

Preparation of Quaternized Carboxymethyl Chitosan and Its Capacity to Flocculate COD from Printing Wastewater

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ABSTRACT: A bioflocculant, quaternized carboxymethyl chitosan (QCMC), was developed by the quaternization of N,O-carboxymethyl chitosan (N,O-CMC) and characterized by FTIR, ¹H-NMR, GPC, and potentiometry. The efficiency of the removal of chemical oxygen demand (COD) in printing wastewater by this flocculant was further reported. Results indicated that the capacity of QCMC to remove the COD from tested wastewater was the best one among the investigated flocculants. The pH had great influence on this capacity and the suitable pH for QCMC to treat the tested wastewater was about 5.0. The utilization of aid-flocculant, especially bentonite, could improve

this capacity obviously, and the increase of mass ratio of bentonite to QCMC resulted in the increase of the capacities of complex flocculant to remove the COD from the tested wastewater. When the mass ratio of bentonite to QCMC was 40, pH of wastewater was 5.0 and amount of complex flocculant in the wastewater was from 2500 to 3142 mg L⁻¹, the removal ratio of COD was more than 80%. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 299–305, 2010

Key words: bioflocculant; quaternized carboxymethyl chitosan; flocculation; COD; printing wastewater

INTRODUCTION

Wastewater from textile effluents is one of the most important pollution sources, the high concentration of chemical oxygen demand (COD), and the presence of dyestuff in this wastewater could result in serious environmental problem. Many techniques have been utilized to treat the wastewater containing dyestuff, such as chemical precipitation,¹ adsorption,^{2,3} photolysis,⁴ oxidation,^{5,6} deoxidization,⁷ biodegradation,⁸ membrane separation,⁹ etc. However, these technologies are either ineffective or expensive when dyestuff is present in the wastewater at high concentrations. Flocculation is a method with highly effective, inexpensive, and easy to operate among the physicochemical treatment processes of wastewater. Consequently, numerous low-cost flocculants have been studied including polyacrylamide (PAM) and its modifying derivatives,^{10–12} polyaluminum chloride (PAC),¹³ polymerized ferrous sulfate (PFS),¹⁴ aluminum sulfate (AS),^{15–17} modifying polysaccharides,^{18,19} etc.

Chitosan (CTS) is a nontoxic, biocompatible, and biodegradable polymer and resulted from deacetylation of chitin, which is the second most abundant natural biopolymer after cellulose.^{9,20} CTS has become of great interest not only as an underutilized bioresource but also as a new functional material with high-potential application in various fields, such as environmental and biomedical engineering. Chitosan has the advantage over synthetic polymers whose use may be limited by the levels of residual toxic monomers. CTS could be used as a flocculant on industrial scale and as an adsorbent for recovering proteins from food-processing factories.²¹

Application of chitosan in the environmental engineering is concerned with its different types, such as chitosan bead,²² chitosan fiber,²³ chitosan resin,²⁴ chitosan membrane,²⁵ etc., but the most extensive one is its water-solubility derivative. Several studies were carried out to improve the properties of these soluble derivatives of chitosan and to enhance their flocculating capacity.^{26–28} To overcome the difficulties associated with the flocculation of a wider range of deleterious molecular species, chitosan-polyanion (CTS-Pol) complexes consisted of chitosan and carrageenan, pectin, or alginate were prepared and used as coagulating agents for treating Cheddar cheese whey.²⁹ The bioflocculants with varying degree of acetylation prepared by homogeneous reacetylation of a highly deacetylated chitosan were tested for elucidating their mechanism of flocculation to model latex particles.³⁰

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In this investigation, an attempt to utilize quaternized N,O-carboxymethyl chitosan (QCMC) as bio-flocculant for treating the printing wastewater from textile effluents was considered. The bioflocculant was characterized by Fourier transform infrared spectra (FTIR), GPC, and $^1\text{H-NMR}$. The substituting degree of quaternization was determined by conductometric method and the substituting degree of carboxymethylation was ascertained by pH-titration. The basic objectives were as follows: (1) to study the flocculation characteristics of QCMC to the dyestuff present in the printing wastewater, (2) to investigate the factors effected on the capacities of QCMC to remove the COD of printing wastewater, and (3) to understand the mechanism of QCMC to flocculate dyestuff. For these purposes, the effect of various factors on the flocculation process, such as pH of the wastewater, bioflocculant dose, type of aid-flocculant, mass ratio of aid-flocculant to QCMC, and amount of complex flocculant composed of bentonite flocculant and QCMC were investigated.

MATERIALS AND METHODS

Materials

Chitosan was purchased from Shanghai Lanji Sci-Tech. Lt. Co. (Shanghai, People's Republic of China) and its degree of deacetylation was determined to be 91.4% by pH titration. The viscosity average molecular weight (M_v) of chitosan is 2.96×10^5 . The aqueous solution of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CTA) was prepared in our laboratory as described elsewhere in Ref. 31, its mass concentration was measured by potential titration to be 497 g L^{-1} . N,O-carboxymethyl chitosan (N,O-CMC) was prepared in our laboratory as described elsewhere in Ref. 32, its substitution degree of carboxymethylation (DS) was 85.6%. 2-Hydroxypropyl trimethylammonium chloride chitosan (HTCC) was prepared in our laboratory according to similar method described in Ref. 33, its substitution degree of quaternization (DQ) was 97.6%. Raw printing wastewater was supplied by Yancheng Huaxin Silk-printing Lt. Co. (Yancheng, People's Republic of China), its initial pH was ca. 8.3. PAM and PAC were purchased from Shanghai Henyi Chem. Lt. Co. (Shanghai, People's Republic of China), industrial grade. Bentonite and diatomite were purchased from Shanghai Haowei Chem. Lt. Co. (Shanghai, People's Republic of China), industrial grade. Sodium hydroxide was purchased from the Third Factory of Chemical Reagent of Tianjin (Tianjin, People's Republic of China), excellent grade. All other chemicals were of reagent grade and purchased from Sinopharm Chemical Reagent Lt. Co. (Shanghai, People's Republic of China). The chemicals were used without purification as received.

Preparation of QCMC

Dried N,O-CMC (8.0 g) was added into reaction bottle. Then, 75.0 mL of 2-propanol and 10 g of NaOH aqueous solution (mass concentration, 40.0%) were added. The mixture was heated to 45.0°C under stirring and alkalized for 1.0 h until the reactant had become a thick liquid material. CTA aqueous solution (24.0 mL) was added into the bottle dropwise in case the temperature was higher than 60.0°C . After this process, the temperature was elevated to 60.0°C and was kept at this temperature for 10.0 h under stirring. Then the pH of mixture was adjusted to ca. 7.0 using HCl solution (mass concentration, ca. 10.0%) and filtered. The resultant dreg was washed by 60.0 mL CH_3OH aqueous solution (mass concentration, ca. 85.0%) for three times, then by 50.0 mL ethanol for three times and filtered. The solid was dried in a freeze drier until its mass quantity was constant and was stored in desiccator for later use.

FTIR and $^1\text{H-NMR}$ spectra analysis

FTIR spectra of CTS, N,O-CMC, HTCC, and QCMC were recorded in the frequency range of $400\text{--}4000 \text{ cm}^{-1}$ using FTIR spectrophotometer (Nicolet Nexux FTIR 670 spectrometer). The samples were formed into pellets with KBr.

$^1\text{H-NMR}$ spectra were obtained with Bruker DRX-500 spectrometer that equipped with a tri-nuclei inverse probe with a Z gradient at 500.13 MHz and $25^\circ\text{C} \pm 0.5^\circ\text{C}$. The $^1\text{H-NMR}$ spectra of samples were measured in D_2O solution except for CTS, which was in $\text{D}_2\text{O-TFA}$ solution, and the samples were dissolved in a 5-mm diameter tube at a concentration of about 20 mg mL^{-1} .

Mensuration of degree of quaternization (DQ) and weight average molecular weights (M_w)

The DQ of QCMC was measured by the potentiometry. Briefly, samples were dissolved in double-distilled water (50 mL) and titrated with 0.100 mol/L aqueous silver nitrate using silver electrode as working electrode and calomel electrode as reference electrode. The titrating curves were constructed by recording conductance ratio (κ) versus volume of aqueous silver nitrate (V_{AgNO_3}) used in mensurating process.

The M_w of samples was measured by gel permeation chromatography (GPC) with poly(ethyl oxide) as standard on a Water-208 apparatus (column: Ultrahydrogel 500 and 1000; eluent: water; flow rate: 1.0 mL min^{-1} ; column temperature: 32°C ; concentration of samples: 0.8 mg mL^{-1}).

Flocculation studies

Flocculant (0.500 g) was dissolved in distilled water (100 mL, pH was ca. 6.4), giving rise to an aqueous

solution with mass concentration of 5.00 g L⁻¹. Printing wastewater (ca. 400 mL) was added into a series conical flasks and the pH of them was adjusted to the preconcentrating value with ca. 0.100 mol L⁻¹ HCl or NaOH aqueous solution, respectively. Then, calculated flocculant solution was added into each of the conical flasks with and without aid-flocculant. The conical flasks were put into an oscillator (SHZ-type, Jingcheng Guosheng experimental instrument factory in Jintian) and were shaken for 30 min. After staying for 5.0 h, some of the upper liquid was taken out and the COD concentration was determined according to literature.³⁴ The removal ratio of COD was determined by the change of its concentration in printing wastewater before and after processing.

$$\text{COD removal ratio \%} = (C_0V_0 - C_1V_1) / C_0V_0 \times 100 \quad (1)$$

where C_0 and C_1 were the COD concentration in printing wastewater before and after processing; V_0 and V_1 were the volume of the printing wastewater before and after processing, respectively.

All experiments were repeated three times and the results were averaged for evaluation.

RESULTS AND DISCUSSION

Characterization of QCMC

The FTIR spectra of CTS, N,O-CMC, HTCC and QCMC were shown in Figure 1. The absorption bands at 1655, 1323, and 1381 cm⁻¹ in the FTIR spectrum of CTS was assigned to primary and tertiary amides, and -CH₃ bend vibration. The characteristic peak at 3359 cm⁻¹ could be attributed to the O-H vibration. Two strong peaks at 1601 and 1416 cm⁻¹

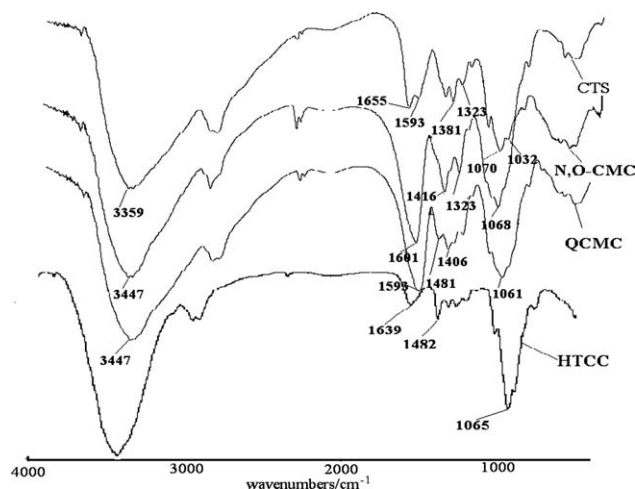


Figure 1 FTIR spectra of CTS, N,O-CMC, HTCC, and QCMC.

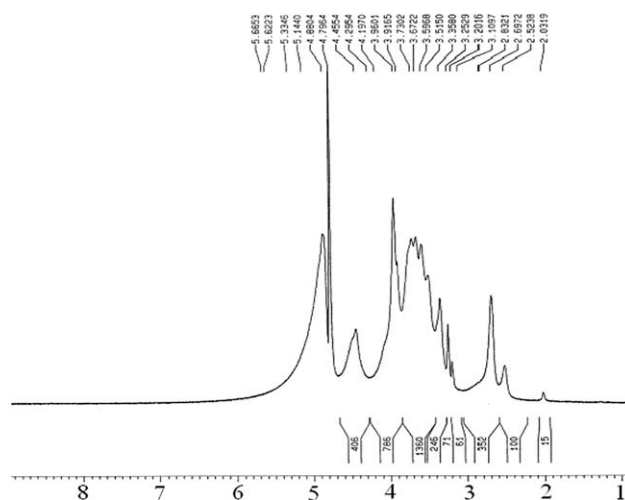


Figure 2 ¹H-NMR spectrum of N,O-CMC.

in the FTIR spectrum of N,O-CMC and 1593 and 1406 cm⁻¹ in the FTIR spectrum of QCMC were ascribed to the asymmetrical and symmetrical stretching of -CO₂⁻ group. In the FTIR spectra of N,O-CMC and QCMC, the C-O stretching band at 1032 cm⁻¹ corresponding to the primary hydroxyl group of CTS disappeared, which confirmed a high carboxymethylation of hydroxyl on the C-6 of sugar unit. Meanwhile, the characteristic peak of second hydroxyl group of chitosan at 1070 cm⁻¹ had shifted to 1061 cm⁻¹ for QCMC and to 1065 cm⁻¹ for HTCC. The peaks appeared at 1482 cm⁻¹ in the FTIR spectrum of HTCC and at 1481 cm⁻¹ in the FTIR spectrum of QCMC were ascribed to the C-H vibration of methyl of quaternary ammonium group, and it indicated the quaternary ammonium group had been introduced into CTS and the N,O-CMC.

The ¹H-NMR spectra of N,O-CMC, HTCC, and QCMC were shown in Figures 2-4. The resonance of 6-substituted and 3-substituted carboxymethyl-

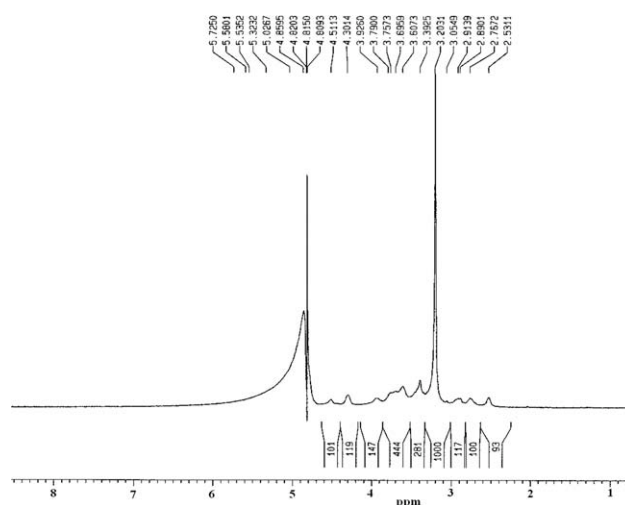


Figure 3 ¹H-NMR spectrum of HTCC.

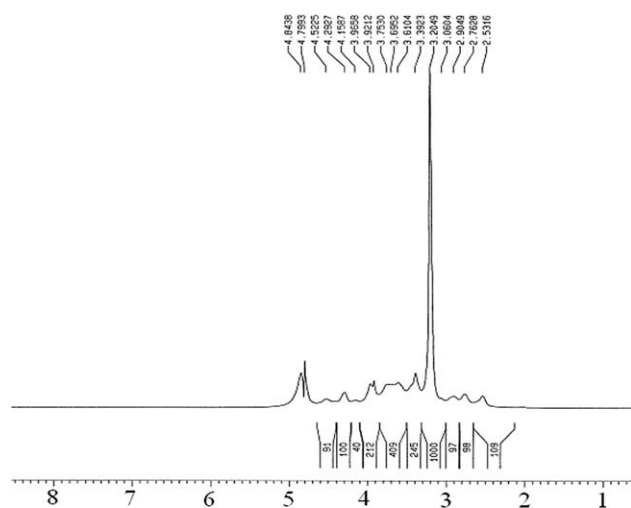


Figure 4 $^1\text{H-NMR}$ spectrum of QCMC.

protons ($-\text{OCH}_2\text{COOD}$) in the $^1\text{H-NMR}$ spectra of QCMC and N,O-CMC appeared in the spectral region of $4.2\text{--}4.6 \times 10^{-6}$ and $4.6\text{--}4.7 \times 10^{-6}$, respectively. Meanwhile, the resonance of 2-substituted carboxymethyl-protons ($-\text{NCH}_2\text{COOD}$) occurred in the spectral region of $3.2\text{--}3.4 \times 10^{-6}$. A stronger resonance appeared in 3.2049×10^{-6} in the $^1\text{H-NMR}$ spectrum of QCMC and in 3.2031×10^{-6} in the $^1\text{H-NMR}$ spectrum of HTCC, which could be attributed to the methyl-protons of quaternary ammonium group. Meanwhile, three new resonances appeared in the 2.7628×10^{-6} , 4.2927×10^{-6} , and 3.3023×10^{-6} in the $^1\text{H-NMR}$ spectrum of QCMC, which could be attributed to the C_1 , C_2 , and C_3 protons of quaternary ammonium group that introduced into the N,O-CMC.

Determining results of M_w and DQ

Results of GPC analysis indicated the M_w of N,O-CMC, HTCC, and QCMC were 3.12×10^5 , 3.93×10^5 , and 4.10×10^5 , respectively. The DQ of QCMC determined by the potentiometry in our investigation was 61.4%. These results were different from the data reported by Carolan, Wu, and Sun et al. The reasons were as follows: (1) the chitosan used in our study and the substitution degree of chitosan derivatives were different from literatures^{32,33}; (2) the N,O-CMC and the condition for preparing QCMC were different from literature.³⁵

Effect of pH on the removal ratio of COD with QCMC as flocculant

Effect of pH on the removal ratio of COD of printing wastewater was investigated on constant initial concentration of COD (760 mg L^{-1}) and amount of bio-flocculant (51.35 mg L^{-1}) with QCMC as flocculant. The results were shown in Figure 5.

The removal ratio of COD by QCMC increased rapidly with the increase of pH of wastewater at the beginning. When the pH was up to ca. 5.0, the removal ratio of COD reached to the maximum (ca. 68%), and thereafter, high pH did not favor for the removal of COD. These results suggested a "chemisorption" mechanism happened between QCMC and dyestuff. QCMC and dyestuff could exist in different form at different pH. In acidic solution, the carboxyl in the QCMC molecular chain existed in the form of $-\text{COOH}$ and the dyestuff existed in the form of cationic colloid, thus the ability of QCMC to remove the COD of printing wastewater mainly depended on the capacity of $-\text{COOH}$ and $-\text{OH}$ to combine with the dyestuff. On the contrary, the existence of $-\text{NH}_3^+$, $-\text{NH}_2^+$, and the quaternary ammonium group was unfavorable for QCMC to combine with these cationic colloid of dyestuff. When the pH was higher than 5.0, more of the carboxyl existed in the form of $-\text{CO}_2^-$ and the dyestuff existed in the form of anionic colloid, the ability of QCMC to remove the COD of printing wastewater mainly depended on the quaternary ammonium group and $-\text{OH}$ to combine with the anionic colloid of dyestuff. When the pH was ca. 5.0, QCMC was mainly existed in the form of amphoteric ion, so it could display a strong polarizing ability to the dyestuff that present in the printing wastewater and endow the flocculant with high-absorbing ability to the dyestuff colloid.

Effects of the type of flocculants on the removal ratio of COD

Effects of the type of flocculant on the removal of COD of printing wastewater were studied at constant initial COD concentration (760 mg L^{-1}), amount of flocculant (51.35 mg L^{-1}), and pH (5.0) with HTCC, PAM, N,O-CMC, QCMC, CTS, PAC, FeSO_4 , MgSO_4 , diatomite, and bentonite as flocculant, respectively. The results were shown in Table I.

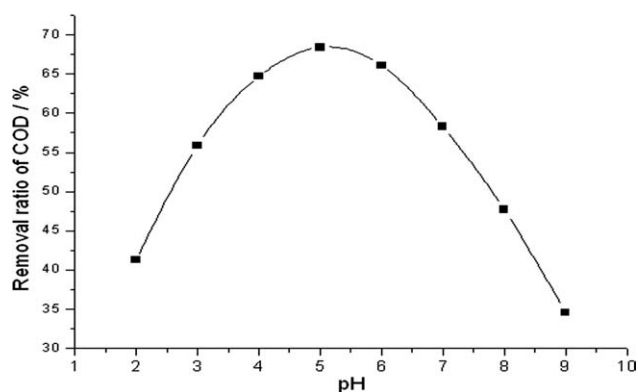


Figure 5 Relationship between pH and removal ratio of COD.

TABLE I
Removal Ratio of COD for Different Flocculant or Aid-Flocculant

Flocculant	COD value before treatment (mg L ⁻¹)	COD value after treatment (mg L ⁻¹)	Removal rate of COD (%)
CTS	760	427	43.8
N,O-CMC	760	363	52.3
HTCC	760	326	57.1
QCMC	760	239	68.5
PAC	760	504	33.7
PAM	760	416	45.2
FeSO ₄	760	695	8.5
MgSO ₄	760	720	5.3
Diatomite	760	729	4.1
Bentonite	760	717	5.7

The capacities of different flocculant to remove the COD of printing wastewater were in the descending order of QCMC > HTCC > N,O-CMC > CTS > PAM > PAC > FeSO₄ > bentonite > MgSO₄ > diatomite. PAC, FeSO₄, and MgSO₄ are typical inorganic compounds that could hydrolyze into hydrophilic colloid in aqueous solution, their removal capacities to the COD of printing wastewater were mainly depended on the absorption ability of the hydrophilic colloids to the dyestuff present in the tested wastewater. The organic property of bentonite endowed it with higher removal capacity to the COD than that of diatomite. PAM, CTS, N,O-CMC, HTCC, and QCMC could form hydrophilic organic colloids in aqueous solution, respectively. These organic colloids could provide with huge specific surface area, which was propitious for the absorption and removal of dyestuff. Meanwhile, the organic property of these hydrophilic colloids could improve their absorption ability to the dyestuff through their affinity. Furthermore, QCMC, HTCC, and N,O-CMC could exert additional electronic-static attraction and these actions were in the descending order of QCMC > HTCC > N,O-CMC. The presence of electronic-static attraction was favorable for the flocculant to adsorb the dyestuff colloid. Although the CTS could show some electronic-static attraction in weakly acidic solution (pH = 5.0), the low solubility resulted in less floccules existing in the wastewater and could not endow CTS with a good capacity to remove the dyestuff of printing wastewater.

Effect of flocculant dose on the removal ratio of COD

One of the parameters that strongly affect the flocculation capacity of bioflocculant was its concentration in the aqueous solution. The relation between the removal ratio of COD and the concentration of flocculant was studied by varying the concentration of

QCMC in wastewater from 12.93 mg L⁻¹ to 114.12 mg L⁻¹ while keeping the pH (5.0) and the initial COD concentration (764 mg L⁻¹) constant. The removal percentage of COD increased from 40.7% to 76.8% when the flocculant dose increased from 12.93 mg L⁻¹ to 89.19 mg L⁻¹ (Fig. 6). However, when the flocculant concentration surpassed 89.19 mg L⁻¹, the removal ratio of COD decreased with the increase of flocculant dose. The reasons were as follows: the increase of flocculant dose could result in much more floccules formed in the wastewater and this trend was favorable for the removal of dyestuff; but when the QCMC in wastewater surpassed a special concentration, the increase of COD resulted from the dissolution of flocculant would exceed the decrease of COD resulted from the removal of dyestuff in aqueous solution and this situation was unfavorable for the COD removal of printing wastewater.

Effect of the type of aid-flocculant on the flocculating capacity of QCMC

Effect of aid-flocculant types on the flocculating capacity to remove the COD of printing wastewater was studied at constant initial concentration of COD (762 mg L⁻¹), amount of flocculant (51.35 mg L⁻¹), pH (5.0), and $m_{\text{Assistant flocculant}}/m_{\text{QCMC}}$ (40.0) with FeSO₄, MgSO₄, diatomite, and bentonite as assistant flocculant, respectively. The results were shown in Table II.

Compared the data of Table II with that of Table I, it could be found that the capacity of QCMC to remove the COD of printing wastewater was improved by using aid-flocculant, and the bentonite improved this capacity more obviously. The reasons were as follows: (1) the use of assistant flocculant could improve the density of QCMC-dyestuff flocs unit and could result in the increase of its flocculation rate; (2) the bentonite possessed some organic property and this property could endow complex

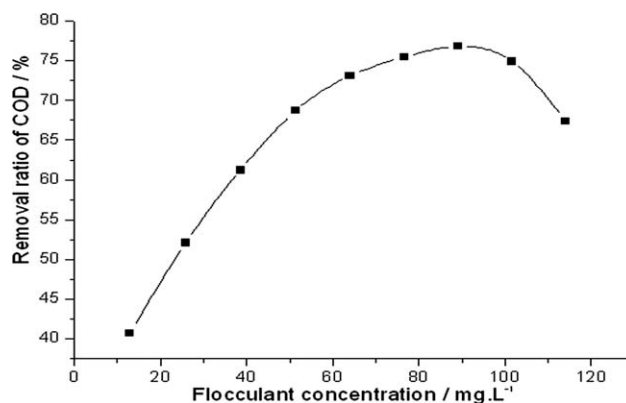


Figure 6 Relationship between the removal ratio of COD and flocculant concentration.

TABLE II
Influence of Type of Assistant Flocculant on the Ability of QCMC to Remove COD of Printing Wastewater

Assistant flocculant	COD value before treatment (mg/L)	COD value after treatment (mg/L)	Removal rate of COD (%)
FeSO ₄	762	216	71.6
MgSO ₄	762	226	70.3
Diatomite	762	187	75.4
Bentonite	762	174	77.2

flocculant with much better ability to combine with dyestuff than other aid-flocculants some extent.

Effect of $m_{\text{Bentonite}}/m_{\text{QCMC}}$ on the removal ratio of COD

Effect of $m_{\text{Bentonite}}/m_{\text{QCMC}}$ on the removal of COD of printing wastewater was studied at constant initial concentration of COD (762 mg L⁻¹), amount of flocculant (51.35 mg L⁻¹), and pH (5.0) with bentonite as aid-flocculant. Results indicated that the increase of aid-flocculant amount could improve the capacity of QCMC to remove the COD of printing wastewater (Fig. 7). The reason was concerned with the absorption ability of bentonite to the dyestuff present in printing wastewater and its ability to improve the flocculation rate of QCMC-dyestuff flocs unit. The increase of bentonite in the complex flocculant resulted in much more dyestuff was adsorbed on floccules of complex flocculant and the improvement of flocculation rate of flocculating colloid.

Effect of complex flocculant dose on the removal ratio of COD

Effect of complex flocculant dose on the COD removal with QCMC-bentonite as flocculant was studied by varying the amount of complex flocculant

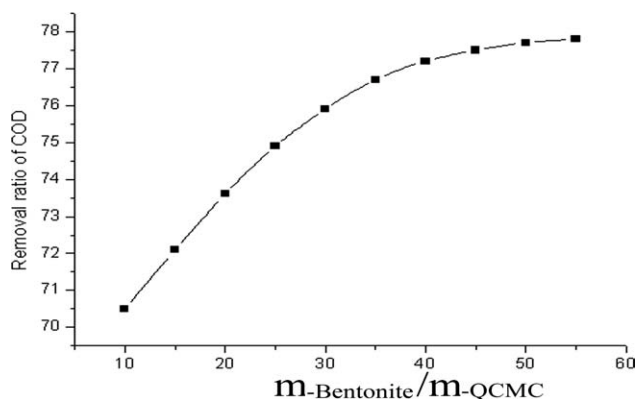


Figure 7 Relationship between the removal ratio of COD and $m_{\text{Bentonite}}/m_{\text{QCMC}}$.

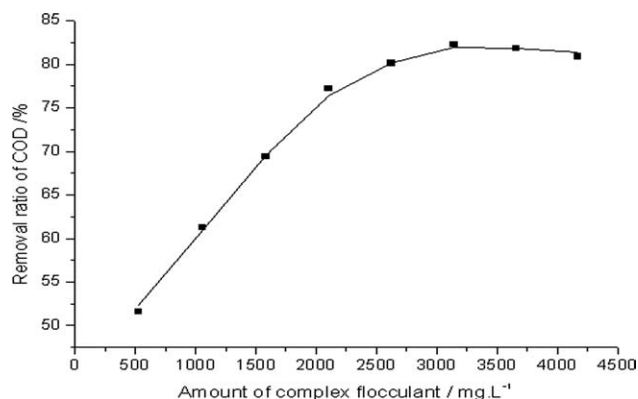


Figure 8 Relationship between removal ratio of COD and the complex flocculant dose.

from 530.1 to 4169 mg L⁻¹ while keeping the pH (5.0), the initial concentration of COD (764 mg/L) and $m_{\text{Bentonite}}/m_{\text{QCMC}}$ (40.0) constant. The removal percentage of COD increased from 51.67 to 82.3 when the complex flocculant dose increased from 530.1 to 3142 mg L⁻¹ (Fig. 8). However, the removal ratio of COD decreased with the increase of complex flocculant dose some extent when the complex flocculant concentration surpassed 3142 mg L⁻¹. The reasons were as follows: the increase of complex flocculant dose could provide much more floccules to combine with the dyestuff presented in the printing wastewater; but when the complex flocculant dose surpassed specifically value, the increase of COD resulted from the dissolving of QCMC in the complex flocculant exceeded the decrease of COD resulted from the removal of dyestuff by flocculation method, this situation was disadvantageous for taking the COD from printing wastewater.

CONCLUSIONS

QCMC was synthesized by the quaternization of N,O-CMC and was utilized as bioflocculant to treat printing wastewater. The capacity of QCMC to remove the COD of wastewater was better than that of HTCC, N,O-CMC, PAM, CTS, and PAC. The use of aid-flocculant, especially bentonite, could improve the flocculating capacity of QCMC, and the increase of bentonite in complex flocculant was favorable for this capacity. When $m_{\text{Bentonite}}/m_{\text{QCMC}}$ was 40, the pH of printing wastewater was 5.0 and the complex flocculant dose was from 2500 to 3142 mg L⁻¹, the removal ratio of COD of wastewater was more than 80%.

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