HCl solution and then reused as adsorbent materials.

Table 2

Sorption characteristics of oxidized cellulose with the same carboxyl content, 5.12%, prepared from cellulose treated with 15% (sample CC5.12SHC15) and 25% (sample CC5.12SHC25) NaOH solution

Adsorbent material	Equilibrium concentration of metal ions (mg/50 ml)		Maximum metal ion binding capacity, As (mg/0.1 g)		Affinity constant, k (50 ml/mg)		Distribution coefficient, D (50 ml/0.1 g)	
	Cu^{2+}	Cd^{2+}	Cu^{2+}	Cd^{2+}	Cu^{2+}	Cd^{2+}	Cu^{2+}	Cd^{2+}
CC5.12SHC15	1.21–40.97	1.07–39.16	11.34	13.50	12.06	19.69	1.07–0.22	1.34–0.28
CC5.12SHC25	0.99–39.15	0.72–38.58	13.19	14.03	19.01	29.06	1.53–0.28	2.47–0.3

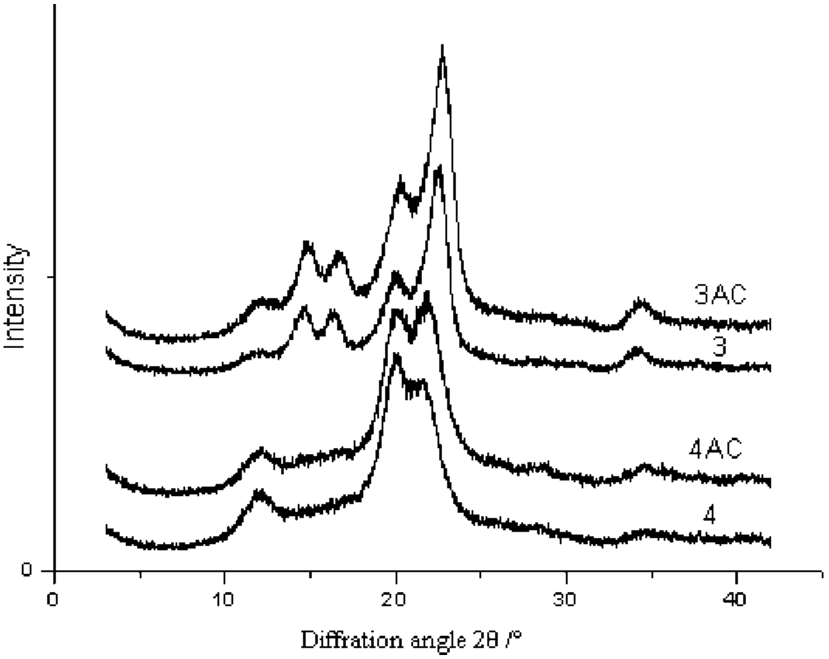


Figure 8. The WAXD patterns of alkaline celluloses and their corresponding oxidized celluloses.

Conclusions

The metal-adsorption characteristics of the oxidized celluloses prepared from natural cellulose pulp treated by different concentration NaOH solution have been investigated. It has been shown that the oxidized celluloses from cellulose treated with 25 wt% NaOH solution have much stronger metal-adsorption capacity, such as higher maximum metal ion binding capacity and higher affinity constant, than the cellulose treated with 15 wt% NaOH solution due to higher accessibility and swellability. However, introducing excess carboxyl groups to alkaline cellulose will reduce metal-adsorption because of the increased water solubility or swellability and degradation of the cellulose base during the oxidation process. The oxidized cellulose with carboxyl content about 5 wt% from cellulose treated by 15 wt% and 25 wt% NaOH solution may be utilized in the areas of wastewater treatment and for heavy metals preconcentration from large volumes of aqueous effluents containing low levels of heavy metals.

Acknowledgements

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