



Preparation and application of cellulose triacetate microspheres

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ABSTRACT

Cellulose triacetate was prepared via reacting of a mixture of acetic anhydride and acetic acid containing sulfuric acid as catalyst with ramie fiber obtained from a biomass of ramie. The cellulose triacetate with a degree of substitution (DS) 2.93 of the ramie fiber was obtained. The honeycomb-like cellulose triacetate microspheres with an average diameter of 14 μm were made from the cellulose triacetate solution. The optimum conditions for preparing the microspheres were determined as cellulose triacetate/dichloromethane ratio 1:7 (w/w), and 0.75% sodium dodecylsulfonate. The cellulose triacetate microspheres were characterized using FT-IR, NMR, XRD, and SEM. Application of the microspheres as an adsorbent for removing disperse dyes in water was investigated under the temperatures from 15 to 50 °C, pHs from 4 to 9, and the weight of cellulose triacetate microspheres from 0.03 to 0.09 g. The cellulose triacetate microspheres exhibited a 16.5 mg/g capability to remove DR dye from water at 50 °C and pH 7.

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1. Introduction

Ramie is an abundant resource in China, and is commonly referred to as “Chinese grass”. As one of the most important natural fibers, the cellulose content in ramie is higher (65–75 wt%) than in other bast fibers such as hemp, flax and jute. Efficient and profitable utilization of the fibers is of great importance [1].

Cellulose acetate is the most important cellulose ester, and is used in the production of oil paint, textiles, filter tips, wrappers, and film [2]. In relation to derivatization of cellulose acetate, cellulose triacetate (CTA) is one of the most important cellulose esters in the cellulose acetate family. It plays an important role in industrial applications due to its low toxicity and low flammability [3–6].

Persistent organic pollutants are present in the environment, and may have long half-lives (years or decades) in soils, water or air [7]. Such pollutants can have harmful effects on the ecosystem, and concerns over resulting health effects in humans and wildlife provide the impetus for research on these topics [8]. Wastewater from textile, paper and other industries contains residual dyes that are not readily biodegradable, and the present study addressed efficient removal of dyes from wastewater.

Previous research has shown that macromolecular materials have high capacity as adsorbents, and can be used to remove organic pollutants from water [9,10]. Furthermore, cellulose acetate is a highly efficient adsorbent due to its porosity [10]. In the present work honeycomb-like CTA microspheres with high specific area were prepared, and were expected to be able to eliminate toxic organic chemicals from water. Preparation of cellulose triacetate from ramie fiber is not only favorable as a low cost route, but also necessary for a sustainable development strategy. The CTA microspheres were synthesized and characterized with FT-IR, NMR, XRD, and SEM. The microspheres showed a broad diameter distribution and rough appearance, and their adsorption ability was quantified using dye solutions.

2. Experimental

2.1. Materials

Ramie fibers were obtained from Hu'nan Yuanjiang Mingxing Co. Ltd. Acetic acid, acetic anhydride, sulfuric acid, anhydrous magnesium acetate, hydrochloric acid, sodium hydroxide, dichloromethane, and alcohol were purchased from Xi'an Chemicals Co. Ltd. Span 80 was purchased from Tianjin kernal chemical reagents development centre. Sodium dodecylsulfonate was obtained from Sinopharm Group Chemical Reagent Co. Shanghai, China. Dyes were purchased from the Xi'an Qinlong Co. Ltd., China. Anhydrous magnesium acetate, sodium dodecylsulfonate dyes, and Span 80 were CP grade, and other chemicals were AR grade and used without further purification.

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2.2. Characterization

FT-IR spectroscopy was performed using a Nicolet 870 spectrometer taking 32 scans for each sample. ^1H NMR spectra in CDCl_3 were recorded with a superconducting Fourier digital NMR spectrometer (Bruker; 300 MHz). X-ray diffractograms were recorded in the range $5^\circ \leq 2\theta \leq 60^\circ$ with a Rigakav D/max-1200 instrument equipped with a graphite monochromator in the diffracted beam, and using $\text{Cu K}\alpha$ radiation with wavelength 0.154 nm at 40 kV and 30 mA. SEM observations on CTA microspheres were carried out using a Philips Quanta 200 instrument. The CTA microspheres were laid down on an aluminum stub using a conductive adhesive tape, and were sputter-coated with gold prior to measurements. The absorbance of dye solution was determined using a UV-vis-NIR spectrometer; model Lambda 950 (Perkin-Elmer Co. Ltd., USA). Dye adsorption was carried out in an incubator shaker at 250 rpm (Shipping Co. Ltd., China).

2.3. Preparation of CTA

Ramie fibers were first swelled with acetic acid for 2 h at room temperature. The swelled fibers (10.0 g) were reacted with a mixture of acetic anhydride (40 mL) and acetic acid (40 mL) containing sulfuric acid as catalyst at 55°C . The amount of catalyst was 0.3–0.8 wt% relative to the mass of ramie fibers. After reaction anhydrous magnesium acetate was added to the reaction mixture to neutralize the sulfuric acid. Acetic acid solution was then added to the reaction mixture. After reaction the solution was poured into water to precipitate CTA, which was isolated from the turbid solution with a centrifugal separator, washed to neutral pH with distilled water and dried at 50°C .

2.4. Preparation of CTA microspheres

A 1.50 g sample of dried (100°C , 2 h) CTA was transferred to a conical flask and 100 mL dichloromethane added. A clear solution of CTA was obtained, and Span 80 was added. A 0.75% solution of sodium dodecylsulfonate (SDS) was obtained by dissolving SDS in distilled water. The CTA/Span 80/dichloromethane solution was added to the SDS solution at 30°C whereupon a white turbid suspension of CTA microspheres was obtained by evaporating the dichloromethane. The microspheres were separated from the dispersion by centrifugal separator and washed with hot water to remove the sodium dodecylsulfonate, then washed several times with alcohol to remove Span 80. CTA microspheres were obtained after drying at 60°C and the yield of the microspheres production was above 95%.

2.5. Calculation of removal rates

The absorbance of the original dye solution and residual solution was measured [11], and the removal rate calculated from:

$$R = \frac{M_0 - M_e}{M_0} = \frac{C_0 - C_e}{C_0}$$

where R is the removal quantity of dye, M_0 is the mass of dye before absorbent, M_e is the mass of dye after absorbent equilibrium, C_0 is the initial concentration of the dye solution, and C_e is the equilibrium concentration of the dye solution. The uptake of the dyes were calculated from [11]:

$$q = \frac{V}{M}(C_0 - C_e)$$

where q is the uptake of the dye, C_0 is the initial concentration of the dye solution, C_e is the equilibrium concentration of the dye

solution, V is the volume of the solution, and M is the mass of the absorbent.

2.6. Degree of substitution of CTA

The degree of substitution (DS) was calculated according to the literature [12,13]. The mass of acetic acid formed during titration was calculated from the equation:

$$\begin{aligned} \text{mass of acetic acid} &= \frac{[(D - C) \times N_{\text{HCl}} + (B - A) \times N_{\text{NaOH}}] \times 6.005}{W} \\ &= \frac{6000DS}{162 + 42DS} \end{aligned}$$

where A is the volume of NaOH consumed by cellulose (mL), B the volume of NaOH consumed by CTA (mL), C the volume of HCl consumed by cellulose (mL), D the volume of HCl consumed by CTA (mL), N_{HCl} the concentration of HCl (mol L^{-1}), N_{NaOH} the concentration of NaOH (mol L^{-1}), and W is the mass of sample (g).

3. Results and discussion

3.1. FT-IR spectroscopy

The IR spectra of ramie fiber and CTA (Fig. 1) exhibited $-\text{O}-\text{H}$ stretching absorption at $3300\text{--}3500\text{ cm}^{-1}$, and $-\text{C}-\text{H}$ stretching absorption at $2900\text{--}3000\text{ cm}^{-1}$. Acetylation of the ramie fiber replaced $-\text{OH}$ by acetyl groups, and the CTA spectrum showed the expected acetyl group vibrations at 1750 ($-\text{C}=\text{O}$) and 1370 cm^{-1} ($-\text{C}-\text{CH}_3$). However, the spectrum of ramie fiber showed only a relatively intense absorption at 1640 cm^{-1} that is attributed to $-\text{O}-\text{H}$ bending vibration, and did not show an absorption band at 1750 cm^{-1} , indicating the absence of $-\text{C}=\text{O}$ group in the ramie fiber molecules. Esterification destroyed many intra- and intermolecular hydrogen bonds of cellulose molecules: the area of the hydroxyl band at $3300\text{--}3500\text{ cm}^{-1}$ in spectrum b is correspondingly smaller than in spectrum a, and the area of the acetyl $-\text{C}=\text{O}$ at 1750 cm^{-1} in spectrum b is larger than in spectrum a. It is clear that acetyl groups were successfully grafted onto the cellulose skeleton and cellulose triacetate was formed.

3.2. ^1H NMR analysis

A ^1H NMR spectrum of CTA is shown in Fig. 2. In the linear molecular structure of CTA, the hydrogen atoms show two clusters of signals (Fig. 2). The proton resonance signals of the glucose ring ($\delta = 3.40\text{--}5.20$ ppm) and the corresponding resonance for the

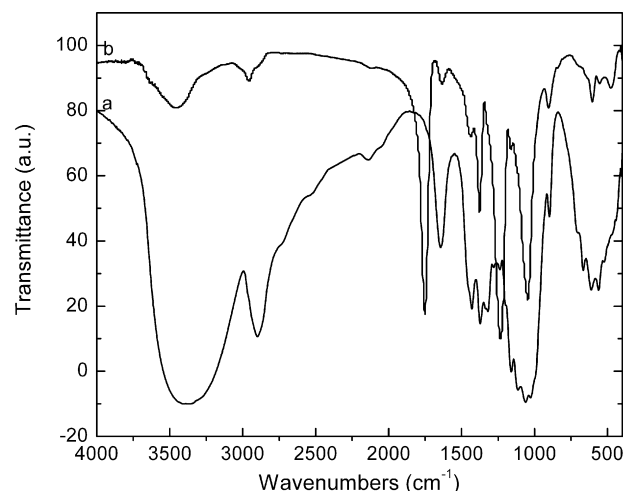


Fig. 1. FT-IR spectra of (a) ramie fiber, and (b) CTA.

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