

Preparation and research of a novel cellulose-based heavy metal adsorbent

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This paper describes a novel cellulose-based heavy metal adsorbing material. The bamboo cellulose was pretreated by plasma (150 V, 120 s), then subjected to epoxidation, amination and ultrasonic enhancement sulfonation reaction to prepare the cellulose-based heavy metal adsorbing material which grafted heavy metal adsorbing groups of N, S into the bamboo cellulose. The treated materials were characterized by FTIR and NMR analysis. The analyses showed that O-containing epoxy groups, N-containing amine group, and S-containing sulfo groups were successfully grafted into the bamboo cellulose.

Keywords: Adsorption, Bamboo fibers, Plasma, Cr(VI), FTIR, NMR

INTRODUCTION

With the rapid development of industry, the problem of heavy metal ion pollution has become increasingly serious. Many technologies and methods have been applied in the removal of heavy metal ions, such as flotation [1], adsorption [2], ion exchange, chemical precipitation, membrane separation [3], electrochemical [4], oxidation/reduction [5], ultra-filtration, and so on. Recent research work has focused on the bio-adsorbent properties of natural cellulose to remove metal ions from wastewater. Cellulose, a polysaccharide polymer, has many reactive surfaces with -OH groups that allow it to participate in a variety of chemical reactions [6], such as esterification [7], etherification [8], oxidation [9], and polymer grafting [10]. Yu [11] reported the magnetically modified sugarcane bagasse with a higher adsorption capacity and a rapid adsorption rate. Experimental results showed that the adsorption capacities of the magnetic sorbent for Pb²⁺ and Cd²⁺ were 1.2 and 1.1 mmol/g, respectively. Esfandiari [12] studied the removal of Mn(II) from groundwater by modified sugarcane bagasse with response surface methodology (RSM). The effects of pH, adsorbent dosage and initial metal concentration on the adsorption of Mn(II) were investigated using response surface methodology (RSM) based on Box-Behnken design. A maximum experimental Mn(II) removal efficiency of 63% for SCB was obtained.

Bamboo is widely cultured in tropical and subtropical areas, especially in Guangxi, China. It has a lot of active hydroxyl groups and can be modified to obtain new properties, such as adsorption of heavy metals. Researchers [13] have found that carboxylated bamboo fibers treated with citric acid have a higher adsorption capacity of Pb²⁺ (127.1 mg/g). Carboxyl group content between 1.99 and 4.13 mmol/g could be obtained by changing the ultrasonic pretreatment time, reaction temperature, reaction time, and the amounts of catalyst and citric acid. Bamboo root biomass [14] was shown to be suitable for the adsorption of Cu²⁺ and Zn²⁺ ions from wastewater. The effects of contact time, adsorbent dose, and initial concentration of the metal solution on metal uptake were evaluated. Equilibrium was reached after 15 to 20 min for both Cu²⁺ and Zn²⁺. The endothermic adsorption process was measured, but its chemical and physical mechanism was not studied.

In the present work, we prepared a bamboo cellulose-based heavy metal adsorbing material for Cr(VI) adsorption. The cellulose was prepared by using plasma treatment, epoxidation, amination, and ultrasonic enhancement sulfonation reactions to graft N and S groups. The surface morphology, and the chemical structure of the bamboo fibers before and after modifications were characterized by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR).

Materials

Natural cellulose (bleached bamboo pulp) was supplied by Guangxi Hwagain Paper Industry of

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China. Diethylenetriamine (DETA), epoxy chloropropane, carbon disulfide, anhydrous cupric sulfate, hydrochloric acid, sodium hydroxide, absolute ethyl alcohol and acetone were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. All these reagents were of analytical grade and used without further purification.

SYNTHESIS OF ADSORBENT

Plasma pretreatment

5 g of bamboo fibers and a certain amount of 2% NaOH were added into a beaker. The moisture content was controlled at 60%. After defibering for 10 min, the mixture was pretreated with plasma (120 s, 150V, 160Pa).

Epoxidation reaction

5 g of plasma-pretreated bamboo fibers and 200 mL of 10% NaOH solution were added into a 250-mL three-stoppered flask. After shaking for 15 min, 15 mL of epichlorohydrin (ECH) solution was added to the flask. The mixture was stirred for 150 min at 50 °C. As a result, epoxy bamboo fibers with an epoxy value of 7.3 mmol/g were obtained.

Amination reaction

5 g of the epoxy bamboo fibers and 200 mL of 3% NaOH solution were then added into a 250 mL three-stoppered flask fitted with a magnetic stirrer. After defibering for 15 minutes, 7 g of diethylenetriamine (DETA) solution was added into the mixture and stirred at 70 °C for 120 min. Zeta potential of the final amino-bamboo fibers was 30.4 mV.

Ultrasonic sulfonation reaction

The amino-bamboo fibers were then treated by an ultrasonic sulfonation reaction as follows: 5 mL of CS₂, reaction temperature of 25 °C, reaction time of 60 min, 14% alkali solution and 200 W of ultrasonic energy.

CHARACTERIZATION OF UNTREATED AND TREATED BAMBOO FIBERS

Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectra of untreated and treated bamboo fibers were recorded on an attenuated total reflection FTIR spectroscope (HP Nexus470, USA) equipped with smart omni-transmission in the range of 650-4000 cm⁻¹. Untreated and treated bamboo fibers were dried in an air-circulating oven at 50 °C overnight. Finally, the samples were prepared by mixing 1 mg of untreated or treated bamboo fibers with 100 mg of KBr followed by pressing the mixture into ultra-thin pellets.

NMR analysis

A common testing method for cellulose structural analysis, ¹³C-NMR analysis was applied to study the structure of untreated and treated bamboo fibers. ¹³C-NMR spectra of the samples were obtained on a Bruker (Germany) AVANCE III equipment at room temperature. Measurements were performed by applying the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence with an interpulse spacing of 200 ms.

ADSORPTION MEASUREMENT OF Cr⁶⁺

The adsorption of Cr(VI) onto grafted bamboo fibers was carried out with a selected amount of adsorbent in 160 mL of Cr(VI) solution at various concentrations. The initial pH of the Cr(VI) solution was adjusted with 0.1 M HCl and NaOH. Then, the adsorption step occurred at 30 °C for 2 h at 150 rpm. Afterwards, the reaction mixture was filtered and the concentration of Cr(VI) in the filtrate was measured by inductively coupled plasma optical emission spectrometry with an Agilent (US) ICP-700 Series OES. The calculation of formaldehyde adsorption on grafted cellulose was following Eq. (1):

$$Q = \frac{(C_0 - C_t)V}{m} - Q_0 \quad (1)$$

Where Q is the adsorption capacity of treated cellulose, mg/g; Q₀ is the adsorption capacity of native cellulose, mg/g; C₀ is the initial Cr⁶⁺ concentration, mg/L; C_t is the subsequent Cr⁶⁺ concentration, mg/L; V is the volume of Cr⁶⁺ solution, mg/L; m is the weight of treated cellulose, g.

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectra of untreated and pretreated bamboo fibers are presented in Fig.1. The featured structures are listed in Table 1. As shown in Fig.1, the new absorption peaks at 1,277.34 cm⁻¹, 993.57 cm⁻¹, and 856.38 cm⁻¹ are due to the presence of an epoxy group, indicating that epoxidation was successful.

The hydroxyl absorption peak at 3000 to 3400 cm⁻¹ was slightly strengthened and widened. This may have been caused by a primary amine N-H stretching vibration and weak absorption from the secondary amine. The IR spectrum of the modified cellulose-based adsorbent displayed an N-H stretching vibration adsorption at 3,332.56 cm⁻¹, a C-H stretching vibration adsorption at 2,934.96 cm⁻¹, the amines of -NH bending vibration adsorption at 1,639.59 cm⁻¹ and 1,456.01 cm⁻¹, as well as a C-N stretching vibration at 1,497.92 cm⁻¹. These

absorption peaks were present in the diethylenetriamine monomer molecule, but were not found in tests of untreated bamboo cellulose.

The peaks at 1,497.92 cm⁻¹, 1,456.01 cm⁻¹, and 1,324.56 cm⁻¹ correspond to bending vibrations of I type C-S, II type C=S, and the presence of a CS₂-NR₂ group, respectively. These molecules indicate that the modified cellulose-based adsorbent was successfully sulfonated.

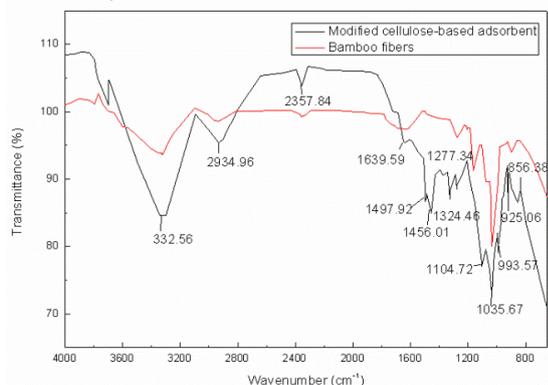


Fig. 1. FTIR spectra of untreated and treated bamboo fibers

Table 1. FTIR spectra peaks of untreated and treated bamboo fibers.

Characteristics	$\Delta\nu$ (cm ⁻¹)		$\Delta\nu$ (cm ⁻¹)/absorbance change	Assignment
	Bamboo fibers	cellulose-based heavy metal adsorbent		
Absorbance change	3331	3332	+1/ Δ	δ O-H
	2930	2934	+4/ Δ	δ C-H (methyl and methylene)
	1640	1639	-1/ ∇	η N-H (in plane) ; δ C=O
		1496	new	I type ϵ C-S (CS ₂ -NR ₂); ϵ C-H
	1455	1456	+1/ Δ	ϵ CH; ζ methyl; ζ methylene
	1373	1373	0	ϵ C-H; ϵ C-O-H
	1337	1336	-1/ ∇	γ OH
		1324	new	II type γ C=S (CS ₂ -NR ₂); γ C-H
	1319	1320	+1/ Δ	γ CH ₂
	1281	1277	-4/ Δ	ϵ CH
	1166	1164	-2/ ∇	ζ C-O-C
	1104	1104	0	δ C-C; δ C-O
	1034	1035	+1/ Δ	δ C-O (cellulose ether bond)
		993	new	δ C-O-C
918	925	+7/ Δ	δ C-OH (out-of-plane)	
	856	new	δ C-O	

Key to symbols: γ : wagging vibration; δ : vibration; ϵ : deformation vibration; ζ : asymmetrical vibration; η : bending vibration; Δ : increase; ∇ : decrease.

NMR analysis

Details of the NMR analysis are shown in Table 2 and Fig. 2. The analysis of the treated

bamboo fibers indicated that the peak shifts from 150 to 200 ppm correspond to C=S and C-S. Chemical shifts at 196, 169, 162, and 150 ppm indicated that C=S and C-S were successfully grafted in the treated fibers. The 100 to 150 ppm shift was caused by C-O. New chemical shifts corresponding to an ether bond in the treated bamboo cellulose occurred at 134, 126, 118, and 103 ppm. The 50 to 100 ppm shift was caused by C-N. A new chemical shift at 83 ppm occurred in the treated bamboo fiber sample. The chemical shift at 56 ppm was strengthened, while the shift at 75 ppm was weakened. This might indicate that the cellulose had a C-N linkage. All NMR analyses of the treated bamboo suggested that the fibers were modified by grafting. In other words, the epoxidation, amination, and sulfonation reactions were successful.

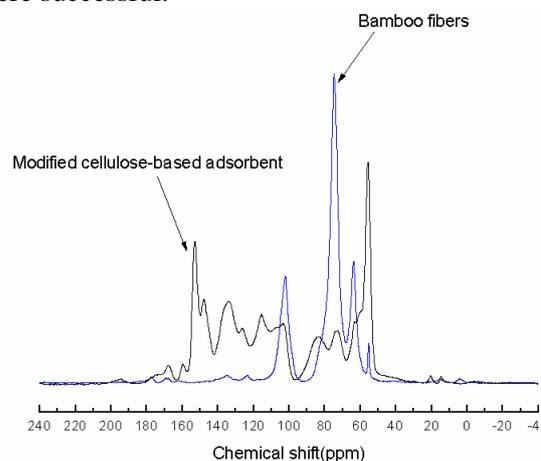


Fig. 2. ¹³C-NMR spectra of untreated and treated bamboo fibers.

Table 2. ¹³C-NMR chemical displacement of untreated bamboo fibers and treated bamboo fibers

Peak shift (ppm)	Bamboo fibers (ppm)	Modified cellulose-based adsorbent (ppm)		Assignment
200-180		196		C=S
180-165		168		C=S and C-S
165-140		159-150		C-S
140-120		132and129		C-O
120-110		116		C-O-C
105-100	101	102		C1, C=N
95-80		82		C-N
80-70	72	71		C-N, C2, C3, C5
70-60	61	61		C6, C-O
60-50	58	58		C4, sugar terminal group C

REGENERATION EXPERIMENTS

The treated bamboo fibers had the advantage of being biodegradable and recyclable. To obtain the

ПОЛУЧАВАНЕ И ИЗСЛЕДВАНЕ НА НОВ АДСОРБЕНТ НА ТЕЖКИ МЕТАЛИ НА ЦЕЛУЛОЗНА ОСНОВА

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(Резюме)

В работата се описва нов материал за адсорбция на тежки метали на целулозна основа. Бамбукова целулоза се третира с плазма (150 V) за 120 секунди, следват епоксидиране, аминирание и ултразвуково ускорено сулфониране за получаването на адсорбента, който е в състояние на вгради тежките метали. Получените материали са изследвани с инфрачервена спектроскопия (FTIR) и ядрено-магнитен резонанс. Анализите показват, че кислород-съдържащите сулфо-групи са успешно включени в целулозата.