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Research paper

Cationic flocculants derived from native cellulose: Preparation, biodegradability, and removal of dyes in aqueous solution

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Abstract

Water-soluble quaternized celluloses with various substitution degrees were prepared. The polymers showed excellent flocculation ability against anionic dyes; this ability was strongly dependent on the substituent degree and not affected by the temperature and pH of the dye solution. The flocculation ability was accurately fitted by a pseudo-second order kinetic model, which enabled reliable predictions of the flocculation behavior. In addition, the flocculation behavior of the anionic dyes followed the Langmuir adsorption isotherm model, whose analysis revealed the maximum anionic dye coagulation/flocculation capacity. The quaternized celluloses could be regenerated by washing in NaOH solution and precipitation in acetone. The quaternized celluloses exhibited good biodegradability, with a maximum degradation of 48% within 48 h using cellulase. These encouraging results indicate that the cationic celluloses could be applicable for use as reusable flocculants for wastewater treatment, leading to an environmentally friendly method to the removal of dyes from aqueous solutions.

Keywords: Cellulose derivatives; Biodegradability; Biopolymeric flocculant

1. Introduction

Dyes are widely used in many industrial applications, including textile, rubber, paper, plastic, and cosmetic ones, among others. More than 10,000 types of dyes are commercially available, and more than 7×10^5 tons per year are produced worldwide [1]. Most of these dyes are not only aesthetically displeasing, but also impede light penetration, retard photosynthetic activity, and inhibit the growth of biota. In addition, many dyes are toxic and carcinogenic [1,2]. About 2% of the industrially produced dyes are discharged directly in aqueous effluents [3], therefore making the elimination of dyes from wastewater before discharge into the environment a fundamental priority.

Among various methods for dye removal such as adsorption [4], coagulation [5], membrane filtration [6], oxidation [7], and biological processes [8], the coagulation/flocculation processes are employed for treating dye-bearing industrial effluents [9] due to its low operating cost and ease to perform. Typical reactants used in these processes are polyelectrolytes derived from inorganic salts of Al or Fe. Although chemical coagulation using these compounds is suitable for dye removal, the process has some drawbacks: the effectiveness of the removal strongly depends on the pH and ionic strength of the effluent, and the treated water may eventually contain high residual Al or Fe ion concentrations [10]. In order to minimize these issues, polysaccharide-based polyelectrolytes are being investigated as more practical alternatives to synthetic polyelectrolytes, due to their biocompatibility and biodegradability [11].

Cellulose, which is the most abundant polysaccharide on Earth, is a prime candidate as precursor of bio-based functional materials. The high degree of polymerization and number of potential chemical modifications of cellulose also make it an attractive candidate for flocculation purposes. For example, sodium carboxymethyl cellulose (CMC), which is a well known water-soluble and anionic cellulose derivative, 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 [12]. In addition, the use of anionic flocculation agents is still infrequent as compared with the use of cationic flocculants. With such a

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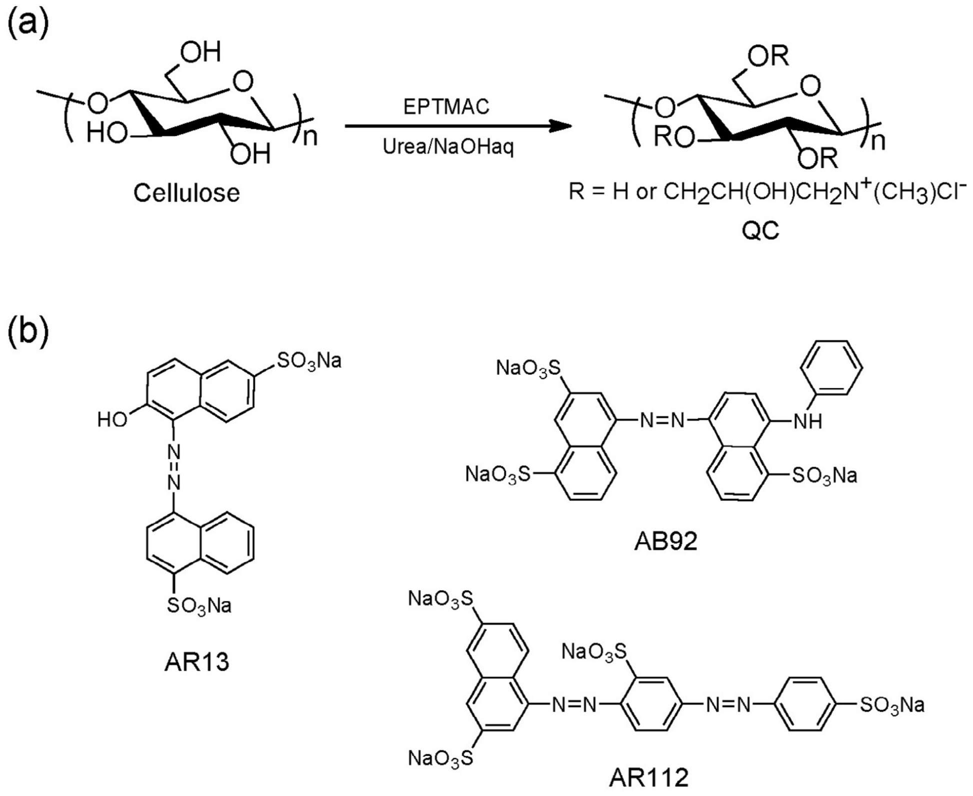

Fig. 1. Scheme of the preparation of quaternized cellulose (QC) from cellulose (a) and structures of the anionic dyes used in study (b).

background, the cationic cellulose derivatives have been paid attention as flocculation agents [13–16].

Water-soluble quaternized cellulose derivatives (QCs) have great potential for various industrial applications because the tertiary ammonium groups in the polymer exhibit intermediate basicity and are permanently charged, independently of the pH of their solutions [13]. Due to their excellent cationic character, QCs could be used as additive in papermaking, as thickener for mineral processing, and as conditioner in hair care products [12]. Recently, QC has been found to exhibit high flocculation ability toward colloidal particles whose surfaces are negatively charged, such as kaolin [13], calcium carbonates [17], and colloidal silica particles [18]. The flocculation performance for these small particles suspended in solutions by QC is related to two major mechanisms. The first mechanism is the charge neutralization of the particles by QC. The second major mechanism concerns the intermolecular bridging between the suspended particles by the QC chains [18]. On the other hand, the flocculation ability and its mechanism of QC toward small compounds such as dye molecules have not been investigated in detail.

In this study, water-soluble QCs having different degrees of substitution (DS) were homogeneously prepared from cellulose dissolved in urea/NaOH solution by the reaction with 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) as a etherification reagent, and their coagulation and flocculation performances toward anionic dyes were investigated (Fig. 1). In addition, the effects of DS, pH, and temperature on the coagulation and flocculation ability, as well as the kinetics and isotherms of the coagulation/flocculation processes were investigated in detail in order to elucidate the corresponding mechanism. Moreover, the possibility of biodegradability and reusing of the QCs was investigated in order to reveal the QCs as an excellent biodegradable and reusable flocculants.

2. Materials and methods

2.1. Materials

Powdered cellulose (an average polymerization degree of 320) was obtained from Wako Pure Chemicals Industries (Japan). EPTMAC was purchased from Sigma-Aldrich Inc. (USA). AcidRed 13 (AR13), AcidBlue 92 (AB92), and AR 112 dyes were purchased from Tokyo Chemical Industry Co. Ltd. (Japan). *Trichoderma viride* (*T. viride*) cellulase ONOZUKA R-10 was purchased from Yakult Pharmaceutical Industry Co., Japan. Sodium carboxymethyl cellulose (CMC, DS = 0.87) was purchased from Wako Pure Chemicals Co., Japan. Other chemicals employed in this work were of a chemically pure grade, and all solutions were prepared with pure water.

2.2. Preparation of QCs

A series of three QCs (labeled **1**–**3**) were prepared from cellulose with EPTMAC according to the method previously reported. Briefly, cellulose (1.26 g, 7.78 mmol per anhydroglucose unit (AGU)) was suspended in 50 mL of 1.5 mol L^{-1} NaOH solution containing 1 g of urea, and the suspension was cooled to 259 K. After 1 h, the temperature of the suspension was set to 271 K and the suspension was vigorously stirred at 800 rpm for 10 min to completely dissolve the cellulose [19]. The temperature of the cellulose solution was set to 298 K, EPTMAC (8.89 g, 58.6 mmol) was then added the solution, and then the reaction mixture was heated at 333 K for 3 h. After cooling to room temperature, the mixture was poured into 300 mL of methanol. The obtained precipitates were washed with a 1:1 mixture of methanol/distilled water to reach neutral pH, and dried under vacuum to obtain the flocculant hereafter labeled QC**1**. The QC**2** flocculant was prepared by a similar method, by changing the feed amount of EPTMAC to 11.8 g (77.8 mmol), whereas QC**3** was prepared by repeating the method used to prepare QC**2** twice. The QCs were stored in a desiccator under vacuum until ready for use.

2.3. *Structural characterization*

Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum II FTIR spectrometer at a resolution of 1 cm^{-1}. The spectra were measured from 4000 to 650 cm^{-1} using an average of 16 scans. NMR spectra of QCs were measured at 363 K in deuterium oxide containing 0.1% 4,4-dimethyl-4-silapentane-1-sulfonic acid as an internal standard using Bruker AVIII 500 MHz spectrometer (Bruker BioSpin GmbH, Germany) equipped with a two-channel 5 mm broadband observe probe. The quantitative ^{13}C NMR spectra were obtained by the inverse-gated ^{1}H decoupling method [19–21] with a flip angle for ^{13}C excitation pulse of 30° and repetition time of 45 s. The ^{13}C NMR chemical shifts were calibrated by referencing to 0 ppm the methyl resonance of the internal standard.

2.4. *Biodegradability test*

Before performing the biodegradability test for QC**1**–**3**, cellulase activity was measured using CMC as a substrate by the following method [22]. A total of 10 mL of the reaction mixture containing 9 mL of 1 (w/v) % CMC in 50 mmol L^{-1} acetate buffer (pH 5.0), and 10 mg of cellulase dissolved in 1 mL of the same buffer solution was incubated at 313 K. After 30 min, the amount of reducing sugars in the mixture was measured by the method of Miller et al. [23]. One unit (U) of the cellulase activity was defined as the amount of enzyme liberating 1 mmol of reducing sugar per min. The protein mass of the cellulase was determined by use of the Bio-Rad protein assay kit (Bio-Rad Co., USA) with bovine serum albumin as the standard [24].

The biodegradability test was carried out using the cellulase according to the method previously reported [22]. Briefly, each QC (100 mg) was dissolved in the 19 mL of 50 mM acetate buffer (pH 5.0), and cellulase dissolved in 1 mL of the same buffer solution was added to the suspension to give a cellulase concentration of 0.20 U/mL. The mixture was incubated at 313 K. After a prescribed period, an aliquot (500 μL) was withdrawn from the mixture, and the amount of reducing sugars in the aliquot was determined by the method described above. The biodegradability of the QCs was determined using the following equation:

$$\text{Biodegradability}\,(\%) = (M_\text{b} \quad M_\text{d})/M_\text{b} \times 100, \tag{1}$$

where M_b is the molar mass of AGU in the QC sample before the cellulase digestion, and M_d is the molar mass of the reducing sugars liberated by the cellulase.

2.5. *Flocculation of dyes*

The flocculation ability of a QC was estimated by the following procedure: a buffer solution (5 mL) containing a dye with an initial concentration (C_0) in the range of 0.050–1 g L^{-1} was poured into a 15 mL polypropylene centrifuge tube, and a precisely weighed amount of QC was added to the dye solution; the mixture was immediately placed in a shaker at 120 rpm and 298 K for 120 min, after which the suspension was left to settle for 5 min. The dye concentration of the filtrate was determined by an Epoch 96-well micro-volume spectrophotometer with a Take3 micro-volume quartz plate (BioTek Instruments, Inc., USA), using a previously prepared calibration curve at 504 nm for AR13, 572 nm for AB92, and 530 nm for AR112. The flocculation ability of a QC at a contact time t (Q_t) was calculated according to Eq. (2):

$$Q_t = \frac{(C_0 - C_t V)}{m}, \tag{2}$$

where C_t is the concentration of the dye at contact time t, V is the volume of the dye solution, and m is the mass of the QC. The buffer solutions used for the adsorption media were 20 mmol L^{-1} citric acid-sodium citrate (pH 3–6), 20 mmol L^{-1} NaH_2PO_4–Na_2HPO_4 (pH 7–8), 20 mmol L^{-1} Tris–HCl (pH 9), and 20 mmol L^{-1} $NaHCO_3$–NaOH (pH 10–11).

2.6. *Recycling experiments*

After the flocculation experiments, the formed floc was recovered by centrifugation at 8000*g* for 10 min. The floc was immersed in 1.5 mol L^{-1} aqueous NaOH solution (20 mL) for 1 h to remove the dye [19], and then 40 mL of acetone was added to the solution to precipitate the QC. After centrifugation at 8000*g* for 10 min, the precipitate was washed with methanol (20 mL) for three times to obtained the regenerated QC. After drying, the flocculation ability of the regenerated QC after *n* cycles was determined by the protocols described above.

3. Results and discussion

3.1. *Structural characterization of the flocculants*

QC**1**–**3** were prepared from cellulose dissolved in the urea/NaOH solution, and the obtained QCs were characterized by FTIR and ^{13}C NMR spectroscopic analyses (Fig. 2). The FTIR spectra of QC**1**–**3** exhibit absorption bands corresponding to the asymmetric —CH_3 stretching vibration at 1481 cm^{-1} and the C—N stretching vibration at 916 cm^{-1}, due to the quaternary ammonium groups substituted at hydroxyl groups of cellulose. In addition, the adsorption bands of cellulose are observed at 1412, 1382, 1318, and 897 cm^{-1}, which can be assigned to the —CH_2 scissoring, —OH bending, O—H deformation, and *β*-glucopyranose ring-breathing vibrations,

Table 1
Degree of substitution (DS) and yields of QC**1**–**3** flocculants.

Flocculant	DS	Yields (g)	Yields (%)*
QC**1**	0.56	1.58	82
QC**2**	0.84	1.75	78
QC**3**	1.33	1.85	65

* Yield (%) of each QC was determined by the Eq. (4).

respectively [25]. The precise DS of the cationic groups substituted in the QC**1**–**3** compounds was estimated from their quantitative ^{13}C NMR spectra through the following Eq. (3):

$$\mathrm{DS} = \frac{I_{CH3}}{3I_{C1}}, \tag{3}$$

where I_{CH3} and I_{C1} are the integrals of the CH_3 and anomeric C1 resonances at 57 and 105 ppm, respectively. The estimated DS can then be used to calculate the yield of each QC through Eq. (4):

$$\mathrm{Yield}(\%) = \frac{Yield(g)}{(162+151.5\times DS)(gmol^{-1})\times 7.78\times 10^{3}(mol)} \times 100(\%). \tag{4}$$

The resulting DS values for QC**1**–**3** were 0.56, 0.84, and 1.33, respectively, and the yields were in range of 65–82% (Table 1).

3.2. *Biodegradability*

Enzymatic degradation of the QCs was performed at 313 K using cellulase. Fig. 3 shows the time dependence of degradation. The cellulase degrades the β-(1,4)-glycosidic bonds of cellulose, while ether bonds in the substituent groups of the cellulose ethers are not degraded by the cellulase [25]. Therefore, the biodegradability in the figure means the percentage of degraded β-(1,4)-glycosidic bonds in the QCs by cellulase. After 48 h of incubation with cellulase, the degradability of the QC**1**–**3** was found to be 48, 32, and 21%, respectively, under the conditions employed. The degradation speed as well a decreased with increase of DS of the QCs. This indicated that the QCs with high DS forbid cellulase to easily contact with the polymer chains, similar to those of other cellulose derivatives [22,26–28].

3.3. *Flocculation of anionic dyes*

3.3.1. *Influence of external parameters*

Flocculation efficiency of the ionic flocculants is generally affected by external parameters such as temperature, pH, and flocculant dosage [3]. In this study, the influence of these parameters on the flocculation ability of QC**1**–**3** was first investigated using the AB92 dye.

The effect of the temperature was investigated in the temperature range of 293–323 K (Fig. 4a). The flocculation ability (*Q*) strongly depends on the DS of the QCs and stays approximately constant in the temperature range investigated: the *Q* values of QC**1**–**3** are 0.321 ± 0.010, 0.400 ± 0.013, and 0.599 ± 0.015 g g^{-1}, respectively, suggesting that the flocculation is determined by charge neutralization between the anionic dye molecules and cationic groups in the QC chains, and that the temperature has no influence on the flocculation of AB92. Therefore, the flocculation mechanism could be described as a homogeneous adsorption process induced by the electrostatic interaction between the anionic dye and the QC chains because physical adsorption processes generally exhibit a strong temperature dependence [29].

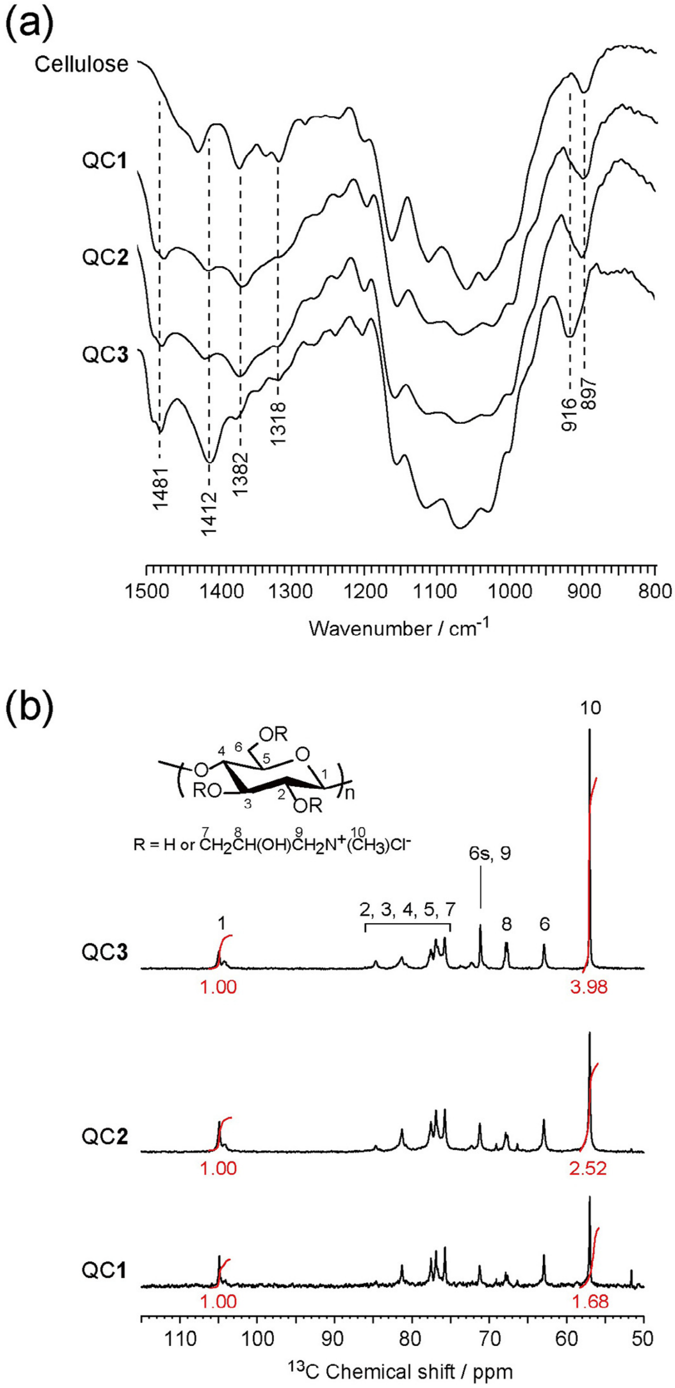

Fig. 2. FTIR (a) and quantitative ^{13}C NMR (b) spectra of QC**1**–**3** flocculants.

Fig. 4b shows the flocculation ability of QC**1**–**3** in the pH range of 3–11. The flocculation performance maintained a con-

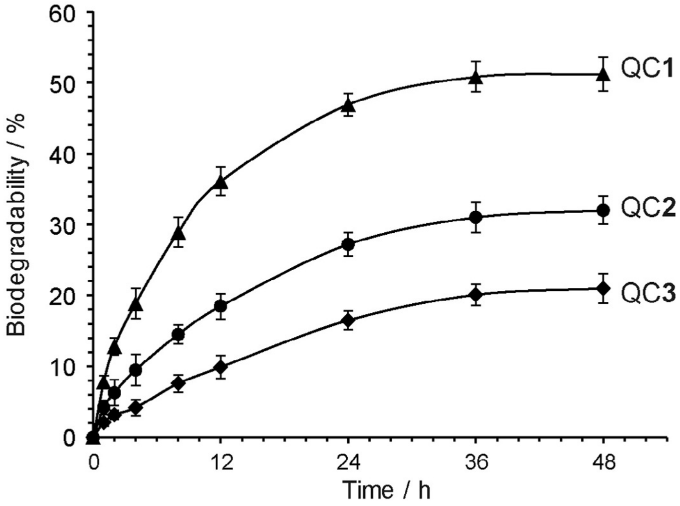

Fig. 3. Cellulase degradation of QC**1**–**3** flocculants.

stant level in the whole pH range, due to the quaternary ammonium groups of the QC chains. As for the previous test (Fig. 4a), also in this case the flocculation of AB92 showed a strong dependence on the DS of the QCs, supporting the finding that the flocculation process occurred via a charge neutralization mechanism.

As shown in Fig. 4c, variable flocculant doses (0–1 g L^{-1}) were exposed to a fixed initial dye concentration to evaluate the influence of the dosage on the flocculation ability of the QCs. The results showed that the flocculation ability increased with increasing flocculant doses up to an optimal value, followed by a decreasing trend with further dose increases. The optimal doses for QC**1**–**3** were 0.40, 0.30, and 0.20 g L^{-1}, respectively. These trends are typical of flocculant systems controlled by a charge neutralization mechanism [25,26]. In particular, when the amount of cationic charge supplied was sufficient for the complete neutralization of the anionic charge, the flocculation of the dye reached the maximum efficiency. Excess of cationic charge following overdosing of the flocculant induces a dispersion restabilization phenomenon and a subsequent decrease in the efficiency of the flocculation process [20,25]. This could be confirmed by the order of Q_t values (QC**1** > QC**2** > QC**3**) at very high flocculant concentrations such as 1.0 g L^{-1}: the excess of cationic charge by the QC flocculants caused electrostatic repulsion between the QC chains in the formed flocs, which resulted in the dispersion of the polymer chains.

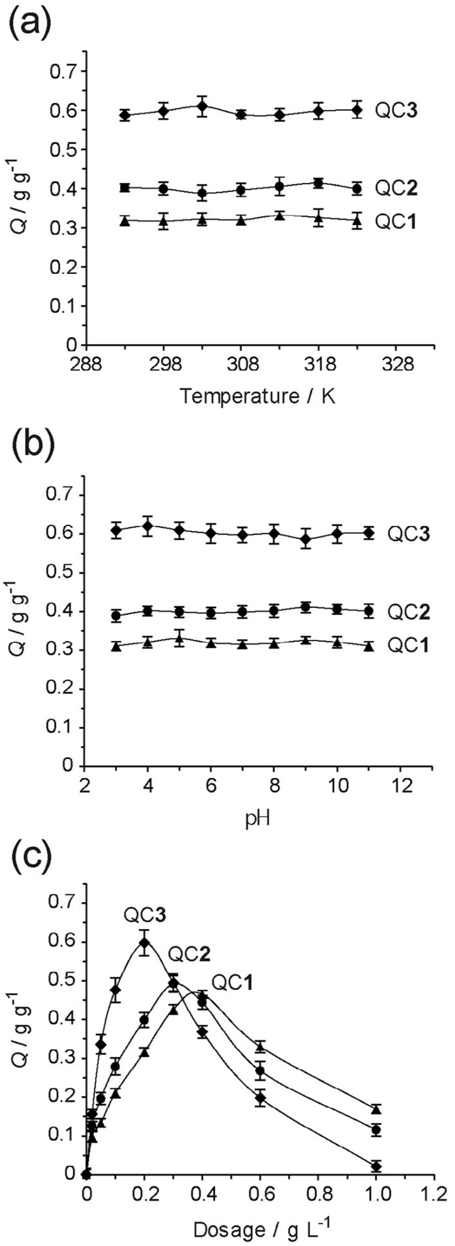

Fig. 4. Influence of temperature (a), pH (b), and flocculant dosage (c) on the coagulation/flocculation of AB92 dye by QC**1**–**3** flocculants. These experiments were performed under the following conditions: flocculant dose 0.20 g L^{-1}; contact time 120 min; saturation concentration of the adsorbate (C_0) 1.0 g L^{-1}; pH 7; temperature 298 K.

3.3.2. Flocculation kinetics

The contact time between dyes and QC chains is another important parameter for understanding the flocculation kinetics [30]. The effect of the contact time on the flocculation ability of QC**3** toward AR13, AB92, and AR112 was investigated at pH 7, and the results are shown in Fig. 5a. The flocculation ability rapidly increased following contact between each dye and the QC, before eventually reaching a plateau at a contact time of 30 min for all dyes. The equilibrium value of the flocculation ability followed the order AR13 > AB92 > AR112, which indicated the charge neutralization mechanism between the anionic sulfonate groups of the dye and the cationic groups of QC chains: AR13, AB92, and AR112 contain 2, 3, and 4 sulfonate groups per molecule, respectively. The amounts of AR13, AB92, and AR112 dyes flocculated by the QC**3** in Fig. 5a were standardized by amounts of sulfonate groups of each dye, and the results were shown in Fig. 5b. If the anionic sulfonate groups of dyes were completely neutralized by the opposite charges of QC**3**, these three curves displayed in Fig. 5b overlapped. However, these anionic dyes were different from each other in their flocculation curves, and the equilibrium value of the standardized flocculation ability followed the order

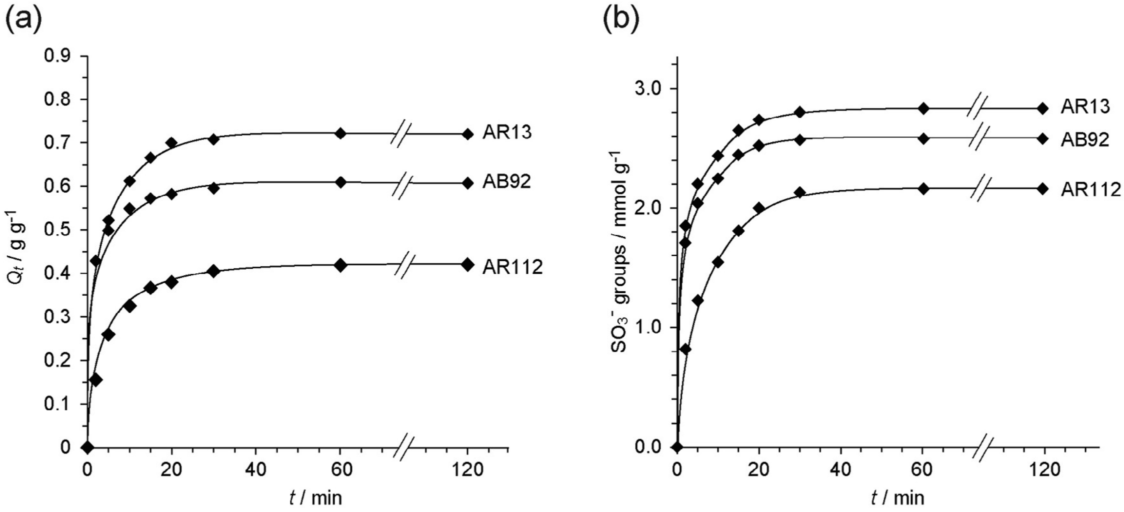

Fig. 5. (a) Time dependence of flocculation of AR13, AB92, and AR112 by QC**3** flocculant at pH 7. The experiments were performed under the following conditions: flocculant dose 0.20 g L^{-1}; saturation concentration of adsorbate (C_0) 1.0 g L^{-1}; pH 7; temperature 298 K. (b) Amounts of anionic sulfonate groups (SO$_3^-$) of AR13, AB92, and AR113 neutralized by the opposite charged groups of QC**3**.

AR13 > AB92 > AR112. This indicates that the flocculation of anionic dyes with QCs depends on the molecular structure of the anionic dyes and that anionic dyes with low number(s) of anionic groups are preferable to achieve efficient flocculation.

Several kinetic models have been previously used to describe the kinetics of dye flocculation, and pseudo-first order [31] as well as pseudo-second order [32] kinetic models have frequently been used to fit the experimental data. The pseudo-first order and pseudo-second order kinetic models are described by the following equations (5) and (6):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad \text{and} \qquad (5)\ \text{and}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}, \qquad (6)$$

respectively, where k_1 and k_2 are the rate constants for the pseudo-first and pseudo-second order models, while Q_e and Q_t are the flocculation abilities at equilibrium and contact time t, respectively. Curve-fitting plots of the flocculation ability of AR13, AB92, and AR112 by QC**1**–**3** using the two kinetic models are shown in Fig. A1, and the fitted k_1, k_2, and $Q_{e,cal}$ parameters are summarized in Table 2, together with the corresponding correlation coefficients (R^2) . For all fitting curves, the R^2 values for the pseudo-second order kinetic model ($R^2 = 0.996$–1.000) were higher than those of the pseudo-first order model ($R^2 = 0.865$–0.991). In addition, the $Q_{e,cal}$ values determined by the pseudo-second order model were more consistent with the experimentally-determined flocculation ability at equilibrium $Q_{e,exp}$, compared with the $Q_{e,cal}$ parameters obtained with the pseudo-first order kinetic model. These results prove that the flocculation of these dyes with QCs completely followed a pseudo-second order adsorption mechanism, and thus that the flocculation behavior by QCs could be predicted over the entire range of contact times using the rate constant k_2 in the same way as the electrostatic adsorption of ionic dyes onto the other polysaccharide-based flocculants [20,25].

Table 2
Kinetic parameters (Eqs. (5) and (6)) for the flocculation of AR13, AB92, and AR112 dyes with QC **1**–**3** flocculants dissolved in aqueous solution at pH 7.0 and 298 K.

Dye	Flocculant	$Q_{e,\,exp}$* (g g^{-1})	Pseudo-first order model			Pseudo-second order model		
			k_1 (min^{-1})	$Q_{e,\,cal}$ (g g^{-1})	R^2	k_2 (g g^{-1} min^{-1})	$Q_{e,\,cal}$ (g g^{-1})	R^2
AR13	QC**1**	0.388	0.135	0.317	0.988	0.670	0.402	0.998
	QC**2**	0.499	0.126	0.352	0.979	0.752	0.511	0.998
	QC**3**	0.711	0.177	0.530	0.984	0.655	0.732	0.999
AB92	QC**1**	0.316	0.186	0.196	0.865	0.786	0.326	0.999
	QC**2**	0.399	0.139	0.219	0.914	0.665	0.406	0.998
	QC**3**	0.599	0.192	0.265	0.906	0.568	0.612	1.000
AR112	QC**1**	0.245	0.122	0.199	0.989	0.871	0.266	1.000
	QC**2**	0.339	0.117	0.297	0.987	0.530	0.342	0.997
	QC**3**	0.411	0.133	0.395	0.987	0.435	0.419	0.998

* Experimentally determined Q_t value at equilibrium ($t = 120$ min).

Table 3
Langmuir, Freundlich, and BET adsorption isotherm coefficients (Eqs. (7)–(10)) for the flocculation of dissolved anionic dyes by CC**1**–CC**3** flocculants.

Dye	CC	$Q_{e,\,exp}$*/g g^{-1}	Langmuir				Freundlich			BET		
			Q_0/g g^{-1}	K_L/g^{-1}L	R_L	R^2	K_F/g L^{-1}	n^{-1}	R^2	Q_m/g g^{-1}	K_b	R^2
AR13	**1**	0.623	0.635	0.0091	0.099	0.998	0.048	0.404	0.942	0.100	−5.89	0.541
	2	0.844	0.869	0.0119	0.078	0.999	0.078	0.377	0.961	0.178	−12.4	0.694
	3	1.060	1.014	0.0459	0.021	0.998	0.243	0.232	0.966	0.253	−9.14	0.854
AB92	**1**	0.511	0.526	0.0082	0.108	0.999	0.037	0.409	0.952	0.067	−3.88	0.512
	2	0.622	0.644	0.0141	0.066	0.999	0.079	0.320	0.975	0.097	−3.62	0.759
	3	0.827	0.845	0.0345	0.028	0.999	0.166	0.259	0.955	0.173	−6.01	0.816
AR112	**1**	0.368	0.399	0.0109	0.084	0.999	0.033	0.375	0.935	0.033	−1.36	0.605
	2	0.458	0.478	0.0193	0.049	0.999	0.064	0.310	0.899	0.052	−1.70	0.714
	3	0.556	0.572	0.0239	0.040	0.999	0.107	0.590	0.949	0.079	−2.70	0.757

* Q_e value at 120 min contact time when C_0 was set to 1.0 g L^{-1}.

3.3.3. *Flocculation isotherms*

Adsorption isotherms represent a key tool for characterizing the interaction between adsorbates and adsorbents. The Langmuir, Freundlich, and Brunauer–Emmett–Teller (BET) isotherms are applied to describe the flocculation behaviors by polymer flocculants [33,34], and were applied here to analyze the flocculation of the anionic dyes by the QC**1**–**3** flocculants.

The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform adsorption energies, with no transmigration of adsorbates in the surface plane. Once an adsorption site is filled by adsorbate, no further adsorption can take place at that site [33]: this results in the surface reaching a saturation point corresponding to the maximum adsorption capacity. Thus, the linear form of the isotherm is represented by:

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e}, \tag{7}$$

where Q_e is the amount of adsorbate on the adsorbant at equilibrium (g g^{-1}), Q_0 is the maximum monolayer coverage capacity (mg g^{-1}), b is the Langmuir constant (L mg^{-1}), and C_e is the equilibrium concentration of adsorbate (mg L^{-1}). As shown in Fig. A2a, the reciprocal flocculation ability at equilibrium Q_e plotted against the equilibrium dye concentration C_e for the flocculation of anionic dyes by QCs strictly obeys the Langmuir isotherm equation, as shown by R^2 coefficients of 0.998–0.999 (Table 3). In addition, the Q_0 values for the flocculation of anionic dyes determined by the Langmuir isotherm model are in good agreement with the equilibrium adsorption abilities of the QCs. By using the Langmuir constant b, the dimensionless separation factor (R_L) could be obtained as:

$$R_L = \frac{1}{(1+bC_0)}. \tag{8}$$

The R_L value allows classifying the adsorption process as unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [35]. As summarized in Table 3, the constants R_L are in the 0.02–0.11 range, indicating favorable adsorption of all dyes onto QCs.

The Freundlich isotherm is an empirical model, whose linear form is given in Eq. (8):

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e, \tag{9}$$

where K_F is the Freundlich constant, corresponding to the maximum adsorption capacity, and the dimensionless constant n^{-1} is an empirical parameter related to the isotherm shape. Based on the n^{-1} values, the adsorption process can be classified as irreversible ($n^{-1} = 0$), favorable ($0 < n^{-1} < 1$), or unfavorable ($n^{-1} > 1$) [34], The $\ln Q_e$ versus $\ln C_e$ plots for each dye flocculation shown in Fig. A2b yield the constants K_F and n^{-1} summarized in Table 3. The estimated n^{-1} values lie in the range of 0.232–0.590, confirming favorable adsorption of the dyes onto QC chains. However, the R^2 coefficients for the Freundlich model are in range of 0.899–0.975, considerably lower than those corresponding to the Langmuir model.

The BET isotherm was developed to describe multilayer adsorption systems, and its linear form is given in Eq. (10):

$$\frac{C_e}{(C_0 - C_e)Q_e} = \frac{C_e(K_b - 1)}{K_bQ_mC_0} + \frac{1}{K_bQ_m}, \tag{10}$$

where Q_m is the amount of adsorbate adsorbed in a complete monolayer (g g^{-1}), K_b a constant representing the energy of interaction with the surface, and C_0 is the saturation concentration of the adsorbate [34]. The Q_m, K_b, and R^2 values for the flocculation of anionic dyes by QC**1**–**3** determined from the BET plots (Fig. A2c) are summarized in Table 3. The R^2 for the BET model ($R^2 = 0.512$–0.854) are considerably lower than those calculated for both Freundlich ($R^2 = 0.899$–0.975) and Langmuir ($R^2 = 0.998$–0.999) isotherm models. In addition, the Q_m values determined by the BET plots are inconsistent with the observed flocculation ability at equilibrium Q_e. These results indicate that multilayer adsorption of dyes onto QC chains, with the associated interactions between anionic dyes, did not occur in the flocculation process of the dyes.

The curve-fitting analysis using the three isotherm models thus shows that the adsorption of the anionic dyes onto the QC chains follow a Langmuir-type adsorption model. The Langmuir adsorption model is derived from the following assumptions: 1) the adsorbed molecules do not interact with each other, and 2) all molecules are adsorbed by the same mechanism. Therefore, the good fit to the Langmuir isotherm model suggests that the flocculation of the dyes follows a

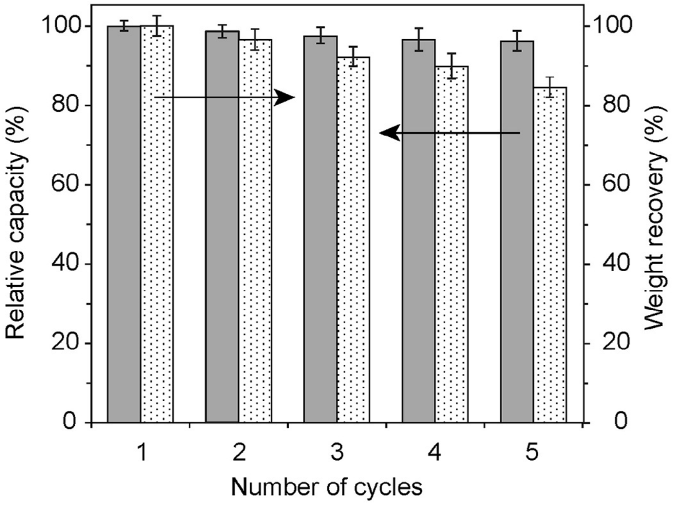

Fig. 6. Flocculation ability (shaded bars) toward AB92 dye and weight recovery upon regeneration (dotted bars) of QC**3** flocculant.

homogeneous mechanism based on charge neutralization between dye molecules and the quaternary ammonium groups of QCs, which is supported by the observation that the flocculation process does not involve physical adsorption. If other interactions besides the electrostatic ones played an important role in the flocculation process, the flocculation behavior would be fitted by the Freundlich or BET adsorption isotherm models, which are generally employed to fit the heterogeneous and multilayer adsorption systems, respectively [36].

3.4. Regeneration and reuse of flocculants

In order to reduce the operating costs of QCs as flocculants, easy regeneration of the adsorbent after dye flocculation is highly desirable. Recycling experiments were thus carried out using QC**3** and the AB92 dye. After flocculation with AB92, QC**3** was recycled as described in experimental section and then used again to carry out the flocculation. Fig. 6 shows no significant losses in the dye flocculation performance even after five cycles despite a weight loss of more than 5% after immersion in NaOH solution and precipitation with methanol. The QC**3** ability to retain its flocculation capacity after several uses highlighted by these results should support a reduction of the operating costs associated to the use of these flocculants for water purification.

4. Conclusions

The present work shows that quaternized celluloses can be used as efficient and recyclable flocculants with high adsorption capacity for anionic dye decontamination. As the flocculation process reaches equilibrium within 30 min, the fast kinetics of the process can permit fast decontamination of pollutants. The flocculation performance is hardly altered by changes in temperature and pH; therefore, the present QCs would survive under a range of different operating conditions. In addition, the efficient regeneration capabilities of the QCs highlighted in this work could significantly reduce the operating costs of wastewater treatments.

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Appendix: Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.reffit.2016.11.015.

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