

Flocculated Decolorization of Vinylsulfone Reactive Dye Solutions with a β -Cyclodextrin-Based Copolymer

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ABSTRACT: A β -cyclodextrin (β -CD)-based copolymer (β -CD-maleic anhydride-*N*-trimethylaminoethylmethacrylate chloride) with good thermal stability was designed and synthesized for flocculated decolorization of Reactive Brilliant Blue KN-R solutions. Jar tests indicated that with the optimal stirring mode as 120 rpm for 5 min and then 40 rpm for 5 min with a flocculant-to-dye ratio of 2 : 5 (w/w), a pH of 8–10, and a temperature of 20°C, the maximum color removal reached. It is reported first in this arti-

cle that, in addition to the polymer bridge and charge neutralization, the covalent bond of the reactive dye to the target flocculant molecules, which had a similar chemical structure to that of cellulose, contributed to the mechanism of flocculated decolorization. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 480–485, 2010

Key words: polysaccharides; radical polymerization; separation techniques; water-soluble polymers

INTRODUCTION

Wastewater from the fabric dyeing industry is a considerable source of environmental contamination. The effluent from the dyeing and finishing processes is characterized by a strong color, high pH, high temperature, high Chemical Oxygen Demand (COD) and low biodegradability.¹ In recent years, reactive dyes have been used most commonly because of their advantages such as ease of application, excellent color fastness, and bright colors. Moreover, the use of reactive dyes is rapidly growing because of the increased use of cellulosic fibers. Nevertheless, 10–40% of reactive dyes are released into dye-bath effluents and, thus, pose serious environmental pollution because they are very sensitive to hydrolysis under the required alkaline dyeing conditions.

Flocculation with cationic polymers, which are endowed with several distinguishing characteristics, such as the formation of large cohesive flocs and versatile tailorability, has been proven to be effective in the removal of dye compounds, in particular water-soluble dyes.^{2–6} It has been increasingly applied for the treatment of dye-bath effluents

because of its technological and, especially, economic aspects.⁷ Decolorization of the waste stream by this method prevents the partial decomposition of dyes, which produces even more potentially harmful and toxic aromatic compounds and, thus, leads to a second pollution.

Currently, the development of more effective, economical, and safer flocculants for decolorization is still in vogue. Natural biomaterials, such as polysaccharides (starch, chitosan, etc.), have attracted more interest because of their eco-friendly, renewable, and cost-effective aspects.^{8–10} Cyclodextrin is a derivative of sugar produced from bacterial action on starch. Among various cyclodextrins, β -cyclodextrin (β -CD) is commercially available at a low cost and has been used extensively.¹¹ In our former study, a β -CD-modified copolymer [β -CD-maleic anhydride (MAH)-*N*-trimethylaminoethylmethacrylate chloride (TMAEMC)] was synthesized from a cationic monomer, TMAEMC, and a β -CD derivative bearing vinyl carboxylic acid groups with an ammonium persulfate and sodium bisulfite redox system as the initiator. This copolymer was proven to be a good flocculant for decolorization of the acid dye solutions. As to the mechanism for flocculated decolorization, charge neutralization played a dominant role, although the inclusion of dye molecules in the cavities of β -CD well maintained in the side chain of β -CD-MAH-TMAEMC also took effect.¹² In this study, we continued to investigate its effect and mechanism for the flocculated decolorization of the reactive dye solutions. Because β -CD or its derivative has the same glucose units as cellulose (Fig. 1), the ionized hydroxyl group of β -CD-modified

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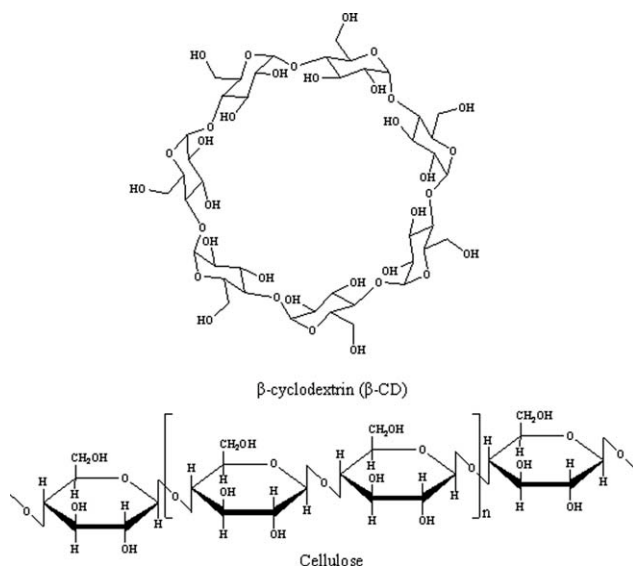


Figure 1 Chemical structure of β-CD and cellulose.

materials certainly would create covalent bonds with the reactive dyes in an alkaline medium, which may be another important factor contributing to the flocculated decolorization properties, apart from the charge neutralization.

Reactive Brilliant Blue KN-R as a representative of reactive dyes was chosen for the jar tests. Studies concerning the effects of the stirring mode, flocculant mass, pH, and temperature of the initial dye solution on the decolorization efficiency were done. The flocculated decolorization mechanism for the given flocculant/dye system was explored by means of Fourier transform infrared (FTIR) characterizations.

EXPERIMENTAL

Materials

β-CD from Wako Pure Chemical Co., Ltd. (Osaka, Japan) was purified two times by recrystallization from water before use. TMAEMC (80 wt % solution in water) was purchased from Sigma-Aldrich. MAH

was purchased from Showa Chemicals (Tokyo, Japan). *N,N*-dimethylformamide was distilled *in vacuo* and stored in 4-Å molecular sieves. All other reagents, including ammonium persulfate, sodium bisulfite, anhydrous alcohol, acetone, and chloroform, were analytic grade made in China and used as received without further purification.

Reactive Brilliant Blue KN-R was purchased from Clariant Chemicals, Ltd. (Shanghai, China), and its structure and characteristics are shown in Table I.

Synthesis of the β-CD-based copolymer

A copolymer bearing natural blocks (β-CD-MAH-TMAEMC) was synthesized according to ref. 12, in which the molar ratio between β-CD and MAH was 1 : 12 and the weight ratio between β-CD-MAH and TMAEMC was 7 : 3.

β-CD-MAH

Yield = 72.8%. ANAL. Calcd for $C_{42}H_{60}O_{35}$ [OCOCH=CHCOOH]₁₀: C, 43.27%; H, 3.96%. Found: C, 43.36%; H, 3.76%.

β-CD-MAH-TMAEMC

The product yield was 86.0%. The ζ potential was 78.60 mV, and the intrinsic viscosity was 0.64 dL/g.

Flocculation experiments

Flocculation experiments were performed with jar-test equipment. Specifically, 200 mL of a dye solution at a concentration of 100 mg/L was transferred to the jar. We added 8 g of NaCl, and the pH of the dye solution was adjusted with 1N H₂SO₄ 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 80–150 rpm for 5 min; this was followed by slower stirring at 20–50 rpm for the next 5–10 min. Then, the

TABLE I
Structure and Characteristics of Reactive Brilliant Blue KN-R

Chemical structure	Dyestuff (color index)	Maximal absorbing wavelength, λ_{max} (nm)	Purity (%)	Molecular weight (g/mol)
	CI Reactive Blue 19 (61200)	595	55	594.5

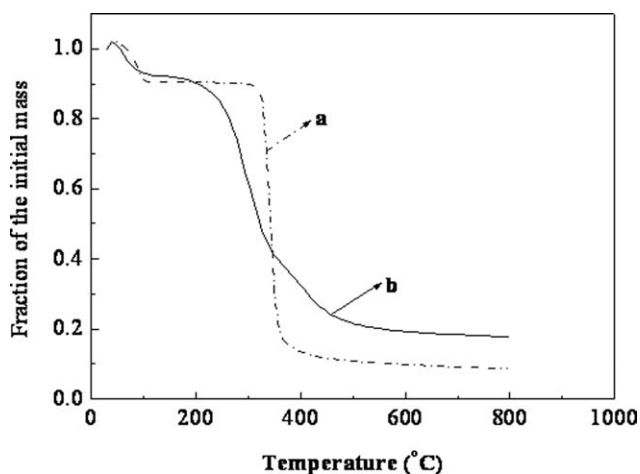


Figure 2 TGA curves of (a) β -CD and (b) β -CD-MAH-TMAEMC.

suspension was allowed to be settled for 3 h. After settling, the sample was collected at the top of the settling beaker (top 1 cm of the water surface) with a syringe, filtered through a membrane, and analyzed for dye content by ultraviolet–visible spectrophotometry (UV2100) from UNIC (Shanghai, China) Instruments Co., Ltd., at a wavelength of 595 nm.

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 are the dye concentrations in the solution before and after flocculation, respectively, and V_0 and V are the volumes of the solution before and after flocculation, respectively.

Instrument analyses

ζ potential was measured by particle microelectrophoresis (Nano-ZS 90, Marlven, England). Element analysis was undertaken with a Vario EL III (Elementar, Germany) elemental analyzer. Viscosity measurements solutions were carried out with an Ubbelohde viscometer at 25°C.⁹ FTIR spectra were recorded on a Nicolet Nexus 470 spectrometer (Nicolet Co., USA) in the optical range 400–4000 cm^{-1} by the averaging of 32 scans at a resolution of 4 cm^{-1} . 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 N_2 .

RESULTS AND DISCUSSION

Thermal stability of the copolymer

The TGA curves of β -CD and β -CD-MAH-TMAEMC are compared in Figure 2.

Obviously, the degradation of β -CD itself took place in one step. However, there were two gradually changing transitions in the TGA scan of β -CD-MAH-TMAEMC. This was mainly because of the existence of two different monomers used for the copolymer synthesis. The decrease in the thermal degradation onset temperature from 328 to 254°C was found after the modification of β -CD. Nevertheless, β -CD-MAH-TMAEMC was thermally stable in the processes of flocculated decolorization in the investigated range of temperature (20–80°C).

Approach of the flocculation mechanism

Generally accepted flocculation theory involves basically two action mechanisms:¹³

- Polymer bridging: The first step is the adsorption of the macromolecular chain onto the surface of a particle to be flocculated, and the second one is polymer bridging, in which the polyelectrolyte adsorbed onto that particle has looped and dangling chains extending some way into the solution, which can attach to nearby particles, resulting in large flocs and accelerated rates of sedimentation.
- Charge neutralization: The macromolecular chain is adsorbed onto the oppositely charged particle surface as a result of strong electrostatic attraction. Therefore, flocculation can occur simply as a result of the reduced surface charge of the particles; this leads to decreased electrical repulsion between them.

In this study, to investigate the interaction between the dye and flocculant molecules, we compared the FTIR spectra of β -CD-MAH-TMAEMC, Reactive Brilliant Blue KN-R, and the formed floc, as shown in Figure 3.

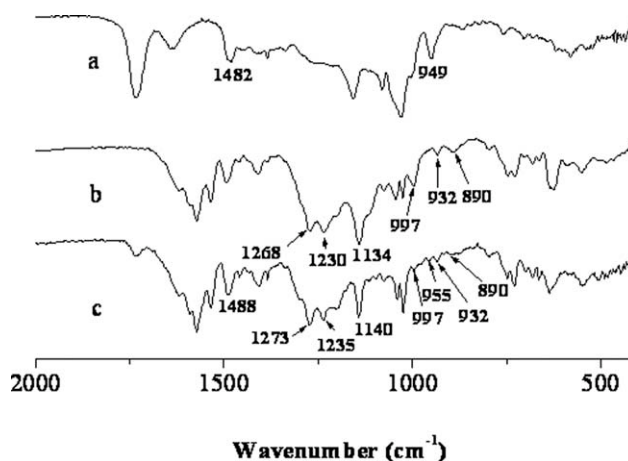


Figure 3 FTIR spectra of the (a) β -CD-MAH-TMAEMC, (b) reactive Brilliant Blue KN-R, and (c) formed floc.

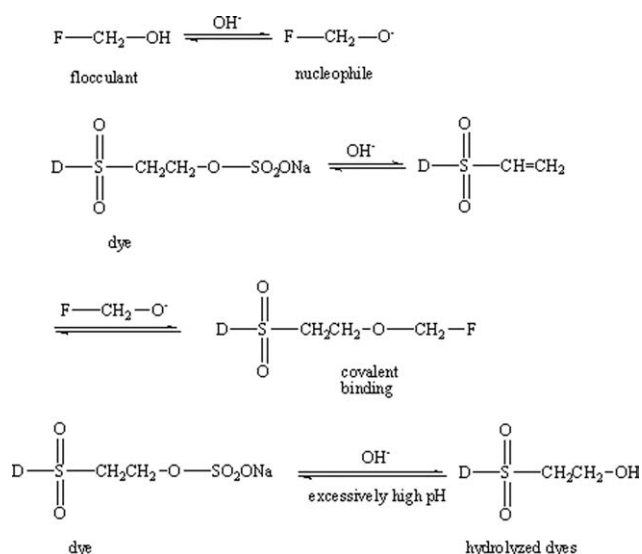


Figure 4 Covalent bond of Reactive Brilliant Blue KN-R to β -CD-MAH-TMAEMC and hydrolysis of the dye molecules in an alkaline medium.

On the one hand, the bands corresponding to the quaternary ammonium groups of the flocculant at 949 cm^{-1} [$\nu(\text{C}-\text{N})$] and 1482 cm^{-1} [$\beta(\text{C}-\text{N})$] in curve a were weakened in intensity and shifted to 955 and 1488 cm^{-1} in curve c, respectively. In addition, the strong bands ascribed to the dye molecules at roughly 1230 and 1268 cm^{-1} [$\nu(\text{SO}_2, \text{as})$] and 1134 cm^{-1} [$\nu(\text{SO}_2, \text{s})$] in curve b also shifted to 1235 and 1273 and 1140 cm^{-1} in curve c, respectively. We presumed that sulfonic groups in the dye molecules reacted with quaternary ammonium groups of the flocculant, and product such as $-\text{N}^+(\text{CH}_3)_3\text{SO}_3^-$ formed in the aqueous solution.¹⁴

On the other hand, the intensity of the bands at 890 and 932 cm^{-1} [$\nu(\text{C}-\text{O}-\text{S})$] and 997 cm^{-1} [$\nu(\text{O}-\text{S}-\text{O})$] were weaker in the spectrum of the formed floc (curve c) in comparison with that of the dye itself (curve b). Accordingly, we inferred that part of the vinylsulfone reactive dye molecules reacted with the flocculant (covalent bond), as shown in Figure 4, which was similar to the dyeing of cellulose fibers with vinylsulfone reactive dyes in an alkaline medium. Concretely, alkali was responsible for the formation of the nucleophile (F-CH₂-O⁻) and the elimination of H₂SO₄ to form the double bond (D-SO₂-CH=CH).¹⁵

As discussed previously, both the charge neutralization and covalent bond contributed to the conglomerates and floccules during the flocculated decolorization processes for the given dye/flocculant system.

Effect of the stirring mode on the decolorization efficiency

In fact, two different stirring steps were needed for the flocculated decolorization process. First, the dye

solution had to be stirred at a relatively high speed to ensure sufficient collision between the dye and flocculant molecules. As a result, the dye molecules could bond to the copolymeric chains of the flocculant, and some flocs were, thus, formed in the aqueous dye solution. Afterwards, the stirring speed had to be slowed so that the formed flocs could continue to grow. However, the concrete speed and time needed for the different two stirring steps needed to be regulated to prevent the destruction of the formed flocs.

Table II lists the different color removals under different stirring modes. For the given dye/flocculant solutions, the optimum stirring mode was as 120 rpm for 5 min and then 40 rpm for 5 min. Moreover, the relatively high color removal of 83.66% explained that β -CD-MAH-TMAEMC synthesized in this study had good decolorization properties for the given dye solutions, which could be correlated to its high ζ potential of 78.60 mV and intrinsic viscosity of 0.64 dL/g.

Effect of the pH on the decolorization efficiency

It was reported that color removal was highly dependent on the pH of the initial dye solution.¹⁶ Figure 5 shows the different color removals at various pH values (5, 7, 8, 10, and 12) with a fixed dose of β -CD-MAH-TMAEMC (10 mg/L) at 20°C. The maximum color removal was attained at pH 8–10. A decrease or an increase in pH led to a reduction of color removal. The reasons can be explained as follows.

When the pH of the initial dye solution was lower than 10, the charge neutralization conflicted with the covalent binding between the dye and flocculant molecules. That is, with an increase in pH, the carboxylic acid ionogenic groups (COO⁻) inverted from the carboxyl groups (COOH) in the flocculant, and the hydroxide ions (OH⁻) partially neutralized the

TABLE II
Effect of the Stirring Mode on the Decolorization Efficiency

Stirring mode	Color removal (%)
80 rpm for 5 min and then 20 rpm for 5 min	67.72
80 rpm for 5 min and then 20 rpm for 10 min	65.68
100 rpm for 5 min and then 30 rpm for 5 min	76.48
100 rpm for 5 min and then 30 rpm for 10 min	71.21
120 rpm for 5 min and then 40 rpm for 5 min	83.66
120 rpm for 5 min and then 40 rpm for 10 min	81.81
150 rpm for 5 min and then 50 rpm for 5 min	82.77
150 rpm for 5 min and then 50 rpm for 10 min	79.42

Conditions: pH = 10, temperature = 20°C, and flocculant mass = 10 mg/L.

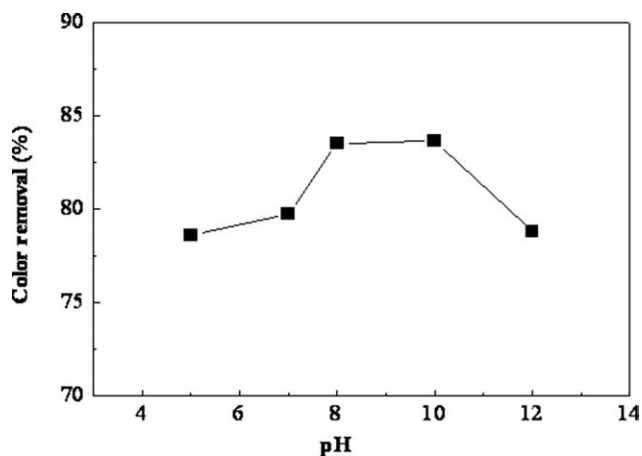


Figure 5 Effect of the pH of the initial dye solution on the decolorization efficiency.

cationic charge of the flocculant; this weakened the electrostatic combination of dye to flocculant. On the contrary, the covalent bonding of dye to flocculant occurred more easily in more alkaline medium. Under this condition, a higher pH made for covalent binding but worked against charge neutralization. The gradual increase of color removal with increasing pH implied that the covalent binding played a dominant role during the flocculated decolorization process, although at the same time, charge neutralization was in operation.

However, at an excessively high pH (>10) of the initial dye solution, part of the dye molecules were hydrolyzed (Fig. 4); this made their covalent bonding to the flocculant impossible. The density of the positive charges of the flocculant was further reduced in stronger alkaline medium; this made the dyes' electrostatic interaction with the flocculant weaken. Relatively poor decolorization effects were thus obtained.

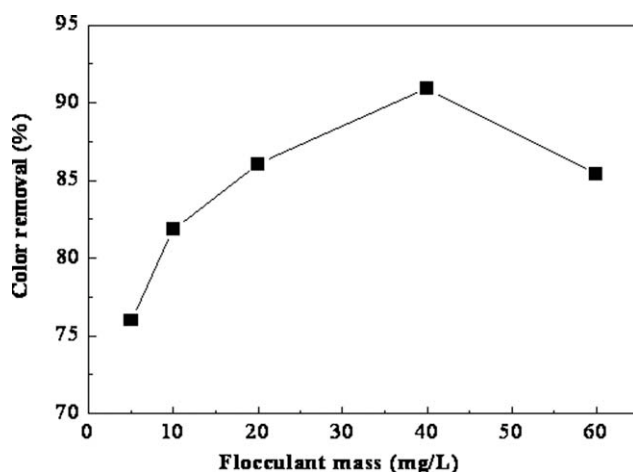


Figure 6 Effect of the flocculant mass on the decolorization efficiency.

As mentioned previously, the pH had to be properly controlled upon the characteristics of the target flocculant and dye for efficient decolorization.

Effects of the flocculant mass on the decolorization efficiency

Figure 6 illustrates the effects of the flocculant mass on the color removal at pH 10 and 20°C.

The color removal increased first and then decreased with increasing dose of β -CD-MAH-TMAEMC. The anionic vinylsulfone reactive dyes, bearing sulfonic groups (SO_3^-), were attracted by quaternary ammonium groups [$\text{N}^+(\text{CH}_3)_3$] in β -CD-MAH-TMAEMC. Moreover, a nucleophilic addition reaction occurred in the vinylsulfone dye/flocculant system. Consequently, the dye molecules could bind together and settle.

However, there was an optimal flocculant dose, 40 mg/L, existing for the given dye solutions. In this case, if more flocculant was ultimately added to the dye solution, the presence of an excess of quaternary ammonium groups (cationic charge) induced a restabilization of the suspension and a decrease in the efficiency of the process.

Effect of the temperature on the decolorization efficiency

Figure 7 shows the different decolorization effects at various temperature of the initial dye solution at pH 10 with a fixed dose of β -CD-MAH-TMAEMC (10 mg/L).

An increase in the temperature limited the improvement of color removal. Because under these conditions, the dye molecules with electrostatic bonding onto the copolymer chains of the flocculant

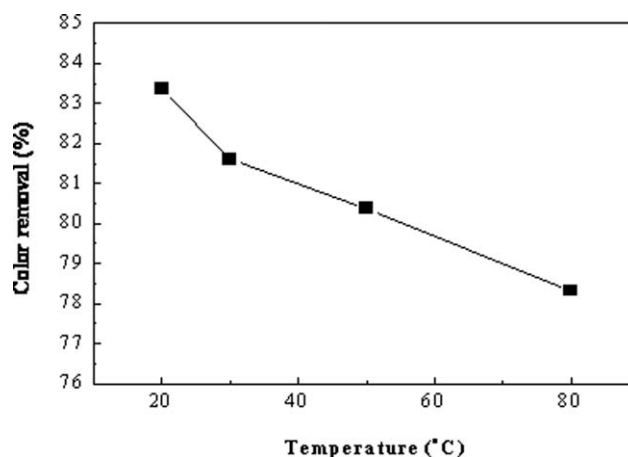


Figure 7 Effect of the temperature of the initial dye solution on the decolorization efficiency.

were released again, which somewhat reduced the decolorization efficiency. However, a small decrease in color removal, from 84 to 78% with an increase in the temperature from 20 to 80°C, implied that the temperature had a small effect on the decolorization efficiency, which might have been due to the covalent binding of the dye to the flocculant.

CONCLUSIONS

The good flocculated decolorization properties of β -CD-MAH-TMAEMC for Reactive Brilliant Blue KN-R solutions were demonstrated by jar tests. With the optimal stirring mode as 120 rpm for 5 min and then 40 rpm for 5 min with a flocculant-to-dye ratio of 2 : 5 (w/w), a pH of 8–10, and a temperature of 20°C, maximum color removal was reached. Furthermore, for the conglomerates and floccules during the flocculated decolorization processes, in combination with the widely accepted polymer bridging and charge neutralization, covalent binding between the reactive dye and target flocculant molecules was simultaneously in operation.

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