Removal of anionic dyes in aqueous solution by flocculation with cellulose ampholytes

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ABSTRACT

Cellulose ampholytes (CAms) prepared from biocompatible and biodegradable carboxymethyl cellulose (CMC) could represent an environmentally friendly alternative for the efficient removal of anionic dyes from water effluents. In order to evaluate their potential for this application, a series of CAms with a degree of cationic substitution (DS_C) between 0.26 and 1.08 were prepared from sodium CMC, by cationization with 2,3-epoxypropyltrimethylammonium chloride. The flocculation ability of the CAms against the anionic dye Acid Red 13 (AR13) was found to strongly depend on the DS_C as well as on the pH of the solution. The highest flocculation ability was observed at lower pH and higher DS_C: a color removal as high as 99% was achieved at pH 3 using a CAm with the highest DS_C. The kinetic analysis revealed that the flocculation of AR13 can be accurately fitted by a pseudo-second order kinetic model, which thus allows to predict the flocculation behavior of CAms under these conditions. Besides AR13, the ampholytes also showed high flocculation ability against Acid Red 9 and Acid Blue 13. The flocculation behavior of these anionic dyes followed the Langmuir adsorption isotherm model, which revealed the maximum flocculation capacity of a CAm for these dyes. Moreover, the analysis of the flocculation isotherm data and the SEM observation of the formed flocs allowed to determine the flocculation mechanism.

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Nomenclature

CMC   Carboxymethyl cellulose
EPTMAC   Epoxypropyltrimethylammonium chloride
CAm   Cellulose ampholyte
DSS   4,4-Dimethyl-4-silapentane-1-sulfonic acid

1. Introduction

More than 7×10^5 ton of dyes are used annually in the chemical industry worldwide, about 10–15% of which are discharged into water as effluents, seriously polluting the environment and affecting human as well as aquatic organisms [1,2]. There are more than ten thousand types of commercially available dyes, most of which are considered toxic [1–3]. In addition, most dyes have complex and very stable aromatic structures, and thus tend to accumulate in nature [4–6]. Industrial treatments to remove dyes can involve oxidation [7,8], coagulation [8,9], flocculation [10,11], ion-exchange [12], photochemical destruction [13], and other methods. In particular, adsorption has been widely used for the removal of dyes from effluents, and activated carbon is conventionally used for adsorbing dyes from wastewaters. However, the use of activated carbon is limited by its relatively high cost and difficult regeneration [14].

Coagulation of dye-containing wastewater has been used for many years either as a pre-treatment or as the main method to treat wastewater due to its low capital cost [15]. Recently, much attention has been devoted to a coagulation-flocculation process for dye removal from water, which employs natural polysaccharides such as sodium alginate [16], carrageenan [17], pectin [18], carboxymethyl cellulose [19], chitosan [20], and carboxymethyl chitin [20]. These compounds are particularly attractive due to their biocompatibility, biodegradability, and anionic properties. However, even though they exhibited promising results, the use of these polysaccharides as anionic flocculation agents is still infrequent. The practical use of anionic polysaccharides as flocculation reagents is limited by their poor solubility in acidic solutions [21,22]. Chitosan, a cationic polysaccharide abundant in nature, exhibits excellent flocculation properties towards anionic dyes and suspended particles with negatively charged surface. The amino groups of chitosan are protonated and thus charged positively in acidic solutions, resulting in facile dissolution and excellent flocculation performance in acidic solutions [22]. On the other hand, the

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poor solubility in neutral and alkaline solutions prevent the use of chitosan as flocculant in these conditions [22].

Among the naturally occurring polysaccharides, cellulose – which is the most abundant natural polymer on earth – represents one of the most environmentally friendly non-food sources for the production of a wide range of eco-friendly products. The high degree of polymerization and number of potential chemical modifications of cellulose also make it an attractive candidate for flocculation purposes [23,24]. For example, sodium carboxymethyl cellulose (CMC), a well known water-soluble cellulose derivative with properties characteristic of an anionic polymer, has shown promising results as an anionic flocculation agent, despite the poor solubility in acidic solutions that limits its practical application as flocculation reagent in these conditions [19]. In addition, cationized cellulose, produced by homogeneous cationization with 2,3-epoxypropyltrimethylammonium chloride (EPTMAC), was reported to exhibit good cationic flocculation ability toward kaolin suspensions [25]. However, as cellulose is highly crystallized by a strong network of inter- and intra-molecular hydrogen bonds, its dissolution requires a time-consuming processing with unpopular solvents such as aqueous sodium hydroxide/urea solution, lithium chloride/dimethyl sulfoxide, tetra-n-butylammonium fluoride/dimethyl sulfoxide, and specific ionic liquids, and/or preswelling by sequential solvent change and heating [26]. In our previous work, cellulose ampholytes (CAms) containing both cationic quaternary ammonium sodium salt and anionic carboxymethyl groups were prepared from homogeneous etherification of CMC dissolved in aqueous solution in the presence of EPTMAC as cationic reagent. The starting CMC material is relatively cheap and easily dissolved in NaOH solution, and its unsubstituted hydroxyls can easily react with EPTMAC to form cationic groups. Thanks to these cationic groups, the obtained CAms could easily dissolve in solutions within a wide pH range and exhibited excellent flocculation performance toward suspended kaolin particles [27]. Similarly, it was reported that several polysaccharide-based amphoteric flocculants, including chitosan [28], amylopectin [29], and starch [30], showed enhanced solubility and good flocculation performance.

In this study, a series of CAms having a different degree of cationic substitution (DS_C) was prepared from CMC with a degree of anionic substitution (DS_A) of 0.60 (Fig. 1(A)), and the effects of several factors on the flocculation ability of the prepared CAms against the Acid Red 13 (AR13) anionic dye in aqueous solution were investigated in detail. In addition, in order to determine the mechanism of interaction between CAm and the anionic dyes during flocculation, we investigated the flocculation behavior of CAm towards Acid Red 9 (AR9), AR13, and Acid Blue 92 (AB92) anionic dyes, which contain 1–3 anionic sulfone groups per molecule, respectively (Fig. 1(B)).

2. Materials and methods

2.1. Materials

CMC ($DS_A = 0.60$, molecular weight (Mw) = 2.6×10^5 g mol^{-1}) was kindly supplied from Dai-ichi Kogyo Seiyaku Co. (Japan). EPTMAC was purchased from Sigma–Aldrich (USA). AR9, AR13, and AB92 were all purchased from Tokyo Chemical Industry Co. Ltd. (Japan). The molecular weights of AR9, AR13, and AB92 were 400.4, 502.4, and 695.6 g mol^{-1}, respectively. Other chemicals were chemically pure grade and all solutions were prepared with pure water.

2.2. Synthesis of CAms

A series of four CAms (labeled **1**–**4**) were prepared from CMC with EPTMAC according to the method previously reported [27]. Briefly, CMC (1.0 g) was dissolved in 1.5 mmol L^{-1} NaOH solution at 277 K, and then EPTMAC (1.4 g) was added dropwise over a period of 20 min. After precipitation with acetone, the obtained precipitates were washed with a 1:1 mixture of acetone/distilled water to reach neutral pH, dried under vacuum, and then milled and filtered through a 40-mesh sieve to obtain CAm **1**. A similar method was used to prepare CAms **2**–**4,** by adapting the feed amount of EPTMAC, which was set to 3.5 g, 4.9 g, and 7.0 g for CAms **2**–**4**, respectively. All CAms were stored in a desiccator under vacuum until ready for use.

2.3. ^{13}C NMR spectroscopy

NMR spectra of the CAms were measured at 353 K in deuterium oxide containing 0.1% 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) as an internal standard using an AV III 500 MHz spectrometer equipped with a 5 mm BBO probe (Bruker BIoSpin GmbH, Germany). The quantitative ^{13}C NMR spectra were obtained by the inverse-gated ^{1}H decoupling method [31] with a flip angle for ^{13}C excitation pulse of 30° and a pulse repetition time of 45 s [32]. The ^{13}C chemical shifts were calibrated by setting the methyl peak of DSS to 0 ppm.

2.4. Flocculation of anionic dyes

Three kinds of anionic dyes, whose structures are shown in Fig. 1(B), were used for the flocculation studies. A buffer solution (10 mL) containing each dye in a concentration range of 50–1600 mg L^{-1} was poured in a glass vial, and the CAm was added to the dye solution. The mixture was immediately placed in a shaker at 120 rpm and 298 K for 1 h, after which the suspension was left to settle for 5 min. The supernatant of the suspension was filtered by using a nylon membrane filter with a pore size of 0.45 μm (Rephile Bioscience, Ltd., USA). The dye concentration of the filtrate was determined by an Epoch 96 well micro-volume spectrophotometer (BioTek Instruments, Inc., USA) with a 96-wells microplate, using an earlier prepared calibration curve at 492 nm for AR9, 504 nm for AR13, and 572 nm for AB92. The percent removal of each dye and the flocculation ability (q_t) of each CAm at contact time t were calculated using Eqs. (1) and (2):

$$(\text{Dye removal})\% = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

$$q_t = (C_0 - C) \times \frac{V}{m} \tag{2}$$

where C_0 (mg L^{-1}) is the initial concentration of dye solution, C (mg L^{-1}) is the concentration of dye solution at contact time t, V (L) is the volume of dye solution, and m (g) is the mass of CAm. 20 mM citric acid-sodium citrate (pH 3–6), 20 mM NaH$_2$PO$_4$–Na$_2$HPO$_4$ (pH 7–8), 20 mM Tris-HCl (pH 9.0), and 20 mM NaHCO$_3$–NaOH (pH 10) were used as buffer solutions for the flocculation media.

2.5. SEM measurements

Scanning electron microscopy (SEM) images of the samples were obtained using a JSM 6330F scanning electron microscope (JEOL Ltd., Japan), using a potential of 1 kV and Au vapor deposition to prepare the sample surface.