



# Synthesis and flocculation property in dye solutions of $\beta$ -cyclodextrin–acrylic acid–[2-(Acryloyloxy)ethyl] trimethyl ammonium chloride copolymer

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## ARTICLE INFO

### Article history:

Received 11 July 2011

Received in revised form 5 September 2011

Accepted 3 October 2011

Available online 8 October 2011

### Keywords:

Cationic

Flocculant

poly ( $\beta$ -CD–AA–DMC)

Decolorization

## ABSTRACT

In aqueous solution a cationic copolymer, poly ( $\beta$ -CD–AA–DMC) was synthesized via free radical copolymerization of acrylic acid (AA) esterified  $\beta$ -CD ( $\beta$ -CD–AA), and a cationic monomer [2-(Acryloyloxy)ethyl] trimethyl ammonium chloride (DMC). The copolymer's structure, morphology and thermal stability were demonstrated by FT-IR, <sup>1</sup>H NMR, SEM and TGA analysis. The flocculation properties of the copolymer were evaluated by the decolorization solutions of two reactive dyes using a jar test method. The decolorization efficiency is influenced by both the nature of the anionic dyes and the pH of the initial dye solution. Electrostatic adsorption played a more important role in flocculation of dyes than bridging of the polymer. Moreover, the inorganic salt decreased the efficiency of color removal.

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## 1. Introduction

Anionic dyes, especially reactive and acidic ones are difficult to eliminate from aqueous solutions because of their relatively complicated structure and poor biodegradability (Anjaneyulu, Chary, & Raj, 2005; Forgacs, Cserhati, & Oros, 2004). Many studies have been carried out to develop the decolorization of dye-containing wastewater with higher efficiency and lower cost (Saratale, Saratale, Chang, & Govindwar, 2011). Currently, flocculation has been widely used as pretreatment to remove colorant from dye-containing wastewater prior to biological processes (Fang, Cheng, & Xu, 2010). High efficiency, low cost and the absence of harmful aromatic compounds are three main advantages of flocculation compare with other treatments. However, anionic dyes, in particular reactive dyes, cannot be easily removed by conventional flocculants such as polyacrylamide (Michelsen, Fulk, Woodby, & Boardman, 1993; Sanghi & Bhattacharya, 2005). Therefore the development of new flocculants suitable for decolorization of anionic dyes is still required.

$\beta$ -Cyclodextrin ( $\beta$ -CD), originating from starch, is eco-friendly, renewable, cost-effective and easily soluble. It has gained increasing interests in the area of flocculants for color removal. However  $\beta$ -CD is inefficient in removing colorants due to its low molecular mass, low charge density and short shelf life due to its biodegradability. Thus, to our knowledge, only a few studies have been reported to use  $\beta$ -CD derivatives as flocculants for decolorization (Jiang, Qi, Wang, & Tian, 2010; Tian, Wu, Zhang, Wang, & Jiang, 2010; Xiao & Cezar, 2005).

An amphoteric  $\beta$ -CD-based copolymer has been synthesized and utilized as flocculants in decolorization of dye-containing wastewater in our previous study. The results indicate that the efficiency of color removal through  $\beta$ -CD-based copolymer can be further improved by modification of  $\beta$ -CD and thereby polymerization of  $\beta$ -CD derivatives (Jiang et al., 2010; Tian, Wu, Zhang, et al., 2010). Accordingly, acrylic acid (AA) is employed to react with  $\beta$ -CD to introduce polymerizable double bonds into  $\beta$ -CD, and a cationic monomer of [2-(Acryloyloxy)ethyl] trimethyl ammonium chloride (DMC) is adopted to charge the  $\beta$ -CD containing copolymer. Consequently, a new cationic instead of amphoteric flocculant based on  $\beta$ -CD has been prepared and characterized by Fourier-transform infrared (FT-IR), <sup>1</sup>H nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR), scanning electron microscope (SEM) and thermogravimetric analysis (TGA). C.I. Reactive Orange 5 (RO 5) and C.I. Reactive Blue 19 (RB 19) are chosen for the jar tests of flocculation as representatives of anionic dyes. The effect on the decolorization's efficiency of the flocculant's mass, the initial dye solution's pH and the salt concentration are evaluated.

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## 2. Experimental

### 2.1. Reagents and materials

The  $\beta$ -CD from Wako Pure Chemical Co. Ltd. (Osaka, Japan) was purified by re-crystallization from water twice prior to use. [2-(Acryloyloxy)ethyl] trimethyl ammonium chloride (DMC), 80 wt.% solution in water and dicyclohexylcarbodiimide (DCC, 99% purity) were purchased from Aldrich. Acrylic acid (AA) was purchased from Showa chemicals (Tokyo, Japan). N,N-dimethylformamide (DMF) was distilled under vacuum and stored in 4 Å molecular sieves. All other reagents including ammonium persulfate (APS), sodium bisulfite (SBS), and acetone were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received without further purification.

The two kinds of reactive dyes used for flocculation experiments were purchased from Dynast Chemicals Co. Ltd. Their structures and characteristics are shown in Table 1.

### 2.2. Synthesis of the $\beta$ -CD-based cationic flocculant

The  $\beta$ -CD derivate containing vinyl groups ( $\beta$ -CD-AA) was synthesized from  $\beta$ -CD and AA (Huang & Fan, 2009), and then  $\beta$ -CD-AA was copolymerized with DMC to prepare a cationic flocculant (poly( $\beta$ -CD-AA-DMC)) for color removal (Jiang et al., 2010). The copolymerization was carried on in an aqueous solution at 45 °C and initiated by APS and SBS redox initiating system. The schematic structure of the cationic copolymer containing  $\beta$ -CD (poly( $\beta$ -CD-AA-DMC)) was illustrated in Fig. 1.

Specifically, 3.0 g of  $\beta$ -CD and 5.5 g of DCC were first dissolved in DMF, and then 1.82 mL of AA was added into the vigorously stirred solution at 30 °C. The reaction was kept at 30 °C for 24 h. The produced suspension was filtered firstly to remove the white solid precipitate, N,N'-dicyclohexylurea. Then a certain amount of acetone was poured into the remained solution to precipitate the product. After separation and filtration, the obtained solid was vacuum-dried at 45 °C and the coarse product was obtained. Lastly, the coarse product was washed with dilute acetic acid, potassium bicarbonate solution and water stepwise, and recrystallized by acetone and a fine product of  $\beta$ -CD-AA was obtained. The product was vacuum-dried at room temperature for 24 h and 80 °C for 72 h.

Thereafter, prescribed amount of  $\beta$ -CD-AA and DMC (6/4, w/w) were dissolved in distilled water in a three-neck flask of which setup with stirrer, nitrogen inlet and outlet, respectively. After bubbling with nitrogen for 15 min, mixed solution of APS and SBS was injected into the flask. The monomer concentration was 20 wt.% and the initiator concentration was 0.5 wt.% relative to monomer. After the copolymerization was conducted at 45 °C for 4 h, the obtained mixture was cooled down to room temperature and poured into acetone. The polymer was precipitated as a white solid, then filtered and washed with abundant acetone. Finally, it was dried in a vacuum oven at 60 °C for 48 h.

### 2.3. Instrumental analysis

FT-IR spectra were recorded on a Nicolet Nexus 470 spectrometer in the optical range of 400–4000  $\text{cm}^{-1}$  by averaging 32 scans at a resolution of 4  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were obtained on a Bruker AV-300 spectrometer using  $\text{D}_2\text{O}$  as solvent. The surface morphology was observed by scanning electron microscope (SEM; Quanta 200, Holland). Calorimetric analyses [weight loss and thermogravimetric analysis (TGA)] were carried out in a TA DSC Q100 (TA Co. Ltd., America) calorimeter at a heating rate of 10 °C/min in  $\text{N}_2$ .

### 2.4. Flocculation experiments

Experiments on dye removal were performed using Jar-Test equipment. Specifically, the dye solution of 50 mL at a concentration of 100 mg/L was transferred into the jar and the pH of dye solution was adjusted with  $\text{H}_2\text{SO}_4$  or NaOH (2 M). Then the prescribed mass of poly( $\beta$ -CD-AA-DMC) was added. The mixture in the jar was rapidly stirred at a speed of 165 rpm for 5 min, followed by a slow stirring at 65 rpm for the next 10 min. Thereafter, the suspension was allowed to be settled for 3 h. After settling, sample was collected after centrifuged (top 1 cm of water surface) using a syringe, and analyzed for dye content by a UV-visible spectrophotometry (UV2100) from UNIC (Shanghai) instruments Co. Ltd. at the wavelengths of 462 nm for RO 5, and 595 nm for RB 19.

The efficiency of color removal was calculated by Eq. (1).

$$\text{Color removal\%} = \left(1 - \frac{CV}{C_0V_0}\right) \times 100 \quad (1)$$

where  $C_0$  and  $C$  denoted the dye concentration in the solution before and after flocculation,  $V_0$  and  $V$  were the volume of solution before and after flocculation, respectively.

## 3. Results and discussion

### 3.1. Characterization of the copolymer

FT-IR spectra of  $\beta$ -CD,  $\beta$ -CD-AA and poly( $\beta$ -CD-AA-DMC) were recorded as curves a, b and c in Fig. 2.

Firstly, an absorption at 1720  $\text{cm}^{-1}$  appears in curve b, while it is not found in curve a. It is due to the stretching vibration of carbonyl's ( $\text{C}=\text{O}$ ) in unsaturated esters [ $\text{CH}_2=\text{CH}-\text{C}(\text{O})-\text{O}$ ] in  $\beta$ -CD-AA. Besides, the intensity of peak in the range of 1600–1650  $\text{cm}^{-1}$  in curve b is stronger than that in curve a, which is attributed to the stretching vibration of  $\text{C}=\text{C}$ . Moreover, another new absorption at 1202  $\text{cm}^{-1}$  assigned to the stretching vibration of esterified linkage [ $\text{C}(\text{O})-\text{O}$ ] in  $\text{CH}_2=\text{CH}-\text{C}(\text{O})-\text{O}$  appears in curve b compared with curve a. The three groups of peaks mentioned above demonstrated that the reaction for esterifying  $\beta$ -CD by AA was realized (Liu & Fan, 2005).

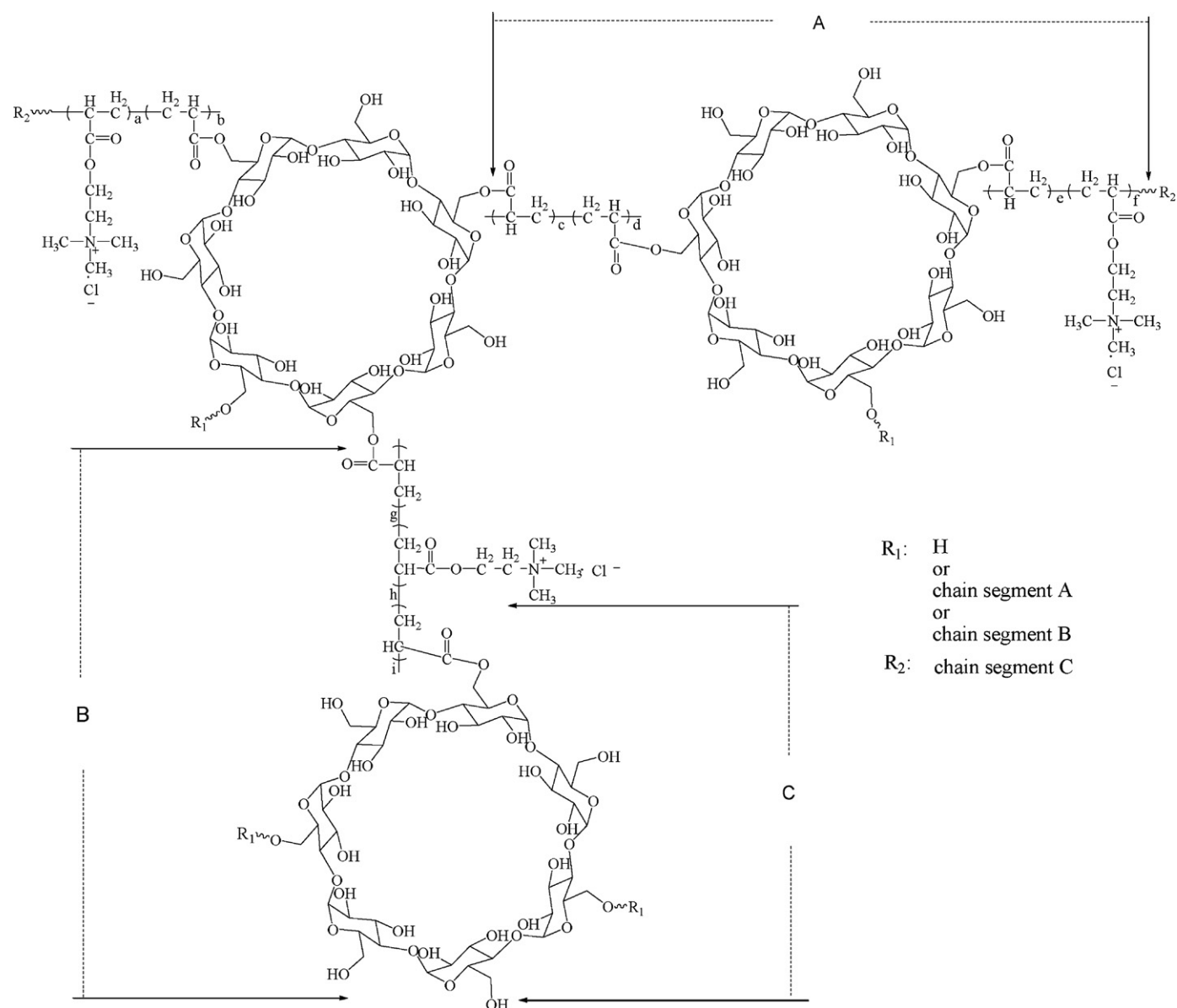
Secondly, characteristic absorptions of  $\beta$ -CD were observed in curves a, b and c at very close wave numbers including 3372  $\text{cm}^{-1}$  [stretching vibration of the hydrogen bonded  $-\text{OH}$ ], 2929  $\text{cm}^{-1}$  [stretching vibration of  $\text{C}-\text{H}$ ], 1414  $\text{cm}^{-1}$  [bending vibration of the  $\text{C}-\text{H}$ ], 1156  $\text{cm}^{-1}$  [symmetrical stretching vibration of  $\text{C}-\text{O}-\text{C}$ ], 1081  $\text{cm}^{-1}$  [asymmetrical stretching vibration of  $\text{C}-\text{O}-\text{C}$ ], 1030  $\text{cm}^{-1}$  [stretching vibration of  $\text{C}-\text{OH}$ ], 946, 756 and 579  $\text{cm}^{-1}$  [skeletal vibration] (Liu & Fan, 2006). These absorptions imply that the structure of  $\beta$ -CD is unchanged in both  $\beta$ -CD-AA and poly( $\beta$ -CD-AA-DMC).

Thirdly, relative to curves a and b, curve c presented the absorption peak at 1486  $\text{cm}^{-1}$  that is due to the bending vibration of methyl groups of ammonium, and 948  $\text{cm}^{-1}$  (overlapped with the band at 946  $\text{cm}^{-1}$ ) that is ascribed to the stretching vibration of quaternary ammonium. These two peaks demonstrated that cationic moieties were incorporated onto the backbone of copolymer (Pal, Malb, & Singh, 2006). Furthermore, free radical copolymerization between  $\beta$ -CD-AA and DMC is validated by the weaknesses of the intensities of peaks at 1600–1650  $\text{cm}^{-1}$  and 1202  $\text{cm}^{-1}$  of unsaturated ester, and as well by the presence of strong absorption peak at 1732  $\text{cm}^{-1}$  of saturated ester linkage [ $\text{CH}_2-\text{CH}-\text{C}(\text{O})-\text{O}$ ] in curve c.

The  $^1\text{H}$  NMR spectra of  $\beta$ -CD-AA and poly( $\beta$ -CD-AA-DMC) are exhibited as curves a and b, respectively in Fig. 3.

As seen in curve a in Fig. 3, the peaks with  $\delta$  ranging from 6 ppm to 7.5 ppm are corresponded to the protons of vinyl groups ( $\text{CH}_2=\text{CH}$ ), which indicates that the esterification of  $\beta$ -CD and AA

Chemical structure	Dyestuff	$\lambda_{\max}$ (nm)	Purity (%)	Molecular weight (g/mol)
	C.I. Reactive Orange 5 (RO 5)	462	55	876.077
	C.I. Reactive Blue 19 (RB 19)	595	55	594.475



**Fig. 1.** Schematic structure of the cationic copolymer containing  $\beta$ -CD.

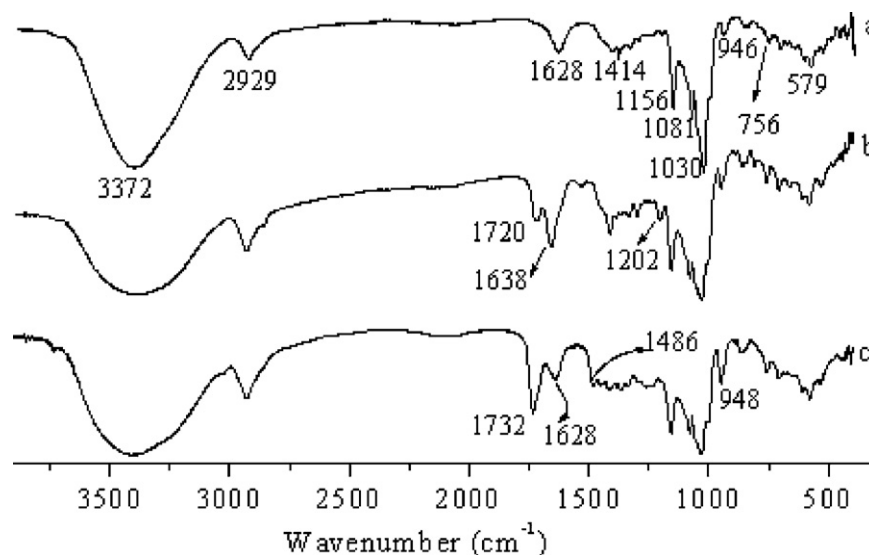


Fig. 2. FT-IR spectra of  $\beta$ -CD (a),  $\beta$ -CD-AA (b) and poly ( $\beta$ -CD-AA-DMC) (c).

occurred and a copolymerizable  $\beta$ -CD derivate that is  $\beta$ -CD-AA bearing active double bonds has been successfully synthesized (Dispenza, Tripodo, LoPresti, Spadaro, & Giammona, 2009). However, as shown in curve b of the spectrum of poly ( $\beta$ -CD-AA-DMC), the peaks of vinyl groups are largely weakened, which suggests that most double bonds ( $\text{CH}_2=\text{CH}$ ) in  $\beta$ -CD-AA has polymerized through an additive reaction. Instead, relative to curve a, curve b showed new peaks of DMC units in the copolymer at 2.40–3.30 ppm ( $\text{CH}_2-\text{CH}$ ), 3.77 ppm ( $\text{N}^+(\text{CH}_3)_3$ ), 4.30 ppm ( $\text{CH}_2-\text{N}^+$ ), and 5.06 ppm ( $\text{C}(=\text{O})\text{O}-\text{CH}_2$ ) (Mespouille, Degee, & Dubois, 2005; Zhu, Qian, Zhang, Tang, & Yin, 2007). Accordingly, the proposed structure of poly ( $\beta$ -CD-AA-DMC) in Fig. 1 is proved.

Moreover, the characteristic peaks of protons in  $\beta$ -CD at 3.5–4.6 ppm and 5.55 ppm exist in both curve a and curve b. It shows that the structure characteristics of  $\beta$ -CD are well maintained in the modified compounds,  $\beta$ -CD-AA and poly

( $\beta$ -CD-AA-DMC) (Biswas, Cheng, Selling, Willett, & Kendra, 2009).

Thermal stability of the original  $\beta$ -CD,  $\beta$ -CD-AA and poly ( $\beta$ -CD-AA-DMC) were analyzed by TGA, the weight loss curves are shown as curves a, b and c, respectively in Fig. 4.

According to Fig. 4, two gradual transitions of degradation can be observed in TGA curve of poly ( $\beta$ -CD-AA-DMC), although there is only one transition of degradation in TGA curves of  $\beta$ -CD and  $\beta$ -CD-AA. Two degradations of poly ( $\beta$ -CD-AA-DMC) are mainly due to the two different segments in its backbone. Compared curves b and c to a, the initial temperature of weight loss of curve b and c is lower than that of curve a, which indicates that the thermal stability of the  $\beta$ -CD-based compound and copolymer become worse compared with  $\beta$ -CD. Nevertheless, poly ( $\beta$ -CD-AA-DMC) is thermally stable enough to be a flocculant based on our flocculated decolorization experiment.

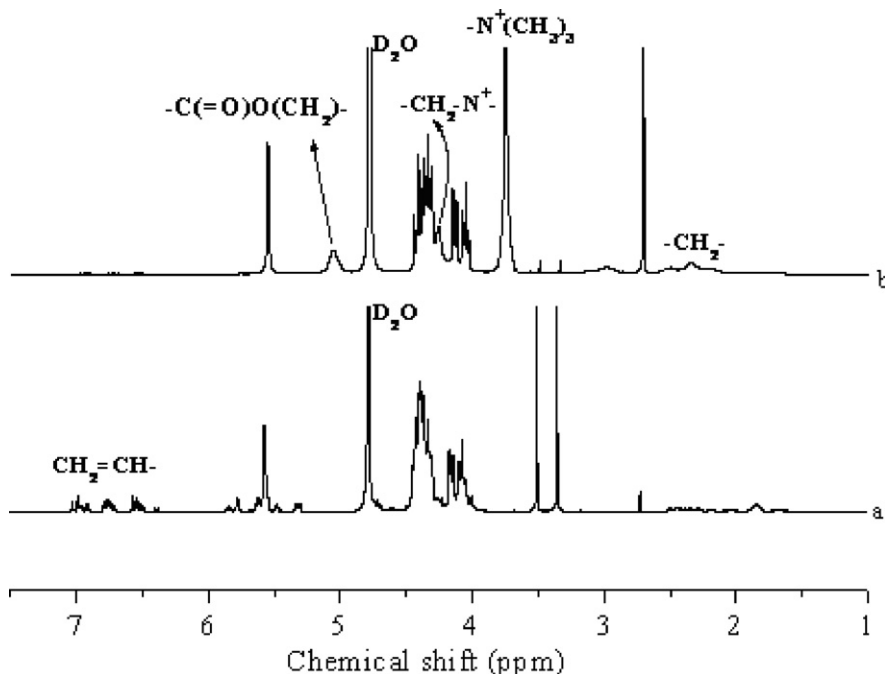


Fig. 3.  $^1\text{H}$  NMR spectra of  $\beta$ -CD-AA (a) and poly ( $\beta$ -CD-AA-DMC) (b) in  $\text{D}_2\text{O}$ .



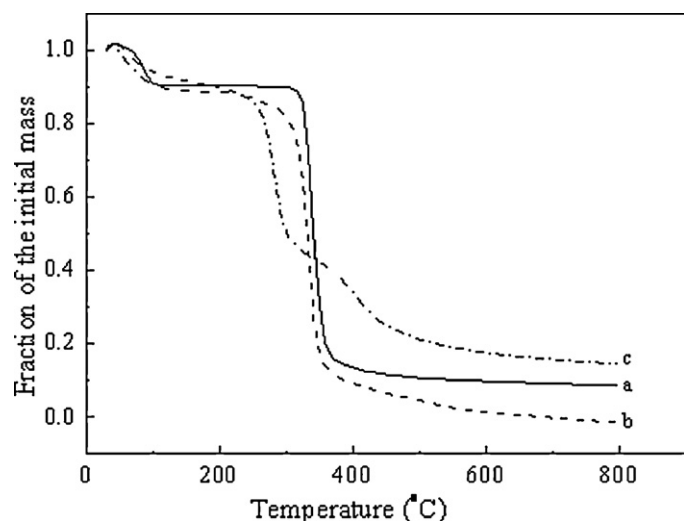


Fig. 4. TGA curves of  $\beta$ -CD (a),  $\beta$ -CD-AA (b) and  $\beta$ -AA-DMC (c).

SEM photographs of the original  $\beta$ -CD and the modified derivatives that are  $\beta$ -CD-AA and poly ( $\beta$ -CD-AA-DMC) are given in Fig. 5a–c.

As seen in Fig. 5a, the original  $\beta$ -CD mainly exists as irregular particle (Biswas et al., 2009). In contrast, Fig. 5b shows that  $\beta$ -CD-AA exists as relatively regular particles with smaller size. Furthermore, after DMC has been grafted onto  $\beta$ -CD-AA by radical polymerization, the obtained poly ( $\beta$ -CD-AA-DMC) mainly exists as irregular and porous clumps as shown in Fig. 5c. In conclusion, morphology and shape of particles of  $\beta$ -CD are changed drastically. It revealed the successful modification of  $\beta$ -CD indirectly, including the esterification between  $\beta$ -CD and AA and the radical polymerization between  $\beta$ -CD-AA and DMC.

### 3.2. Decolorization of poly ( $\beta$ -CD-AA-DMC) as a flocculant

#### 3.2.1. Effect of the pH of the initial dye solution and the flocculant dosage

Generally, decolorizing the dye-containing solutions by flocculation is a process to remove the anionic dyes through forming large agglomerates with a certain kind of macromolecules with appropriate length of molecular chain and positive charges. As a result, both electrostatic adsorption and bridging action could be employed to explain the decolorization processes. Nevertheless, to tell which one is more influential depends on many factors such as pH and ionic strength of the dye solution and the flocculant concentration (Ochoa-Gómez et al., 2009). The influence of pH and dose of poly ( $\beta$ -CD-AA-DMC) on the efficiency of color removal is presented in Fig. 6.

The efficiency of color removal of poly ( $\beta$ -CD-AA-DMC) can be higher than 90% according to Fig. 6. In general, the more the poly ( $\beta$ -CD-AA-DMC) is dosed, the more the dyes are removed, unless the cationic charge of the polymer is high enough to neutralize the anionic charge of dyes. The excess of cationic charges in polymer will lead to re-stabilization of suspension so that decrease the efficiency of flocculation.

The efficiency of removal of RO 5 is higher than that of RB 19 as pH is 7 and dose of poly ( $\beta$ -CD-AA-DMC) is lower than 140 mg/L. It can be explained by the different  $\zeta$ -potential of the dyes. According to Table 1, RO 5 contains more sulfonic groups ( $-\text{SO}_3^-$ ) than RB 19, which means that RO 5 might have higher  $\zeta$ -potential than RB 19. Therefore, the decoloring efficiency of RO 5 is higher than that of RB 19.

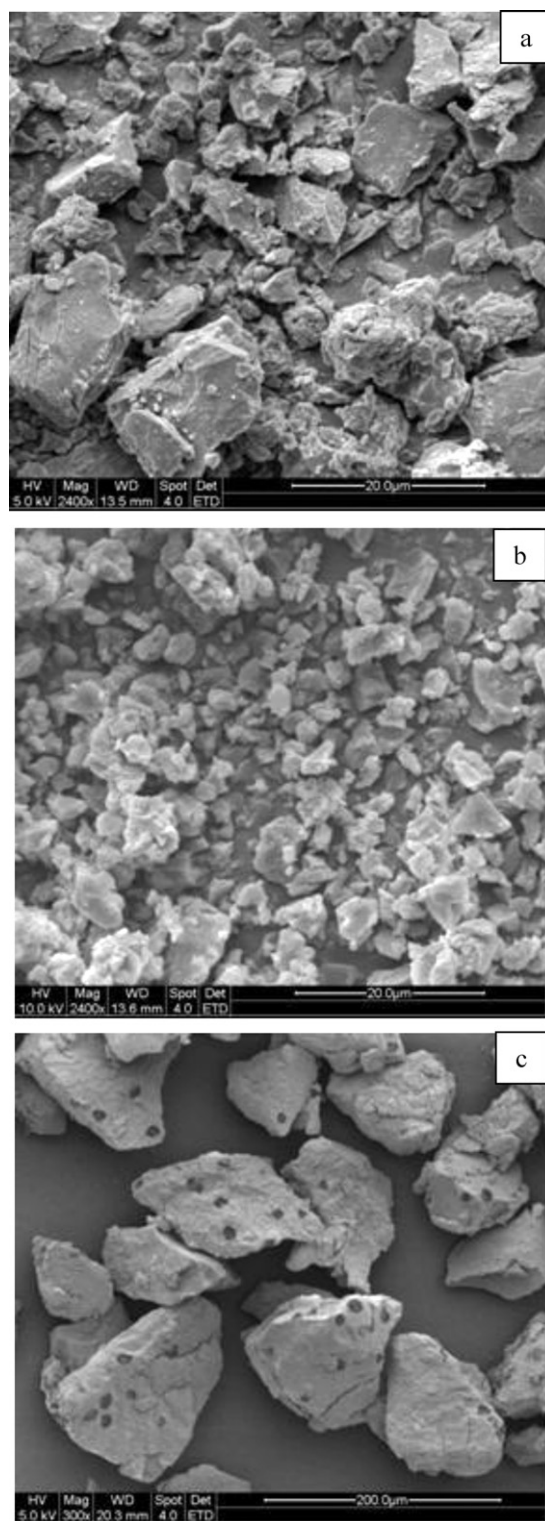


Fig. 5. SEM microphotographs of surfaces. (a)  $\beta$ -CD, (b)  $\beta$ -CD-AA and (c) poly ( $\beta$ -CD-AA-DMC).

On the other hand, the lower pH of solution is benefit for the efficiency of decolorizing both dyes' solutions. Wherein, the removal of RO 5 is influenced by pH more than that of RB 19. Especially, 140 mg/L of poly ( $\beta$ -CD-AA-DMC) is utilized in the neutral solution of RO 5, while only 120 mg/L is enough in the acidic solution, to achieve the highest efficiency of decolorization. The influence of pH

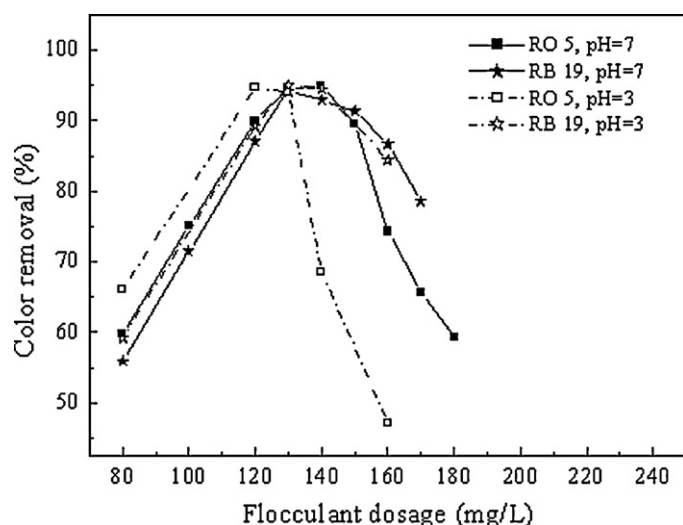


Fig. 6. Effects of flocculant dosage on the decolorization efficiency of the two dye solutions at different pH values.

also demonstrates that electrostatic adsorption plays a dominant role in decolorization by flocculation.

### 3.2.2. Effect of the salt concentration

Inorganic salt such as NaCl is generally adopted in dyeing process of textiles with reactive dyes. As its perfect solubility in water, NaCl remains in the effluents unavoidably. The effect of concentration of NaCl on the efficiency of color removal has been studied. The dose of poly ( $\beta$ -CD-AA-DMC) and the pH of solution are fixed at 140 mg/L and 7, respectively. The results are exhibited in Fig. 7.

In both dyes' solutions, the efficiency of decolorization decreases with the increasing of the dosage of NaCl, as seen in Fig. 7. However, the influence of the salt on the efficiency of decolorization of RO 5 solution is stronger than that of RB 19 solution. It could be explained as follows. First of all, the ionic macromolecular segments curl instead of extending in a solution with a relatively high salt concentration, which reduces the chance of bridging of polymer chains (Tian, Wu, Liu, & Xie, 2010). Moreover, ionization of dye molecules is prevented by adding  $\text{Na}^+$ , as shown in Eq. (2). The  $\text{Na}^+$  possibly decreases the surface potential of anionic dyes ( $\text{DSO}_3^-$ ) and thus weakens the electrostatic interactions between

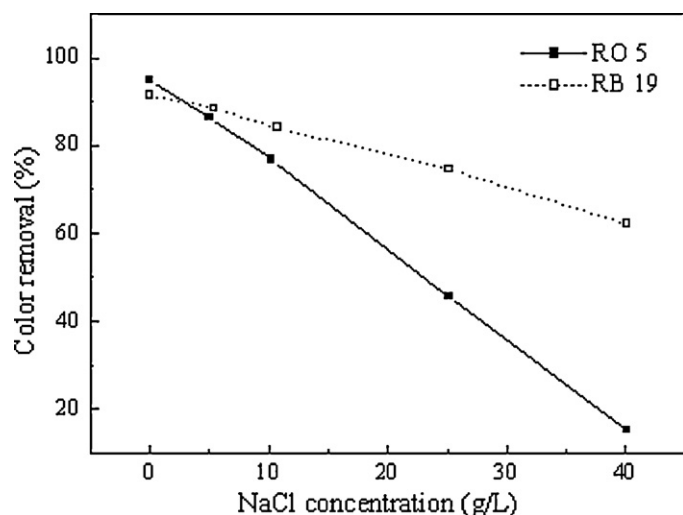


Fig. 7. Effects of salt concentration on the decolorization efficiency at neutral pH.

the anionic dyes and the cationic flocculant, poly ( $\beta$ -CD-AA-DMC). Accordingly, the decolorization efficiency decreased.



Obviously, the prevention of ionization is more serious for RO 5 solutions due to the presence of more sulfonic groups. Thus the added salt has stronger effects on color removal of the RO 5 solutions as faster depression of the decolorization efficiency with increasing the salt concentration takes place in the case of the RO 5 solutions. Thus, the electrostatic adsorption is the main mechanism for flocculated decolorization for the given flocculant/dye solution system.

## 4. Conclusions

A novel cationic flocculant,  $\beta$ -CD-based copolymer named as poly ( $\beta$ -CD-AA-DMC), with efficiency of decolorization higher than 90% has been synthesized. FT-IR and  $^1\text{H}$  NMR testified the chemical structure of the copolymer, SEM displayed the morphology of the copolymer's particles, and TGA showed the variation of thermal stability of  $\beta$ -CD derivatives with the introducing of polymerizable structure of AA and cationic monomer of DMC.

Further, the decolorization property of poly ( $\beta$ -CD-AA-DMC) was demonstrated by flocculation of two kinds of anionic dyes that are RO 5 and RB 19. The efficiency and mechanism of decolorization depend upon the structural nature of the anionic dyes and the pH of the dye solutions to be flocculated. For the given examples of flocculant/dye solution, electrostatic adsorption played a dominant role for the color removal at both acidic and neutral pH, and the bridging effect of long chain of polymer could not be neglected synchronously. The more sulfonic groups do the dyes have, or the more acidic are the dye solutions, the higher is the efficiency of color's removal. Moreover, adding an inorganic salt such as NaCl had decreased the efficiency of color's removal. More depression of the decolorization efficiency took place in the RO 5/poly ( $\beta$ -CD-AA-DMC) solution system, compared with RB 19.

## Acknowledgements

This research was financially supported by National Natural Science Fund of China (No. 20704018), the Fundamental Research Funds for the Central Universities (No. JUSRP10902, JUSRP10904) and the Open Project of State Key Lab of Pulp and Paper Engineering in South China University of Technology (201031).

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