



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 $1750\text{ (}-\text{C}=\text{O})$ 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 ($\delta = 3.40\text{--}5.20\text{ ppm}$) and the corresponding resonance for the

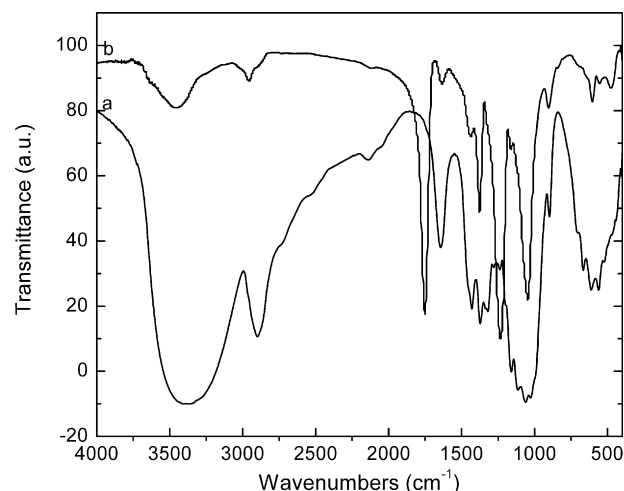


Fig. 1. FT-IR spectra of (a) ramie fiber, and (b) CTA.

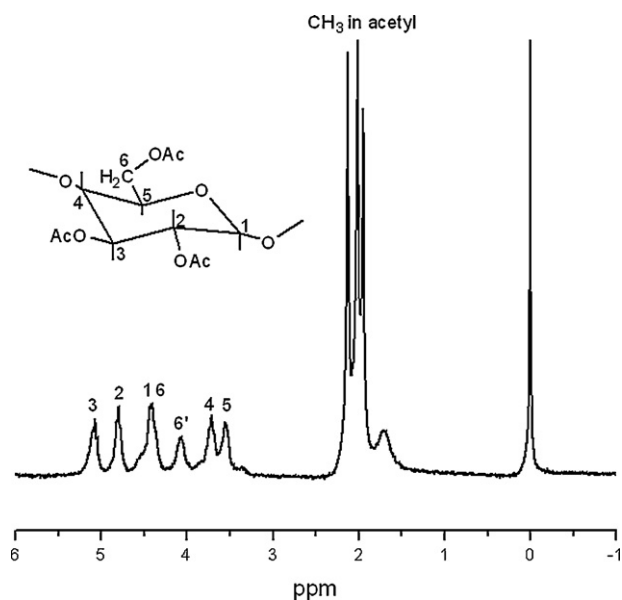


Fig. 2. ^1H NMR spectrum of CTA.

methyl protons of the acetate group ($\delta = 1.80\text{--}2.20$ ppm) are shown in Fig. 2. The chemical shifts are in good agreement with previously reported observations [14]. It is possible to calculate *DS* at the free reactive site from ^1H NMR spectra after peracetylation of the cellulose acetate derivatives with acetyl- d_3 -chloride. The *DS* value of the CTA was calculated from the ratio of the area corresponding to the proton resonance of the glucose ring ($\delta = 3.40\text{--}5.20$ ppm) to the corresponding resonance for the methyl protons of the acetyl group ($\delta = 1.80\text{--}2.20$ ppm) [14]. The *DS* value obtained by the proton NMR method was 2.93, in excellent agreement with reported values [12,15].

3.3. X-ray diffraction

X-ray diffractograms of ramie fiber (curve a) and CTA (curve b) are shown in Fig. 3. Compared with the diffraction peaks in curve a, curve b is a typical pattern of CTAII as reported by Zugenmaier [16].

The difference of the two diffraction patterns demonstrated the total transformation of the cellulose structure to the structure of CTA. The main reason for the change in the diffraction patterns may

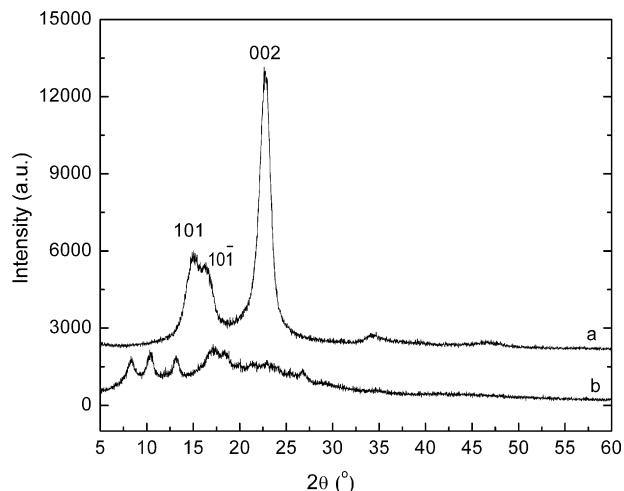


Fig. 3. XRD patterns of (a) ramie fiber and (b) CTA.

be penetration of the reagent into the crystalline region of cellulose, reacting and promoting formation of amorphous structures.

Acetylation began in a multiphase system. Acetyl groups were initially grafted onto the cellulose surface leading to gradual dissolution in the reaction mixture, exposure of fresh cellulose surface, and continuation of the acetylation reaction until the reaction mixture became homogeneous. The reaction is represented by Scheme 1.

There are three active hydroxyl groups in each glucose ring of the cellulose chains. The high degree of crystallinity of cellulose arises from the intra- (1) and inter-molecular (2) hydrogen bonds shown in the reaction scheme. The structure of the crystalline regions of cellulose was progressively destroyed by the acetylation reaction, and the crystallinity decreased accordingly.

3.4. Scanning electron microscopy

Fig. 4 shows SEM micrographs of CTA microspheres prepared. When the CTA/Span 80/dichloromethane solution was added to aqueous sodium dodecylsulfonate solution and the dichloromethane evaporated, honeycomb-like CTA microspheres with a broad distribution of diameters (Fig. 4 a) were obtained.

Fig. 5 shows that the diameters of CTA microspheres are mostly in the ranges from 10 to 16 μm , indicating that CTA microspheres prepared has a well-distribution diameter.

CTA is soluble in dichloromethane solution, but precipitates in water. In the sedimentation system, due to the low solubility of dichloromethane in water and with the help of the surfactant (sodium dodecylsulfonate), an “oil in water” emulsion was formed. When CTA molecules dissolved in the dichloromethane drop were attacked by surrounding water, the CTA microspheres precipitated. Span 80 was added to the reaction mixture to produce pores in the CTA microspheres. When the CTA microspheres were treated with alcohol, the Span 80 dissolved in the alcohol and the honeycomb-like microspheres were obtained (Fig. 4b).

3.5. Measurements of CTA sorption

The adsorption capacity of CTA microspheres was determined by measuring the absorbance of a dye solution before and after dye was adsorbed by the microspheres. The two types of dyes used were Disperse Red S-R (DR) and Reactive Brilliant Red X-3B (RB).

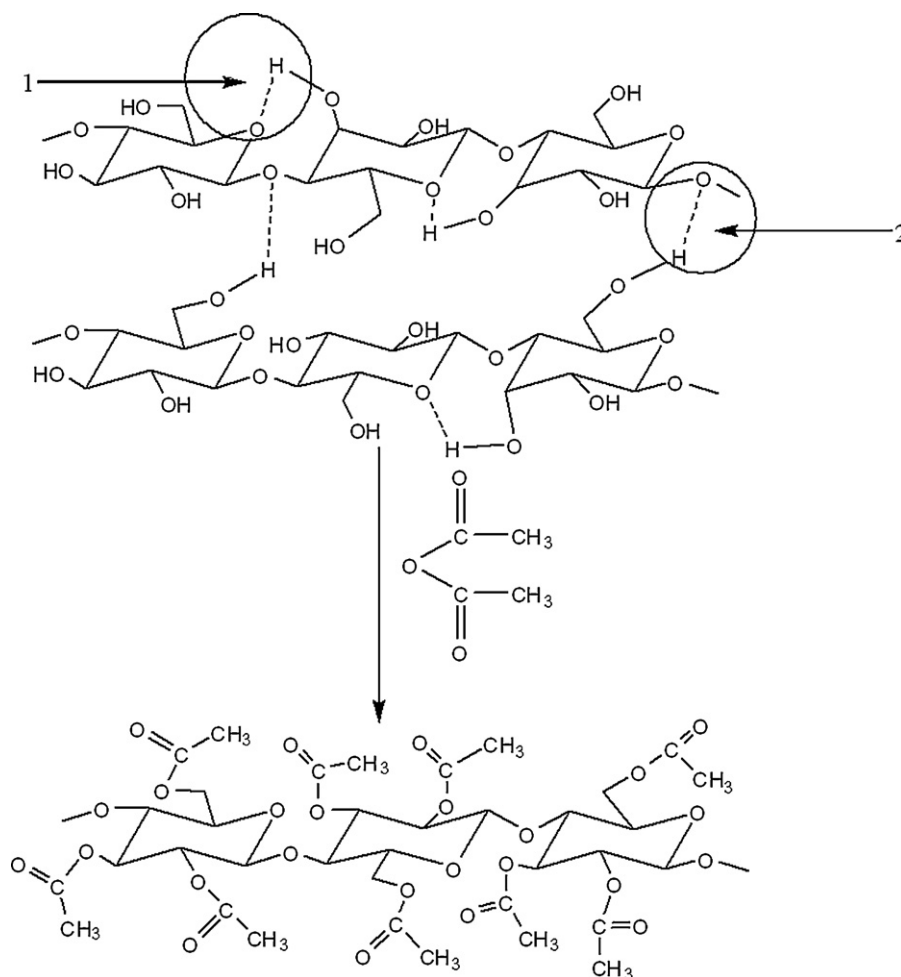
3.5.1. The relationship between removal rates and amount of CTA microspheres

CTA microspheres were added to 50 mL of the DR solution (40 mg L^{-1}), with pH 7, at 15°C . The removal rates of the CTA microspheres for dye solution are shown in Fig. 6. The dye removal rates clearly increased with increased mass of the CTA microspheres. With larger mass of microspheres, the removal rate increased slowly from 1 to 7 h, but much more rapidly at longer times. This trend may be due to the poor reactivity of the CTA and DR at 15°C . At the low temperature, the dye molecules diffused to the CTA surface slowly, and the adsorbent capability of CTA was low. With increase of time, more and more dye molecules reached the surface of the CTA microspheres and led to a remarkable increase of the removal rate for DR. The rate of desorption increased with increase of time until equilibrium was reached between adsorption and desorption, at which point the rate of removal became almost constant.

3.5.2. The relationship between removal rate and temperature

Fig. 7 shows the removal rates of DR (40 mg L^{-1} ; pH 7) by 0.09 g CTA microspheres at different temperatures. It is apparent that temperature is the predominant factor in the adsorption process.

During the adsorption process, CTA attracts the dye molecules from the water solution. Dye adsorption is strongly favored at



Scheme 1. Acetylation of ramie fiber.

higher temperatures primarily because diffusion of dye molecules is more rapid at higher temperature, and the flux of dye molecules to the surface of the surface of CTA microspheres is correspondingly larger. When the dye molecules enter the amorphous region of CTA molecules, the dye molecules are trapped by hydrogen bonding. Because of the strong adsorption of CTA microspheres for DR and the rough surface which gives a high specific surface area of the microspheres, adsorption of DR is very efficient at 50 °C.

3.5.3. The relationship between removal rate and solution pH

The effect of pH variation on dye removal rate, for 0.09 g CTA microspheres and 40 mg L⁻¹ dye, at 50 °C, is shown in Fig. 8. It is apparent that dye removal is more efficient at pH 7 than in either acidic or alkaline conditions. The main reason is the reduced stability of CTA in acidic or alkali solutions, in which deacetylation of the ester can occur and the rate of deacetylation is increased at elevated temperature. The resulting conversion of acetyl to -OH

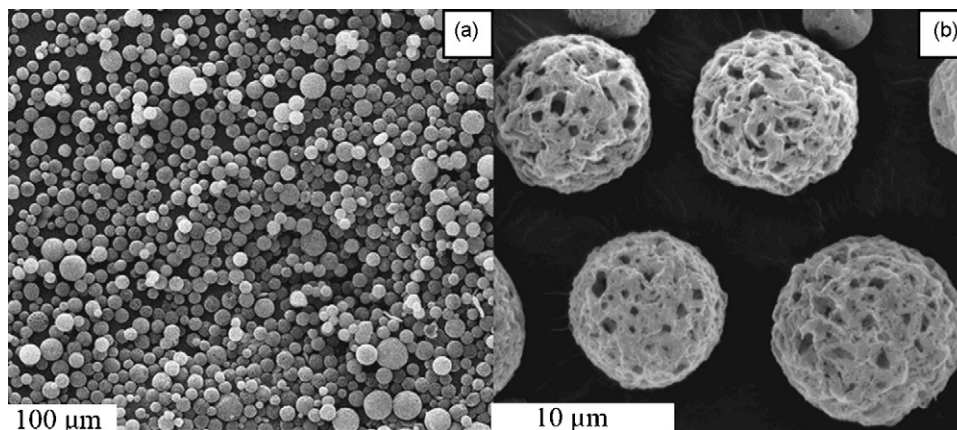


Fig. 4. SEM micrographs of CTA (a: 300×, b: 5000×).

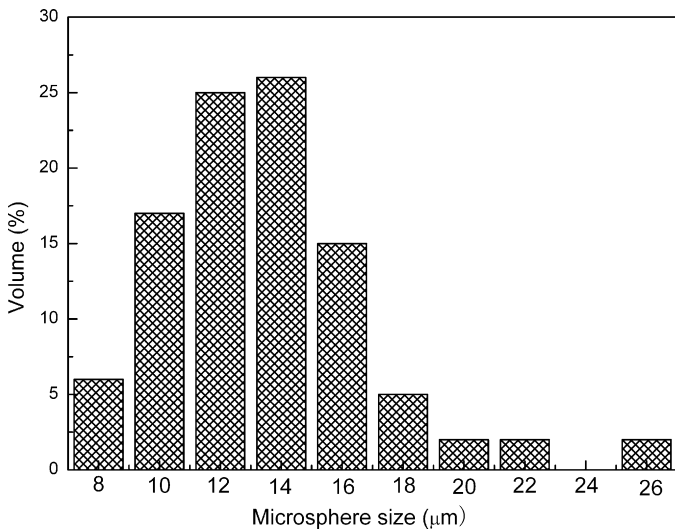


Fig. 5. The size distribution of CTA microspheres.

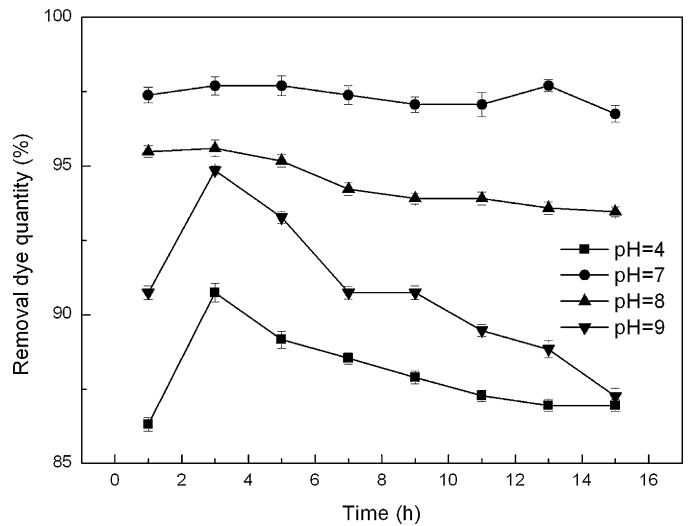


Fig. 8. The relationship between removal dye quantity and solution pH.

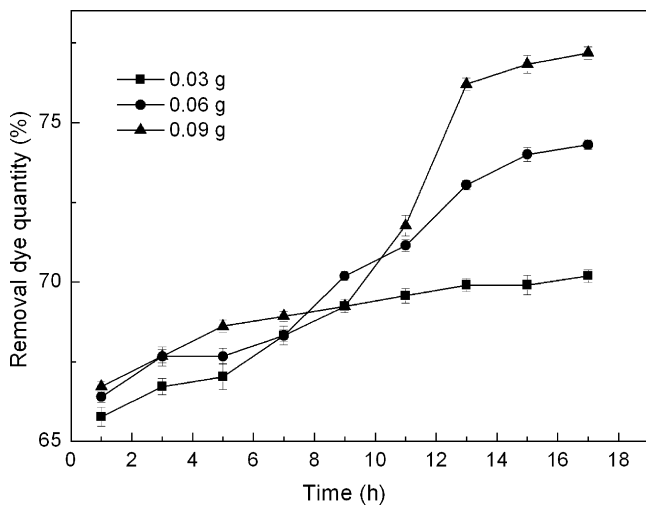


Fig. 6. The relationship between removal dye quantity and CTA mass.

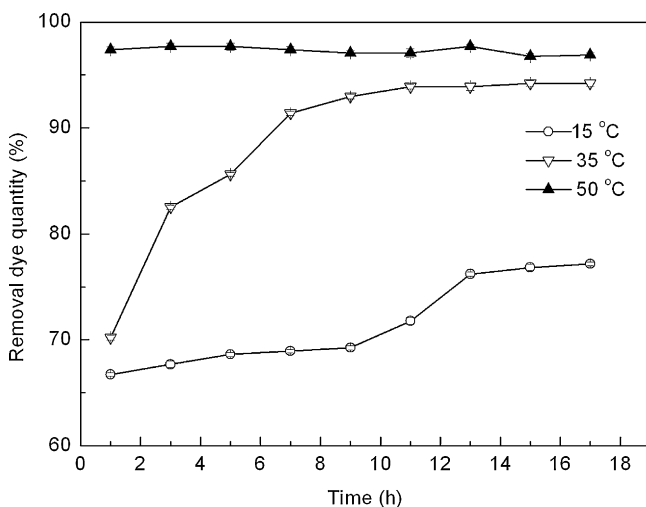


Fig. 7. The relationship between removal dye quantity and temperature.

groups reduces the ability of CTA to trap DR and the dye removal rate decreases. Although the removal rate was reduced at all pHs (relative to pH 7), the change in removal rate was different for each pH. At pH 8 the characteristics of the solution are very similar to those of a neutral solution, deacetylation occurred to only a small extent, and the rate of dye removal was only slightly smaller than at pH 7. At pH 4 and 9 CTA should be deacetylated to a greater extent, and the removal rates were significantly smaller than at pH 8. The time dependence of the dye removal rate at pH 4 and 9 may be due to an adsorption–deacetylation equilibrium in the system. In the early stages the adsorption of dye on CTA microspheres was faster than deacetylation; after about 3 h deacetylation occurred more rapidly than adsorption and the dye removal rate decreased.

3.5.4. The adsorption capability of CTA microspheres for different dyes

Fig. 9 gives adsorbent quantities for two dyes used. In these experiments the quantity of CTA was 0.09 g, the dye concentration was 40 mg L^{-1} , and the experiments were conducted at 50°C and pH 7. The data show that the dye removal rate was essentially independent of time for both dyes, but the adsorbent quantities for DR was much larger than for RB. This effect is due to the different

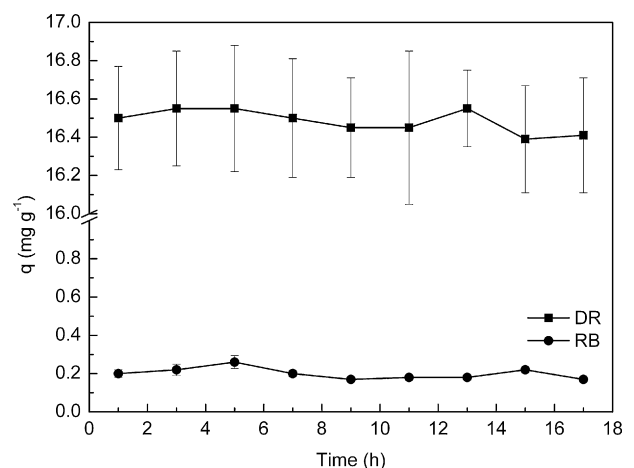


Fig. 9. The adsorbent quantities of the CTA microspheres for different dyes.

structures of the dyes causing different sorption capacities of CTA microspheres. Because the three hydroxyl groups in the cellulose were replaced by acetyl, there were few polar groups (such as –OH and –COOH) in the glucose rings. Also, the hydrogen atom in DR is more easily trapped by hydrogen bonding to the acetyl oxygen in CTA molecules. RB will react with –OH groups, but the hydroxyl groups in CTA were replaced completely, thus the sorption capacity for DR was larger than for RB. The sorption capacity mechanism of CTA microspheres for different dyes will be further studied in our work.

4. Conclusions

We provided a new method to prepare cellulose triacetate from ramie fiber obtained from a biomass of ramie, which is an abundant resource in China, and is commonly referred to as “Chinese grass”. The cellulose triacetate microspheres can be prepared from the cellulose triacetate solution. The optimum conditions for preparing cellulose triacetate microspheres were determined as the cellulose triacetate/dichloromethane ratio of 1:7 (w/w), and 0.75% sodium dodecylsulfonate. The honeycomb-like cellulose triacetate microspheres were formed with an average diameter of 14 μm with large specific surface area as confirmed by SEM. The cellulose triacetate microspheres showed a 97% removal rate for removing disperse dye from water at 50 °C.

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