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Effect of hydrolysis degree of hydrolyzed polyacrylamide grafted carboxymethyl cellulose on dye removal efficiency

Tao Cai · Zhen Yang · Haijiang Li · Hu Yang · Aimin Li · Rongshi Cheng

Abstract In this present work, a series of hydrolyzed polyacrylamide grafted carboxymethyl cellulose (CMC-*g*-HPAM) was prepared. The structure and solution properties of CMC-*g*-HPAM were characterized by FTIR, ^{1}H-NMR, elemental analysis and zeta potential measurements. The graft copolymers were applied as flocculants to remove methylene blue (MB), a cationic dye, from aqueous solutions. In comparison with its precursors, carboxymethyl cellulose (CMC) and polyacrylamide CMC-*g*-PAM, CMC-*g*-HPAM exhibited higher removal efficiencies. Furthermore, the flocculation performance of the copolymers was significantly improved with the increase of the hydrolysis degree, and the MB removal efficiency was more than 90 % when the hydrolysis degree of CMC-*g*-HPAM was higher than 80 %. More importantly, image analysis in combination with fractal theory demonstrated that the graft copolymers could produce notably denser and larger flocs, which was of great significance in practical water treatment. The improved flocculation performance was ascribed to both charge neutralization and bridging effects.

Introduction

With the rapid development of modern industrial sections, such as dyeing, printing, textile, leather, and coating industries, the environmental pollution is becoming more and more serious, which has been drawn much attention. Dyes are the main pollutants in the sewage from the aforementioned industries (Crini 2006; Zahrim et al. 2011). It is estimated that more than 70,000 tons of dyes are discharged in the world every year. Dyes exert serious influences on the environment in two main aspects. On the one hand, they are highly visible and interfere with light penetration in the receiving water bodies thereby disturbing the biological processes. Many dyes degrade into compounds that are toxic and hazardous to mammals and aquatic organisms. On the other hand, most dyes are organic compounds of which the excess would increase the chemical oxygen demand (COD) of the water body (Beltran-Heredia et al. 2009; Zahrim et al. 2011). Among all these dyes, methylene blue (MB) is one of the most commonly used substances for dyeing cotton, wood and silk. MB can cause eye burn which is very harmful to human and animals.

T. Cai · H. Yang (✉) · A. Li
State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, People's Republic of China
e-mail: yanghu@nju.edu.cn

T. Cai · Z. Yang · H. Li · R. Cheng
School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

Even worse, MB can also increase heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, and tissue necrosis in humans (Tan et al. 2008; Vadivelan and Kumar 2005). Thus, removal of dyes from wastewater becomes a significant issue, and environmental regulations in many countries have made it mandatory before discharging wastewaters (Crini 2006; Mishra et al. 2006).

In recent years, various combined techniques, including flocculation, adsorption, filtration, oxidation, and electrolysis, have been developed to remove dyes from wastewaters (Beltran-Heredia et al. 2011; Dukkanci et al. 2010; Fang et al. 2010; Rafatullah et al. 2010; Sabah and Cengiz 2004). Therein, flocculation is one of the most widely applied methods in primary purification due to its low cost and easy operation (Bratby 2006; Hogg 2000). The choice of flocculants during a flocculation process is significant to the final effect. Until now, inorganic metal-based flocculants and synthetic polymeric ones are two of the most extensively applied flocculants. However, the increased concentration of metal ions of inorganic flocculants or residual noxious monomers in synthetic ones when these chemicals are used may have potential disadvantages to both ecosystem and human health (Bratby 2006; Hogg 2000; Li et al. 2005).

Nowadays, great attention has been paid to natural polymer based flocculants, since they are considered as wide-resourced, nontoxic, environment-friendly and high-efficient materials. They have been even acclaimed as "Green Flocculants of twenty-first Century" (Xiao and Zhou 2005). Among them, cellulose is one of the most important natural polymers, and the first most abundant one in the world (Gao and Tang 1996). In term of its novel characteristics, cellulose and its derivatives have a very wide application in many fields such as pharmaceutical, food, paper, and building material industries (Gao and Tang 1996; Klemm et al. 2005). In addition, cellulose also has good water purification effects because it has abundant free –OH groups on the chain, enabling efficient removal of metal ions and organic matters from water for excellent chelating effect. However, owing to poor water solubility and relatively low chemical reactivity, application of cellulose as a flocculant is always limited. To overcome those shortcomings, modified cellulose materials have been manufactured, and carboxymethylation is a conventional and useful method for chemical modification. Among them, carboxymethyl cellulose

(CMC) is the simplest one. After introducing the carboxyl group, not only the solubility of cellulose has been greatly improved for destroying the original ordered structure, but also the negative charges on CMC can enhance the electrostatic attraction with some cationic matters such as MB. Additionally, grafting copolymerization is also an efficient way for chemical modification. It is well known that polyacrylamide (PAM) is widely used in flocculation (Lee et al. 2011) and show high flocculation efficiency. PAM can produce dense flocs for bridging flocculation effect, which are usually favored in water treatment. Thus, grafting PAM onto CMC is more promising, since the tailored graft copolymers have combined the advantages of both (Sanghi et al. 2006; Yang et al. 2012).

Moreover, it has been widely accepted that floc properties also count much in the flocculation process in addition to impurity removal efficiency. Dense flocs are preferred in order to produce lower sludge volumes and reduce the disposal and handling cost. Previous work (Mandelbrot 1983; Yang et al. 2012) has proven that the irregular flocs can be treated as geometrically fractal objects. Consequently, fractal dimension, a powerful parameter in fractal theory, can be used to describe the compactness of flocs. Larger fractal dimension indicates denser flocs, and is favored in flocculation. According to the space dimension, fractal dimensions can be divided into several forms. One commonly applied fractal dimension is two-dimensional one (D_2) (Chakraborti et al. 2000; Yang et al. 2012), defined by the power law relationship between the projected area (A) and the characteristic length (l), which can be measured by image analysis (IA) (Chakraborti et al. 2000; Mandelbrot 1983; Yang et al. 2012).

In the current work, PAM was grafted onto CMC with ammonium persulfate as the initiator. In order to further improve the flocculation performance for removal of MB, a cationic dye, the graft copolymers were hydrolyzed under an alkaline condition (Song et al. 2011). By controlling the hydrolysis time, a series of hydrolyzed polyacrylamide grafted carboxymethyl cellulose (CMC-g-HPAM) with different degree of hydrolysis (DH) was obtained. The structure and solution properties of the final copolymers were characterized by Fourier transform infrared (FTIR), ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra, zeta potential (ZP) and elemental analysis measurements. The effect of hydrolysis degree on the MB removal efficiency was systematically evaluated.

Besides, the properties of flocs were especially investigated in detail combined with the fractal theory (Liao et al. 2006; Moghaddam et al. 2010).

Experimental

Materials

Carboxymethyl cellulose (CMC) was purchased from Sinopharm Chemical Reagent Co., Ltd. Its viscosity with the concentration of 20 g L^{-1} is 800–1,200 MPa·s at 25 °C and its weight-average molecular weight is 150,000 g mol^{-1}. The substitution degree of carboxyl group is approximately 68.69 %. Acrylamide (AM) (Nanjing Chemical Reagent Co., Ltd.), ammonium persulfate (Shanghai Lingfeng Chemical Reagent Co., Ltd.), MB (Tianjin Chemical Reagent research institute) were used without further purification. All other chemicals were purchased from Nanjing Chemical reagent Co. Ltd. Distilled water was used in all experiments.

Preparation of CMC-g-HPAM

A desired amount of solid CMC was dissolved in 100 mL distilled water. After 30 min of stirring under N$_2$, a certain amount of ammonium persulfate was added as the initiator. Before the dropwise addition of the acrylamide monomer aqueous solution, the CMC solution was kept for 5 min for pretreatment by the initiator to suppress the formation of the PAM homopolymer. The mass ratio between CMC and AM is 1:5. The reaction was carried out for 3 h under N$_2$. Then, the mixture was precipitated in acetone. The solid product was filtered and washed by ethanol, then extracted using acetone as the solvent in a Soxhlet apparatus for 48 h for removal of impurities (Ali and Singh 2009; da Silva et al. 2007) and finally vacuum dried at 60 °C. The obtained product was CMC-g-PAM, which had a PAM grafting ratio of 323 %, calculated by weighting method as shown below.

$$\text{Grafting ratio}(\%) = \frac{w_g - w_o}{w_o} \times 100\% \qquad (1)$$

where w_o and w_g are the weight of raw CMC and CMC-g-PAM, respectively. Then, a specific amount of CMC-g-PAM was added into 100 mL mixed solution containing ethanol and 3 mol L^{-1} sodium hydroxide aqueous solution (V$_{ethanol}$: V$_{NaOH}$ = 85:15).

The hydrolysis reaction was carried out at 55 °C. After finishing the reaction, the mixture was filtered. Then, the solid product was washed by a mixed solution of ethanol and water (V$_{ethanol}$: V$_{water}$ = 85:15) and finally vacuum dried at 60 °C. The detailed synthesis process of CMC-g-HPAM has been described in Scheme 1.

For preparation of various CMC-g-HPAM samples with different hydrolysis degree, various hydrolysis time for each reaction has been carried out, which was 10, 30 min, 1, 1.5, 3, 4, and 6 h, respectively. The final corresponding products were named CMC-g-HPAM1, CMC-g-HPAM2, CMC-g-HPAM3, CMC-g-HPAM4, CMC-g-HPAM5, CMC-g-HPAM6, and CMC-g-HPAM7, respectively. The hydrolysis degree of various CMC-g-HPAM samples was calculated according to Eq. (2) as shown below based on elemental analysis method.

$$DH(\%) = \frac{\omega_{CMC-g-PAM} - \omega_{CMC-g-HPAM}}{\omega_{CMC-g-PAM}} \times 100\%$$

$$(2)$$

where $\omega_{CMC\text{-}g\text{-}HPAM}$ and $\omega_{CMC\text{-}g\text{-}PAM}$ are the N/C ratio in CMC-g-HPAM and CMC-g-PAM, respectively, which were obtained from an elemental analyzer model of Elementar vario ELIII. The calculated DH of various samples including other details were all listed in Table 1.

Characterization

Fourier transform infrared (FTIR) spectra of various samples were recorded on a Bruker Model IFS 66/S FTIR spectrometer. The interval of measured wave numbers was 600–3,800 cm^{-1}.

^{1}H NMR spectra of different samples were carried out using a Bruker AVANCE Model DRX-500 spectrometer, operating at 500 MHz with D$_2$O as solvent.

ZP of various sample solutions was measured using a Malvern Model Nano-Z Zetasizer. Here, dilute hydrochloric acid and sodium hydroxide aqueous solutions were employed to adjust the pH of various solutions.

Flocculation experiment

A MB aqueous solution with concentration of 100 mg L^{-1} was employed as synthetic wastewater. After addition of a desired amount of flocculants as
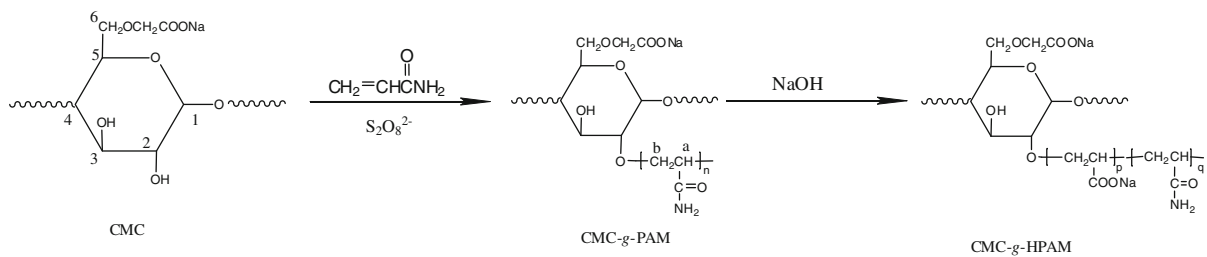
Scheme 1 Preparation process of hydrolyzed polyacrylamide grafted carboxymethyl cellulose

Table 1 Flocculation performance of various flocculants for removal of MB from aqueous solutions

Flocculants	Hydrolysis time (min)	DH (%)	Dosage$_{opt}$ (mg/L)[a]	Highest colour removal efficiency (%)	D_2[b]	R^2	Average l (μm)[b]
CMC	N/A	N/A	150	55.3	1.89	0.952	45.8
CMC-g-PAM	N/A	0	200	66.2	1.83	0.869	133
CMC-g-HPAM1	10	28.6	200	69.6	1.84	0.876	137
CMC-g-HPAM2	30	52.7	150	79.7	1.85	0.852	163
CMC-g-HPAM3	60	69.0	150	84.6	1.80	0.874	175
CMC-g-HPAM4	90	73.8	100	87.8	1.89	0.909	226
CMC-g-HPAM5	180	81.9	150	90.4	1.93	0.888	249
CMC-g-HPAM6	240	82.9	100	91.2	1.95	0.928	257
CMC-g-HPAM7	360	83.2	100	89.2	1.96	0.972	263

[a] Optimal dosage where the plateau of the high colour removal efficiency onsets

[b] At the highest colour removal efficiency

solid powder into 100 mL synthetic wastewater, the mixture was fast stirred at 200 rpm for 3 min, followed by a slowly stirring at 50 rpm for 10 min, and finally left to settle for 2 h. The supernatants were collected using a syringe and filtrated through a membrane with 0.45 μm pore diameter. An UV–visible spectrophotometry (Model UV-2401, Shimadzu Co.) was used to measure the concentration of residual dye in water. A calibration curve of MB was prepared in advance. The absorbance was measured at the wavelength of 662 nm. The colour removal efficiency was calculated as follows:

$$\text{Colour Removal Efficiency}(\%) = \frac{C_0 - C}{C_0} \times 100\,\%$$
(3)

where C_0 and C were the dye concentrations in the solution before and after flocculation, respectively (Yang et al. 2011).

Floc properties were measured by IA according to our previous work (Yang et al. 2012). After flocculation, the flocs were carefully withdrawn from the beakers and transferred into a glass dish. A Leica Model DMLP microscope equipped with a digital camera (Victor Company of Japan, Ltd.) was used to take photos. Then, A and l were derived from the photos using Image-pro® Plus 6.0. In this work, l was defined as the largest projection length and employed to evaluate the floc size. D_2 was obtained from the slope of the log–log plot of A and l (Chakraborti et al. 2000; Liao et al. 2006; Lin et al. 2008; Mandelbrot 1983).

$$A \propto l^{D_2}$$
(4)

where A is the projected area of flocs. For guaranteeing the reliability of the calculated D_2, more than 50 data points have been collected randomly in each plot.

Result and discussion

Characterization of the CMC-g-HPAM

The detailed preparation process of CMC-g-HPAM was described in experimental part and summarized in

Scheme 1. The FTIR spectra of CMC, homopolymer PAM, CMC-g-PAM and various CMC-g-HPAM samples were illustrated in Fig. 1. From Fig. 1a, the FTIR spectrum of CMC showed characteristic peaks of C = O around 1,590 cm^{-1} and hydroxyl groups on the glycosidic ring appeared around 3,300 cm^{-1}. As for the FTIR spectrum of CMC-g-PAM as shown in Fig. 1c, the overlapped peaks around 1,660 and 1,610 cm^{-1} were assigned to the amide I and II bands, respectively, and a shoulder peak appeared at 3,190 cm^{-1} was ascribed to N–H stretching vibration, which were both well consistent with those of PAM as shown in Fig. 1b. In addition, since the prepared samples were washed and extracted by acetone in the Soxhlet apparatus thoroughly, and the homopolymer of PAM, initiator, monomer and other unwanted residues have been successfully removed (Ali and Singh 2009; da Silva et al. 2007) the detected PAM chain should be chemically grafted on the backbone of cellulose chain. Furthermore, in comparison with the FTIR spectrum of CMC-g-PAM, those of various hydrolyzed CMC-g-PAM, CMC-g-HPAM, with different hydrolysis time in Fig. 1d–f, it was found that the intensity of the characteristic peak at 1,660 cm^{-1} due to C = O of amide group decreased whereas that at 1,560 cm^{-1} corresponding to C = O on carboxyl group increased with the increase of hydrolysis time. It was due to the fact that amide groups in graft PAM were consumed gradually and more carboxyl groups produced, which confirmed that the hydrolysis reaction occurred. Furthermore, the hydrolysis degree of
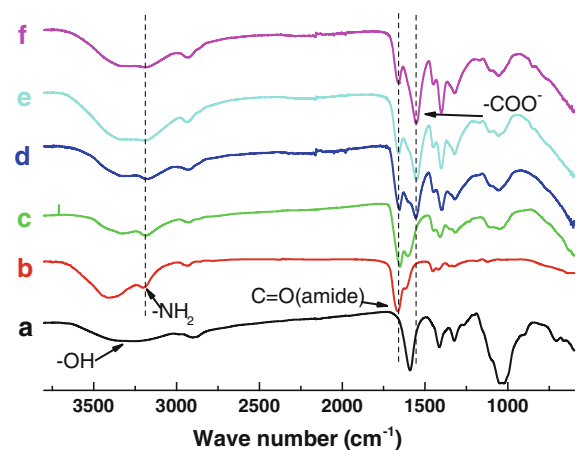
various CMC-g-HPAM samples was calculated according to Eq. (2) based on elemental analysis method and listed in Table 1. DH of hydrolyzed samples increased with increasing hydrolysis time and reached a plateau at approximately 3 h.

In addition, the ^{1}H NMR spectra of various samples as shown in Fig. 2 provided further evidences of the structure changes. The overlapped signals between 3.10 to 4.30 ppm in Fig. 2a were assigned to the protons H1–H6 on the glycosidic ring of carboxymethyl cellulose. The new intense peaks at around 1.58 and 2.14 ppm in Fig. 2b–f were corresponding to the characteristic signals of methylene (Hb) and methine (Ha) protons in the PAM chains (Yang et al. 2012) respectively. Moreover, the signals of CMC-g-HPAM as shown in Fig. 2d–f turned broader than those of CMC-g-PAM in Fig. 2c. It may be due to the fast spin–spin relaxation time (T_2) resulting from the fact that hydrolysis reaction has destroyed the regular structure of samples and chain segments are more mobile.

As for the detailed grafted point of hydrolyzed polyacrylamide in the final products, based on previous reported works (Guo et al. 2013; Wang et al. 2013), the grafted point of hydrolyzed polyacrylamide may be C2 or C3 on glucopiranose ring. Furthermore, since ammonium persulfate was applied as initiator here, the glucopiranose ring would not be broken during the grafting reaction. In addition, the C2–OH was on the axial bond while the C3–OH was on the
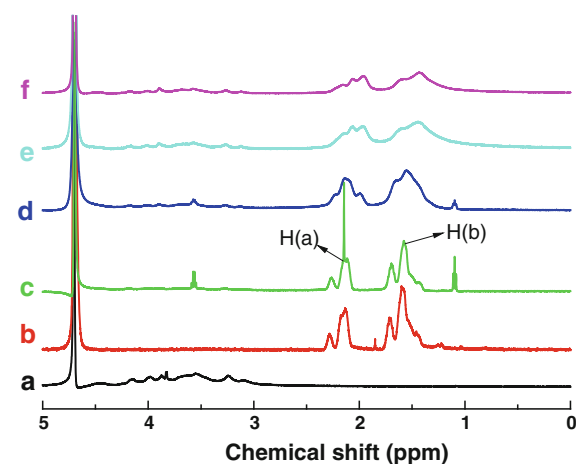

Fig. 1 FTIR spectra of various samples: a CMC; b PAM; c CMC-g-PAM; d CMC-g-HPAM2; e CMC-g-HPAM4; f CMC-g-HPAM6

Fig. 2 ^{1}H NMR spectra of various samples: a CMC; b PAM; c CMC-g-PAM; d CMC-g-HPAM2; e CMC-g-HPAM4; f CMC-g-HPAM6

equatorial bond, therefore C2 was more active than C3. So it could be inferred roughly that the grafting reaction has more probability to take place on C2. However, further experiments are very necessary for confirming the fine structure of the cellulose based flocculants.

In addition, it was well known that charge properties of ionic flocculants would affect the flocculation efficiency greatly (Wang et al. 2009). Hence, the pH dependences of ZP of various samples solutions were measured at the beginning and demonstrated in Fig. 3.

Based on Fig. 3, it was found that ZP of CMC was less negative than that of each CMC-*g*-HPAM but more than that of CMC-*g*-PAM. It was ascribed to the fact that more carboxyl groups were produced in the final products with the hydrolysis process, resulting in the decease of ZP. Furthermore, the ZPs of different CMC-*g*-HPAM samples decreased further when increasing the reaction time and hydrolysis degree. As for CMC-*g*-PAM, the non-ionic PAM branch chains would screen the charges on the CMC backbone and reduce the surface charge (Song et al. 2009). It was interesting to observe from Fig. 3 that, in the pH range from 8.0 to 13.0, ZP values of CMC-*g*-HPAM increased with the increase of pH. The reason for this trend could be explained as follows: Before pH at 8.0, more –COO⁻ groups were formed and thus the zeta potential decreased as the pH increased; then, at pH around 8.0 or 9.0, nearly all the carboxyl groups were deprotonized; after that, with pH increase further which need more NaOH, the ionic strength in solution increased greatly. Since the number of –COO⁻ has already reached saturation, the increased ionic
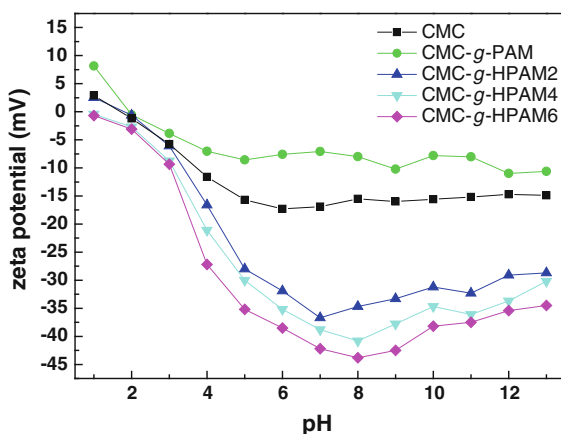
strength would compress electrical double layer of flocculants much more and the flocculants chains were surrounded with a growing number of sodium ions. As a result, zeta potential of flocculants increased and became close to zero.

Flocculation performance of CMC-*g*-HPAM

pH Effects on the optimal dosage and colour removal efficiency

Then, CMC-*g*-HPAM was employed as flocculants for removal of a cationic dye, MB, from aqueous solutions. Among numbers of external parameters which can affect the flocculation efficiency of ionic flocculants, pH was usually one of the most important ones (Sand et al. 2010). Thus, pH effects on the optimal dosage and colour removal efficiency of CMC-*g*-HPAM for flocculation of MB were studied and the results were summarized in Fig. 4. Here, dilute hydrochloric acid and sodium hydroxide aqueous solutions were employed to adjust the pH of various dye solutions.

As revealed in Fig. 4, under acidic condition, the required optimal dosages were relatively high but the corresponding colour removal efficiencies were relatively low. However, under alkaline condition, the situations were fully reversed and the flocculation performance of CMC-*g*-HPAM turned better with lower dosage required yet higher removal efficiencies. As was known, MB is a typical cationic dye and bear positive charge in aqueous solution. As for CMC-*g*-HPAM, the negative charges of flocculants were relatively weak at pH lower than 7.0 based on their ZP profiles as shown in Fig. 3, since most of carboxyl groups on the CMC-*g*-HPAM were protonized. As a consequence, the electrostatic attractions between flocculants and positively charged dye were not strong. Nevertheless, under alkaline condition, the carboxyl groups of flocculants were deprotonized and formed –COO⁻ groups, which is in favor of flocculation of MB by neutralizing effect.

Besides, it was found from Fig. 4 that the optimal pH for the removal of MB was pH at 9.0 instead of the highest one (pH = 11.0) in tested pH range. This phenomenon could be ascribed to two factors. On the one hand, the increased zeta potential of the flocculants as illustrated in Fig. 3 engendered weaker electrostatic attraction between the flocculants and
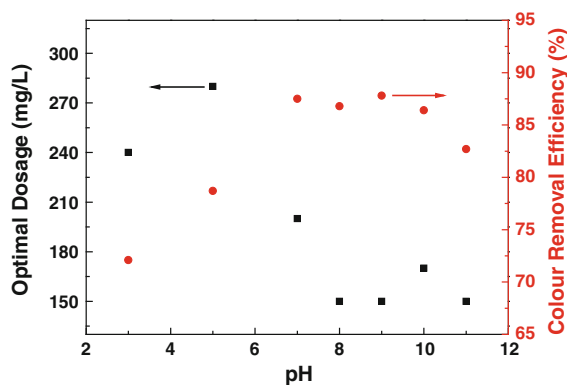

Fig. 3 Zeta potential–pH profiles of various samples

Fig. 4 The pH effects on optimal dosage and colour removal efficiency of CMC-*g*-HPAM4 at 25 °C and initial MB concentration of 100 mg/L

Fig. 5 The colour removal efficiency of different CMC based samples using various dosages at pH 9.0 and initial MB concentration of 100 mg/L

positively charged dye. On the other hand, large numbers of hydroxyl groups (OH⁻) at high pH surrounded the MB molecules tightly through charge attraction, which also prevented the attraction between CMC-*g*-HPAM and dye molecules and reduced the colour removal efficiency (Yang et al. 2013). Since the flocculant had the highest colour removal efficiency and the lowest dosage at pH 9.0, this optimal pH level was selected in further flocculation experiments.

Effect of the DH of the flocculants

Then, the flocculation performance of CMC, CMC-*g*-PAM and various CMC-*g*-HPAM samples for removal of MB was investigated at pH 9.0, and the results were all presented in Fig. 5. The detailed optimal dosages of various flocculants and their corresponding colour removal efficiency based on Fig. 5 were listed in Table 1.

From Fig. 5 and Table 1, the colour removal efficiency of CMC-*g*-PAM has been improved in a minor way but the optimal dosage was slightly increased in comparison with those of CMC. They were resultant from two opposite effects. On the one hand, the flexible PAM chains on the comb-like copolymer of CMC-*g*-PAM enhanced the probability of netting and seizing more MB molecules around from aqueous solutions, which engendered better flocculation performance. On the other hand, the surface charge on the flocculants has been partially screened after PAM chains grafting onto CMC backbone according to its ZP profile as shown in
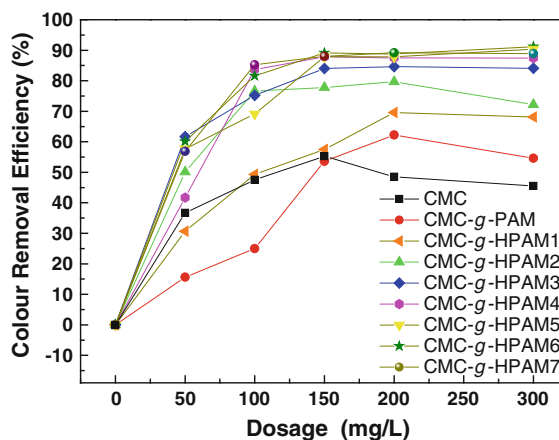
Fig. 3, which reduced the charge neutralization flocculation effects. Therefore, more flocculants were required.

Then, it was also found from Fig. 5 and Table 1 that various CMC-*g*-HPAM samples all showed better flocculation performance for removal of dye from aqueous solutions than their two precursors, CMC and CMC-g-PAM. Most of CMC-*g*-HPAM had higher colour removal efficiency but lower optimal dosage. It was ascribed to more carboxyl groups and active flocculation sites on the flocculants, which also further confirmed that charge neutralization effect was the main flocculation mechanism in this case. However, it was interesting that the colour removal efficiency of each CMC-*g*-HPAM as shown in Fig. 5 all increased with increasing dosage and then reached a plateau at its optimal dosage, but did not decreased with the increase of dosage further. As was known, the colour removal efficiency-dosage profiles always showed an up-climax-down trend, when the flocculation process was controlled only by charge neutralization mechanism (Ghimici et al. 2010; Ghimici and Nichifor 2010; Yang et al. 2011). The up-plateau trend and wider flocculation window of CMC-*g*-HPAM in current system as shown in Fig. 5 revealed that bridging flocculation effect had also much contribution to the dye removal besides charge neutralization effect, since numerous grafted HPAM chains were on the CMC backbone.

Furthermore, the flocculation performance of CMC-*g*-HPAM has been improved significantly with

increasing hydrolysis time and hydrolysis degree based on Fig. 5 and Table 1. According to Fig. 5, the dependence of the hydrolysis degree on the colour removal efficiency after reaching flocculation equilibrium has been summarized in Fig. 6. It was obvious that the colour removal efficiency increased linearly with hydrolysis degree increased. When the hydrolysis degree of CMC-*g*-HPAM was higher than 80 %, the colour removal efficiency was larger than 90 %. The enhanced flocculation performance was ascribed to the hydrolysis effect and production of more carboxyl groups and active flocculation sites on the graft chain. On the one hand, the carboxyl groups were mainly deprotonized and existed as carboxyl anions at pH 9.0, and the increased negative charges on the flocculants made the electrostatic attraction forces between CMC-*g*-HPAM and MB stronger. As a result, charge neutralization flocculation effect was distinctly improved. On the other hand, the side HPAM chains with increased negative charge would result in a more extended morphology due to the intra-molecular electrostatic repulsion, which further enlarged the probability of getting close to free MB in wastewater. Therefore, the bridging flocculation effect has been also improved. In terms of the cooperative effects of the aforementioned two flocculation mechanisms (Rasteiro et al. 2008), better flocculation performance of CMC-*g*-HPAM was obtained.

In addition, the flocculation performance of CMC-*g*-HPAM would be beneficial to higher hydrolysis degree. It was also found that the hydrolysis degree
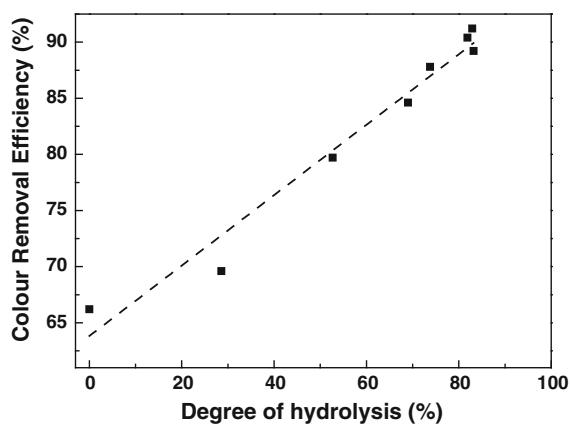
would reach a plateau at hydrolysis time around 3 h according to Table 1. Therefore, the hydrolysis process should be controlled within 3 h for better flocculation performance and saving energy.

Floc properties

Besides flocculation efficiency, floc properties are also very important in real water treatment, and larger and denser flocs are usually preferred for reducing the cost of disposal of and handling the sludge, as mentioned above. Hence, the flocs properties, including floc size (*l*) and D_2, under each optimal condition were also measured through IA method, which were listed in Table 1 too. In this work, *l* was defined as the largest floc length and employed to evaluate the floc size. D_2 was obtained from the slope of the log–log plot of *A* and *l* (Chakraborti et al. 2000; Liao et al. 2006; Lin et al. 2008; Mandelbrot 1983). Although the values of the determination coefficient R^2 were not quite close to 1.0 based on Table 1, D_2 were still very reliable. Because more than 50 data points have been collected randomly in every plot.

From Table 1, the flocs size turned much larger after PAM chains grafted, and the average *l* of flocs by CMC-*g*-PAM was near three times of that by CMC. Furthermore, the hydrolyzed graft copolymer flocculants would produce even larger flocs than CMC-*g*-PAM, and the size of flocs increased with increasing hydrolysis degree. The larger size of flocs produced by CMC-*g*-HPAM was due to the enhanced bridging flocculation effect resulting from more extended morphology of flocculants for the intra-molecular electrostatic repulsion of the charged hydrolyzed PAM graft chain.

In addition to flocs size, the flocs by CMC-*g*-HPAM with higher DH also had denser structure with larger D_2. When the hydrolysis degree was higher than 80 %, D_2 of the flocs by CMC-*g*-HPAM was more than 1.9 and very near to 2.0, the largest value in theory, which indicated higher strength of flocs and stronger charge attraction between flocculants and dyes. However, CMC could also produce flocs with higher D_2, which may be due to higher charge density on the backbone of CMC or certain efficient attraction way with MB.

Anyway, the flocs with larger size and compacted structure produced by CMC-*g*-HPAM would be beneficial for rapid separation and low handling cost, which further indicated that CMC-*g*-HPAM was a kind of efficient flocculants.

Fig. 6 The effect of hydrolysis degree on the colour removal efficiency after reaching flocculation equilibrium based on Fig. 5

Conclusion

In this work, a kind of novel flocculants, CMC-*g*-HPAM, has been prepared successfully by hydrolysis of PAM grafted carboxymethyl cellulose under strong alkaline condition. In comparison with its precursors, CMC and CMC-*g*-PAM, CMC-*g*-HPAM exhibited much better flocculation performance for removal of MB, a cationic dye, from aqueous solutions, i.e., remarkably higher colour removal efficiency and considerably larger and denser flocs. Investigation of pH effect indicated that higher dye removal efficiency would take place at alkaline conditions. Furthermore, the flocculation performance of CMC-*g*-HPAM has been improved significantly with increasing hydrolysis time and hydrolysis degree. Based on experimental results, hydrolysis time was better controlled in 3 h. The final improved flocculation performance of CMC-*g*-HPAM was ascribed to the cooperative effects of the charge neutralization and bridging flocculation mechanisms. Above all, CMC-*g*-HPAM could be regarded as a kind of cost-efficient flocculants in future water treatment work.

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