New amphoteric flocculant containing beta-cyclodextrin, synthesis, charaterization and decolorization properties

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ABSTRACT

To react with the cationic monomer, N-trimethylaminoethylmethacrylate chloride (TMAEMC), a β-CD derivative carrying vinyl carboxylic acid groups (β-CD-MAH) was designed and synthesized via esterfying reaction between β-CD and maleic anhydride (MAH). Whereafter, a water-soluble amphoteric flocculant, the copolymer of TMAEMC and β-CD-MAH (β-CD-MAH-TMAEMC) has been synthesized by means of free radical copolymerization using the ammonium persulfate (APS) and sodium bisulfite (SBS) redox system as the initiator. The copolymer structure was demonstrated by FT-IR, ^{1}H NMR, SEM characterizations. Its excellent flocculated decolorization properties were evaluated with Acid Light Yellow 2G solutions using a jar test method. With the mass ratio of 1/10 (w/w) between the flocculant and dye, and at pH 4 and 20 °C of the initial dye solution, the maximum color removal reached. The charge neutralization played a dominant role during the flocculated decolorization process, although the inclusion of dye molecules into the cavities of β-CD well maintained in side chain of β-CD-MAH-TMAEMC also contributed to the conglomerates and floccules.

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1. Introduction

Color is the first contaminant to be recognized in the dyebath effluents and the presence of very small amount of dye in water is highly visible and undesirable. Thus decolorization is the principal task for dyebath effluents' treatment. During the past three decades, several physical, chemical and biological methods, e.g., flocculation, precipitation, extraction, evaporation, adsorption on activated carbon, ion-exchange, oxidation and advanced oxidation, incineration, electrochemical treatment, biodegradation and membrane filtration have been reported and attempted for the removal of dyes in wastewater [1,2]. Among them, flocculation is widely applied for the technological and especially economic reasons. It has been proved to be effective in removing dye compounds, in particular water-soluble dyes [3–9]. Otherwise, decolorization of the waste stream by this method is not due to a partial decomposition of dyes which produces some even more potentially harmful and toxic aromatic compounds and thus leads to a second pollution, but due to the removal of dye molecules from the dyebath effluents.

At present, development of more effective, safer and cheaper flocculants is still in expectation. The use of natural biomaterials such as polysaccharides is in vogue due to their ecofriendly, renewable and cost-effective aspects [2,10,17].

Cyclodextrins (CDs) are series of oligosaccharides produced by *Bacillus macerans* during the enzymatic degradation process of starch and related compounds. Among various CDs, β-cyclodextrin (β-CD), consisting of seven glucose units (Fig. 1), is commercially available at a low cost and has been used extensively [11]. The structure of β-CD takes the form of a toroid or a hollow tapering cone. The interior of the toroid, or the central nano-cavity, is hydrophobic as a result of the electron-rich glycosidic oxygen atoms. Consequently, hydrophobic molecules or groups can be included into the cavities of β-CD in the presence of water, if their dimensions correspond to those of the cavities. Currently, it has been applied in wastewater treatment due to its ability to form inclusion complexes with many pollutants, including dyes [11–16].

Nevertheless, based on the widely accepted flocculation mechanism—charge neutralization and bridging, β-CD itself was not suitable for decolorization because of its low molecular weight and charge density. In addition, the biodegradability reduces its shelf life and needs to be appropriately controlled. Thereby, β-CD-based water-soluble copolymer with high density of positive charge and molecular weight has potentially good flocculated decolorization effects for anionic dye solutions.

In the present work, a novel amphoteric flocculant was synthesized from a cationic monomer, N-trimethylaminoethyl-methacrylate chloride (TMAEMC) and a β-CD modified reactive one carrying vinyl carboxylic acid groups, using the ammonium persulfate (APS) and sodium bisulfite (SBS) redox system as the initiator.

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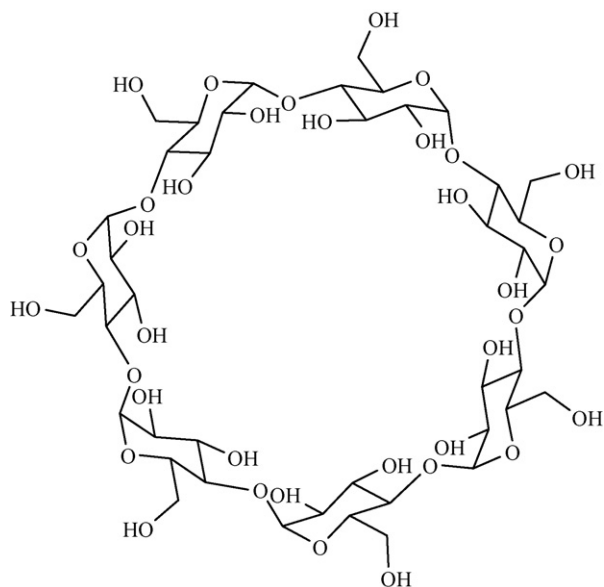
Fig. 1. Chemical formula of β-CD.

Fig. 2. Chemical structure of Acid Light Yellow 2G.

The obtained copolymer was characterized by Fourier-transform infrared (FT-IR), ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR), intrinsic viscosity, zeta potential, scanning electron microscope (SEM). Its flocculated decolorization properties were also tested with Acid Light Yellow 2G solutions using the jar test method. Studies concerning the effects of flocculant mass, pH and temperature of the initial dye solution on the decolorization efficiency were especially evaluated.

2. Experimental

2.1. Materials

β-CD from Wako Pure Chemical Co. Ltd. (Osaka, Japan) was purified two times by recrystallization from water prior to use. N-Trimethylaminoethylmethacrylate chloride (TMAEMC), 80 wt.% solution in water was purchased from Sigma–Aldrich. Maleic anhydride (MAH) 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), anhydrous alcohol, acetone and chloroform were analytic grade made in China, and used as received without further purification.

The dye of Acid Light Yellow 2G was purchased from Clariant Chemicals (China) Ltd. and its structure and characteristics were exhibited in Fig. 2 and Table 1, respectively.

2.2. Synthesis of β-CD-based reactive monomer

The β-CD derivative (β-CD-MAH) carrying vinyl carboxylic acid groups was designed and synthesized as in Fig. 3.

Specifically, 5.6820 g of β-CD (0.005 mol) was dissolved in 30 mL DMF, and 2.4515 g of MAH (0.025 mol) was added afterwards. The mixture solution was heated at 80 °C for 10 h under vigorously stirring. After the reaction was completed, the mixture was cooled
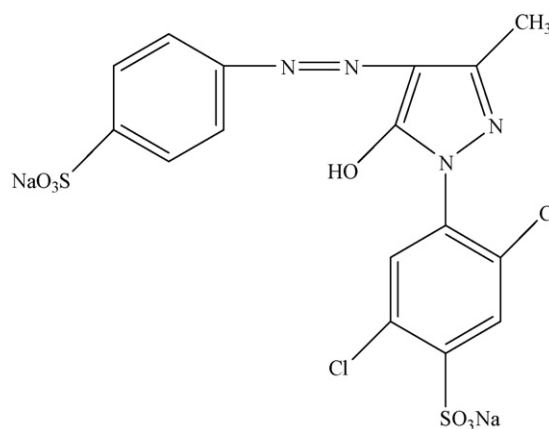
down to room temperature, and then, poured into 30 mL chloroform. A white precipitate was obtained and filtrated, washed at least three times with large amount of acetone, finally, dried in a vacuum oven at 60 °C for 48 h.

The product yield: 6.1489 g (75.6%).

Element analysis: specifically, for a molecular formula of $C_{42}H_{65}O_{35}[OCOCH=CHCOOH]_5$, the theoretic calculation is C: 43.66%; H: 4.69%, and the actual measurement is C: 43.61%; H: 4.66%.

2.3. Synthesis of amphoteric copolymer

Amphoteric copolymer (β-CD-MAH-TMAEMC) used as flocculant for decolorization was copolymerized via TMAEMC and β-CD-MAH in aqueous solution at 45 °C using APS and SBS redox system as the initiator (Fig. 4).

Specifically, total 2 g of β-CD-MAH and TMAEMC (4/6, w/w) were dissolved in 8 mL of distilled water, then 0.0495 g of APS was added. After bubbling with nitrogen gas for 15 min to remove oxygen, 0.0226 g of SBS dissolved in 2 mL distilled water was added by an injector. The copolymerization was conducted at 45 °C for 5 h. The obtained mixture was cooled down to room temperature and poured into 30 mL anhydrous alcohol. A white precipitate was filtrated and washed with abundant acetone, then dried in a vacuum oven at 60 °C for 48 h.

Finally, the copolymer solution was further purified using a dialysis bag with a cut-off of 7000 for 48 h and then freeze-dried to a constant weight.

The product yield: 1.5166 g (75.8%); zeta potential: 89.95 mV; intrinsic viscosity: 0.671 dL/g.

2.4. Instrument analyses

Zeta potential of β-CD-MAH-TMAEMC was measured by Particle Micro Electrophoresis (Nano-ZS90, Marlven) manufactured in England. Element analysis of β-CD-MAH was undertaken with a Vario EL III elemental analyser.

Viscosity measurements of β-CD-MAH-TMAEMC solutions were carried out with an Ubbelohde viscometer at 25 °C. The viscosities were measured in dilute aqueous solutions. The pH of the

Table 1
Characteristics of the tested dye.

Name of dye (abbreviation)	Dyestuff (color index)	λ_{max} (nm)	Purity (%)	Molecular weight (g/mol)
Acid Light Yellow 2G	Acid Yellow 17 (C.I. 18965)	404	55	551.3

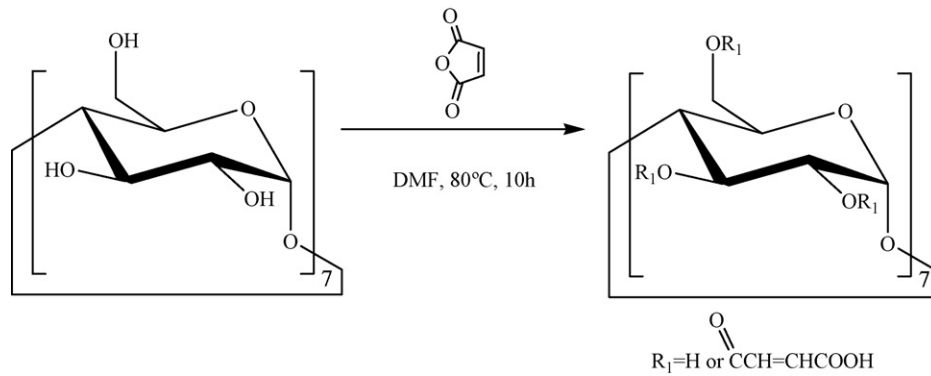**Fig. 3.** Synthesis of the β-CD-based reactive monomer (β-CD-MAH).

aqueous solution is neutral. The time of flow for solutions was measured at four different concentrations. From the time of flow of copolymer solution (t) and that of the solvent (t_0, for distilled water), relative viscosity ($\eta_{rel} = t/t_0$) was obtained. Specific viscosity was calculated from the relation, $\eta_{sp} = \eta_{rel} - 1$. Then, the reduced viscosity (η_{sp}/C), and the inherent viscosity ($\ln \eta_{rel}/C$) were calculated, where C is the copolymer concentration in g/dL. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots [17], i.e. η_{sp}/C versus C and $\ln \eta_{rel}/C$ versus C, to zero concentration.

FT-IR spectra of β-CD, β-CD-MAH and β-CD-MAH-TMAEMC were recorded on a Nicolet Nexus 470 spectrometer in the optical range of 400–4000 cm^{-1} by averaging 32 scans at a resolution of 4 cm^{-1}.

^{1}H NMR spectra of β-CD-MAH and β-CD-MAH-TMAEMC were obtained on a Bruker AV-300 spectrometer using D$_2$O as the solvent.

The surface morphologies of β-CD, β-CD-MAH and β-CD-MAH-TMAEMC were observed by scanning electron microscope (SEM; Quanta 200, Holland).

2.5. Flocculation experiments

Experiments on dye flocculation were performed using Jar-Test equipment. Specifically, the dye solution of 100 mL at a concentration of 100 mg/L was transferred into the jar and the pH of dye solution was adjusted with 1N H$_2$SO$_4$ and 1N NaOH. Then the prescribed mass of β-CD-MAH-TMAEMC was added. The mixture in the jar was rapidly stirred at a muddler speed of 120 rpm for 5 min, followed by a slow stirring at 40 rpm for the next 10 min. Thereafter, the suspension was allowed to be settled for 3 h. After settling, sample was collected at the top of the settling beaker (top 1 cm of water surface) using a syringe, filtrated through a membrane and analyzed for dye content by a UV–vis spectrophotometry (UV2100) from UNIC (Shanghai) instruments Co., Ltd. at the wavelength of 404 nm.

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

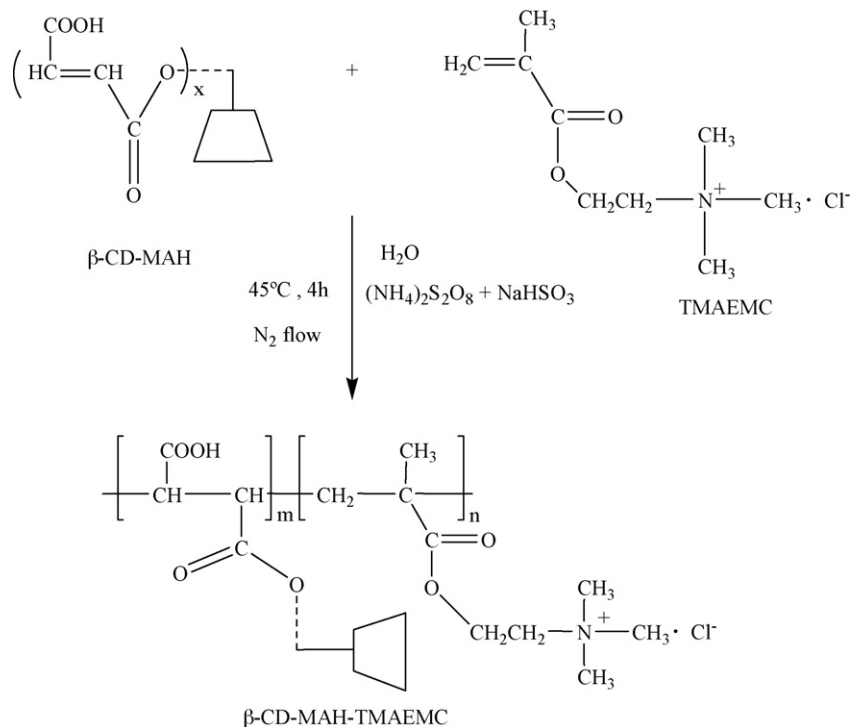$$\text{color removal}\,(\%) = \left(1 - \frac{CV}{C_0 V_0}\right) \times 100 \tag{1}$$

Fig. 4. Synthesis of amphoteric copolymer containing β-CD.

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 β-CD, β-CD-MAH and β-CD-MAH-TMAEMC were shown in Fig. 5.

It could be seen that an intensive absorption band at 1727 cm^{-1} appeared in curve *b* but was absent in curve *a*, which was due to the carbonyl (C=O) stretching vibration of ester groups and carboxylic acid groups in β-CD-MAH. Actually, the band at 1628 cm^{-1} in curve *a* was due to the first overtone of O–H bending, which was overlapped by the band owed to the C=C stretching vibration at 1644 cm^{-1} in curve *b*. Besides, another new band at 1216 cm^{-1} corresponded to the stretching vibration of C(O)–O in C=C–C(O)–O appeared in curve *b* compared with curve *a*. All these indicated that the esterfying reaction successfully occurred between β-CD and MAH [18].

The bands for β-CD at 3391 cm^{-1} [ν(O–H)], 2931 cm^{-1} [ν(C–H)], 1156 cm^{-1} [ν (C–O–C, s)], 1081 cm^{-1} [ν (C–O–C, as)], 1031 cm^{-1} [ν (C–OH)] [19] and the other absorption bands for β-CD including 1414, 944, 758 and 582 cm^{-1} appeared nearly at the same wavenumbers in curves *a*, *b* and *c*. It could be inferred that the structure characteristics of β-CD were well maintained in both β-CD-MAH and β-CD-MAH-TMAEMC. And that the hydroxyl groups existing in the original β-CD had been partially replaced, which was well consistent with the result from elemental analysis, $C_{42}H_{65}O_{35}[OCOCH=CHCOOH]_5$.

Furthermore, the bands at 1475 cm^{-1} assigned to the bending vibration of methyl groups of ammonium and at 954 cm^{-1} (overlapped with the band at 944 cm^{-1}) corresponded to the stretching vibration of quaternary ammonium appeared in curve *c*, which was not presented in curve *b*. This was a clear proof of incorporation of cationic moiety onto the backbone of copolymer [20]. Otherwise, disappearance of the bands at 1644, 1216 cm^{-1} in curve *c* validated the free radical copolymerization between β-CD-MAH and TMAEMC.

^{1}H NMR spectra of β-CD-MAH and β-CD-MAH-TMAEMC were presented in Fig. 6.

Relative to the unmodified β-CD, additional peaks were observed in Fig. 6a. Namely, signals at about 6.54 and 6.24 ppm could be ascribed to the protons of vinyl groups (CH=CH), indicating that β-CD-MAH bearing double bonds had been successfully prepared after esterfying reaction between β-CD and MAH [21]. However, they vanished in the spectrum of β-CD-MAH-TMAEMC, Fig. 6b, suggesting the disappearance of double bonds (CH=CH) after free radical copolymerization. It is noticeable that new absorp-
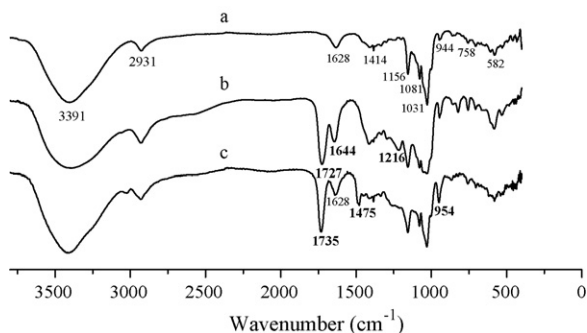
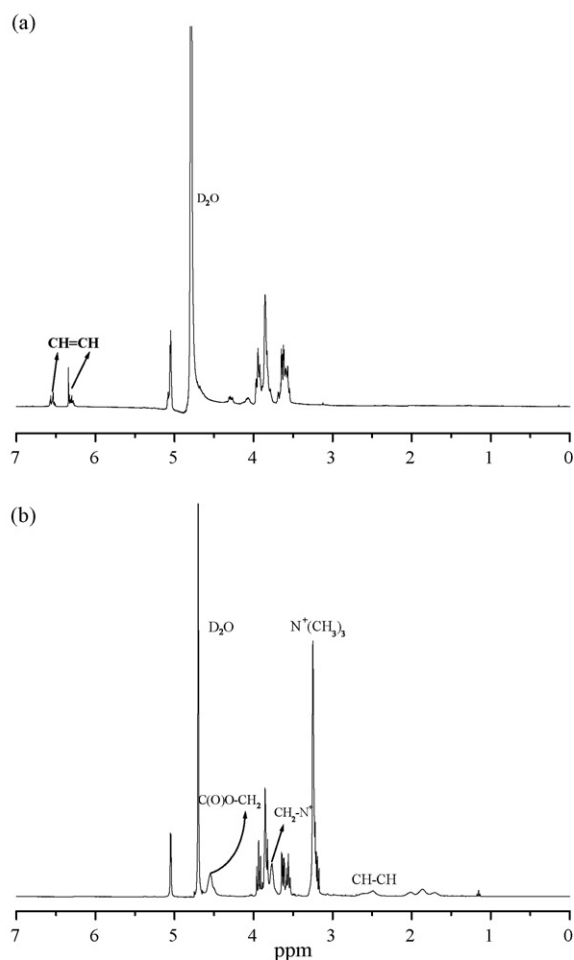**Fig. 5.** FT-IR spectra of β-CD (a), β-CD-MAH (b) and β-CD-MAH-TMAEMC (c).

Fig. 6. ^{1}H NMR spectra of β-CD-MAH (a) and β-CD-MAH-TMAEMC (b) in D$_2$O.

tions were found in Fig. 6b at 2.4–2.7 ppm (CH–CH). Besides, Fig. 6b also shows strong absorptions at 3.25 ppm (N$^+$(CH$_3$)$_3$), 3.77 ppm (CH$_2$–N$^+$) and 4.55 ppm (C(O)O–CH$_2$) which were related to ATMEAC cells in the copolymer [22,23]. Accordingly, the proposed structure of β-CD-MAH-TMAEMC in Fig. 4 was confirmed.

Moreover, signals of protons in β-CD (3.5–4.3, 5.05 ppm) existed in both curves *a* and *b*, which further implied that the structure characteristics of β-CD were well maintained in both the β-CD-MAH and β-CD-MAH-TMAEMC [24].

SEM images of surfaces of β-CD, β-CD-MAH and β-CD-MAH-TMAEMC were exhibited in Fig. 7.

β-CD particles in Fig. 7a had irregularly shaped crystals [25]. In contrast, a compact and homogeneous powder-like structure was observed in Fig. 7b, whose dimensions were evidently smaller than those of β-CD crystals. After free radical copolymerization between β-CD-MAH and TMAEMC, particles/aggregates were found in the product, Fig. 7c. In conclusion, the drastic change in the morphology and shape of particles revealed the occurrence of esterfying reaction and free radical copolymerization.

3.2. Approach of the flocculation mechanism

In order to investigate the interaction between the dye and flocculant, FT-IR spectra of β-CD-MAH-TMAEMC, Acid Light Yellow 2G and the formed floc were compared in Fig. 8.

In curve *c*, the intensity of bands at 954 cm^{-1} [ν (C–N)], 1475 cm^{-1} [δ (C–N)] and 1735 cm^{-1} [ν (C=O)] was much weaker than that in curve *b*, which was possibly due to the low content of
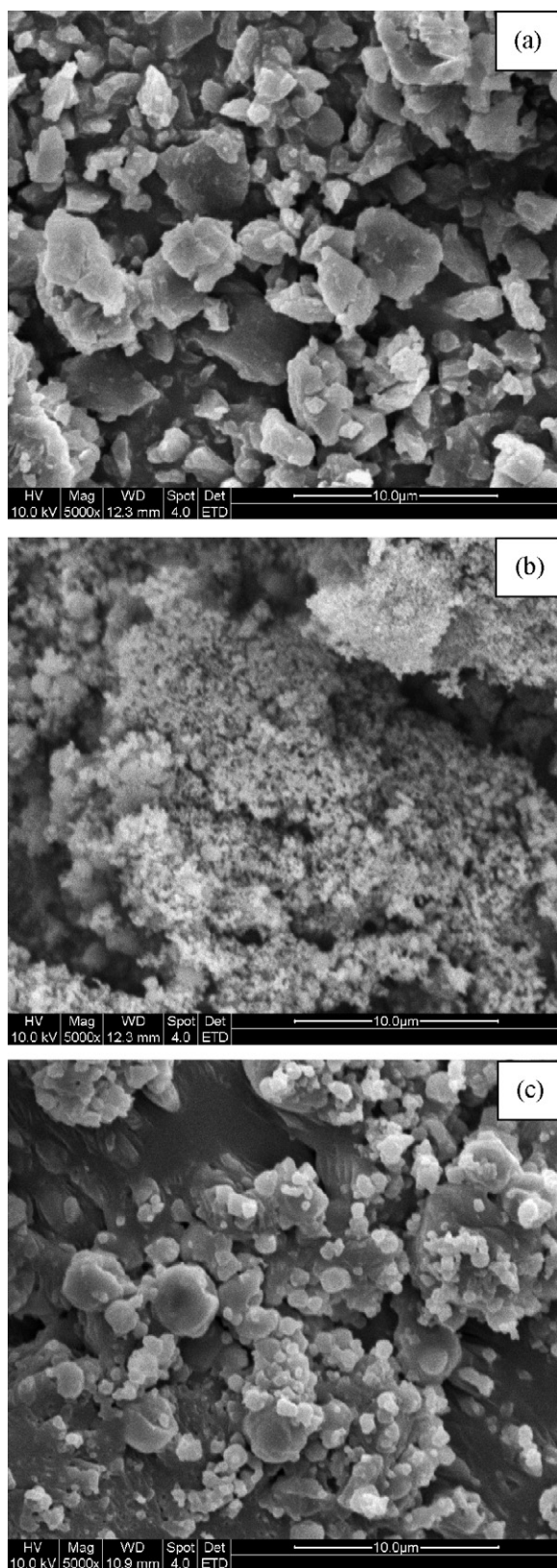
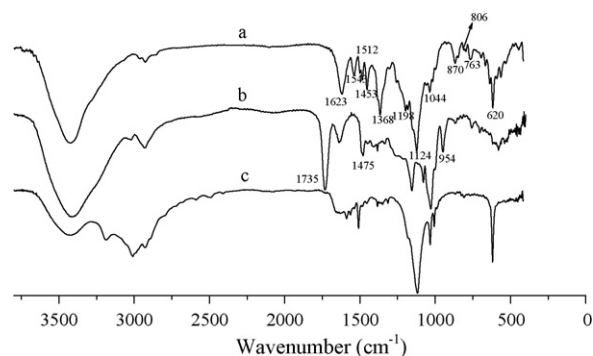Fig. 7. SEM microphotographs of surfaces. (a) β-CD, (b) β-CD-MAH and (c) β-CD-MAH-TMAEMC.

Fig. 8. FT-IR spectra of Acid Light Yellow 2G (a), β-CD-MAH-TMAEMC (b) and formed floc (c).

flocculant in the formed floc. Whereas, strong bands corresponded to the dye molecules at 1000–1250 cm^{-1} [ν (SO$_3$)], 620 cm^{-1} [ν (C–Cl)] appeared in the spectrum of the formed floc (curve c). It could be presumed that sulfonic groups in the dye molecules reacted with quaternary ammonium groups of flocculant and product like –N^{+}(CH$_3$)$_3$SO$_3$$^{-}$– in the aqueous solution formed [7], as schemed in Fig. 9.

However, the bands assigned to the phenyl at 700–900 cm^{-1} [γ (C–H)], 1400–1600 cm^{-1} [ν (C$\cdots$C)], and the band at 1368 cm^{-1} [δ (CH$_3$)] were evidently weakened in intensity in the spectrum of the formed floc (curve c) relative to that of the dye itself (curve a), suggesting that these groups in the dye molecules might be included into the β-CD cavities.

Otherwise, the change of bands in the range of 2500–3800 cm^{-1} and at 1623 cm^{-1} in curves a, b and c might be ascribed to the intermolecular hydrogen bonds formed in the dye/flocculant system.

As discussed above, apart from the charge neutralization, inclusion also contributed to the conglomerates and floccules during the flocculated decolorization process for the given dye-flocculant system.

3.3. Effects of pH on the decolorization efficiency

As known that color removal was highly dependent on the pH of the initial dye solution [10]. Fig. 10 illustrated the effects of pH (2, 4, 7 and 10) on the decolorization efficiency for 100 mL dye solutions of 100 mg/L at 20 °C using fixed dose of β-CD-MAH-TMAEMC (10 mg/L).

It could be seen that varying pH of the initial dye solution, the color removal reached a maximum before increasing again. The optimal pH was observed at 4. In general, acidic dye solutions brought higher color removal. But at an excess low pH of the initial dye solution, the color removal showed a decreasing trend.

The reason could be explained as follows. On the one hand, as afore-mentioned that the flocculated decolorization was attributed to the electrostatic interaction between the anionic dye molecules and the quaternary ammonium groups (cationic charges) in side chain of β-CD-MAH-TMAEMC (Fig. 9), in combination with the inclusion of dye molecules into the cavities of β-CD well maintained in side chain of β-CD-MAH-TMAEMC. On the other hand, more hydrophobic dye molecules could be included into the hydrophobic cavities of β-CD more easily [14,15]. Acid Light Yellow 2G used in this study became more hydrophilic with increasing pH of the initial dye solutions.

In the range of pH 4–12, at a relatively higher pH of the initial dye solution, the carboxylic acid ionogenic groups (COO^{-}) transferred from the carboxyl groups in the flocculant and hydroxide ions (OH^{-}) partially neutralized the positive charges of the flocculant. The density of positive charges of the flocculant was thus reduced,
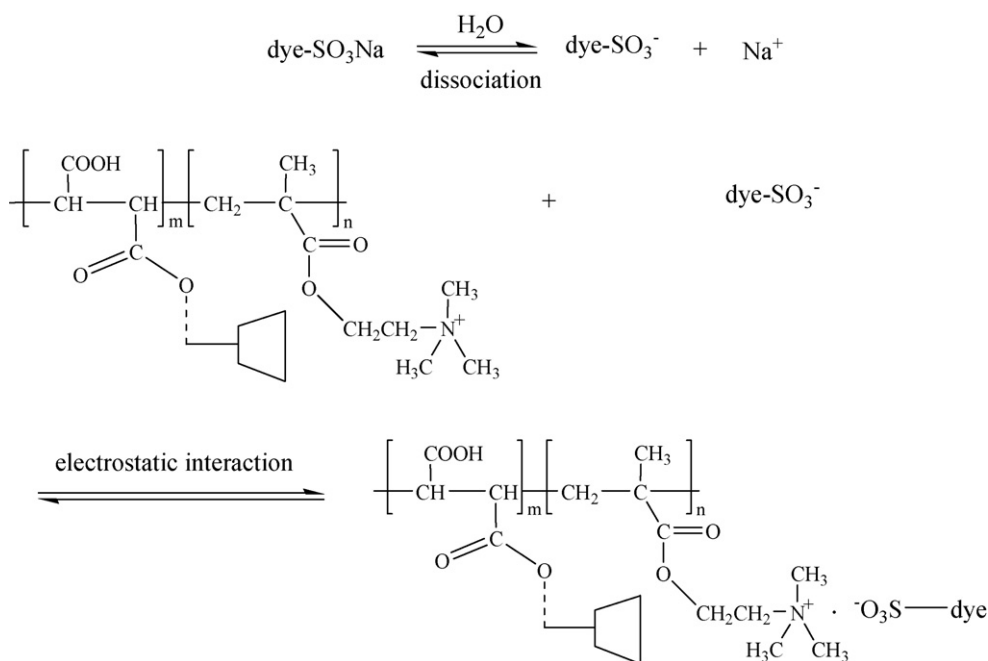
Fig. 9. The mechanism of electrostatic interaction between the anionic dye and amphoteric flocculant.

weakening its electrostatic binding to dye molecules. Besides, dye molecules under this condition became more hydrophilic, making their inclusion into the hydrophobic cavities of β-CD more difficult. Therefore, the decolorization efficiency was depressed with increasing pH of the initial dye solution in the range of pH 4–12.

But at an excessively low pH (lower than 4) of the initial dye solution, the sulfonic groups (SO_3^-) in Acid Light Yellow 2G converted into sulfo acid (SO_3H). As a result, negative charges of the dye molecules were reduced, making the electrostatic binding of dye molecules to flocculant decrease in strong acid medium.

As mentioned above, pH should be properly controlled upon the characteristics of the target flocculant and dye for efficient decolorization.

Nevertheless, the maximum color removal at pH 4 was close to 90%, as presented in Fig. 10. This explained that β-CD-MAH-TMAEMC synthesized in this study had excellent decolorization properties for the given dye solutions, which could be correlated to its high zeta potential of 89.95 mV and intrinsic viscosity of 0.671 dL/g.
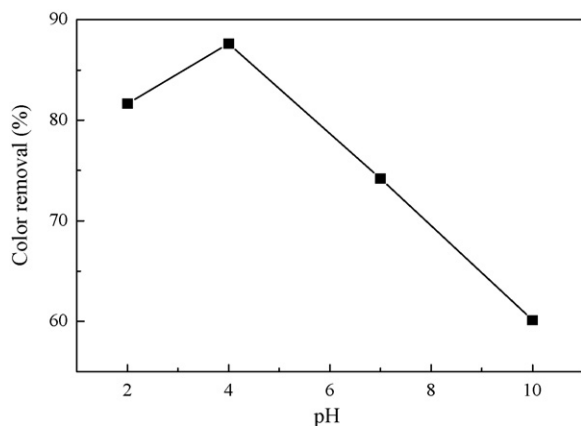
3.4. Effects of the flocculant mass on the decolorization efficiency

Fig. 11 illustrated the effects of flocculant dose on the decolorization efficiency for 100 mL dye solutions of 100 mg/L at pH 4 and 20 °C.

It could be seen that the color removal increased first and then decreased with increasing dose of β-CD-MAH-TMAEMC. This was the typical curve of a flocculation system controlled by charge neutralization mechanism [7]. The anionic dye, bearing sulfonic groups (SO_3^-), was electrostatically attracted by quaternary ammonium groups ($N^+(CH_3)_3$) in β-CD-MAH-TMAEMC: this reaction allowed neutralizing the anionic charges of dyes that could bind together and settle. There was an optimal flocculant dose (10 mg/L) existed for the given dye solution. When the amount of quaternary ammonium groups reached the complete neutralization of anionic charges, the color removal reached a maximum. Thereafter, if more flocculant was ulteriorly added into the dye solution, the presence of an excess of quaternary ammonium groups (cationic charges)
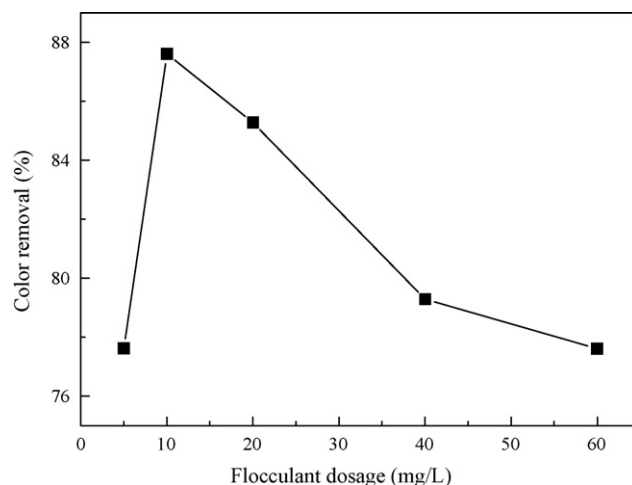

Fig. 10. Effect of pH of the initial dye solution on the decolorization efficiency.

Fig. 11. Effect of the flocculant mass on the decolorization efficiency.
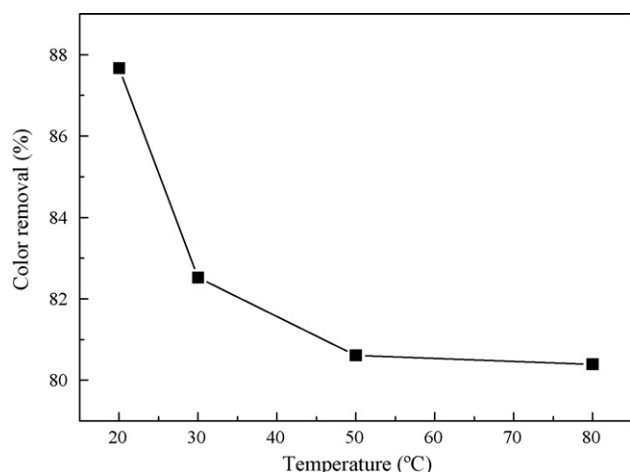
Fig. 12. Effect of temperature on the decolorization efficiency.

induced a re-stabilization of the suspension and a decrease in the efficiency of the process [7].

3.5. Effects of temperature on the decolorization efficiency

Fig. 12 illustrated the effects of temperature on the decolorization efficiency for 100 mL dye solutions of 100 mg/L at pH 4 using fixed dose of β-CD-MAH-TMAEMC (10 mg/L).

It could be seen that an increase in temperature made against the improvement of color removal. Because dye molecules bond onto the copolymer chains or included into the cavities of β-CD would be released again, reducing the decolorization efficiency. However, a small decrease of color removal from 88 to 80% with an increase of temperature from 20 to 80 °C implied that temperature had a small effect on the decolorization effects.

4. Conclusions

A novel synthetic polymer bearing natural blocks, β-CD-MAH-TMAEMC, was prepared through free radical copolymerization and used for flocculated decolorization of Acid Light Yellow 2G solutions. The FT-IR and ^{1}H NMR spectra confirmed the occurrence of copolymerization between the cationic monomer (TMAEMC) and β-CD-based derivative bearing vinyl carboxylic acid groups (β-CD-MAH). The flocculation experimental results demonstrated the excellent decolorization efficiency of β-CD-MAH-TMAEMC synthesized in this study. The maximum color removal reached at pH 4 and 20 °C of the initial dye solution, with a mass ratio of 1/10 (w/w) between the flocculant and dye. As to the decolorizing mechanism for the given dye/flocculant system, the charge neutralization played a dominant role, although simultaneously the inclusion of dye molecules into the cavities of β-CD well maintained in side chain of β-CD-MAH-TMAEMC contributed to the conglomerates and floccules during the flocculated decolorization process.

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