Enhanced coagulation of titanium tetrachloride aided by the modified compound bioflocculant

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Abstract

The compound bioflocculant (CBF) was modified by graft copolymerization of acrylic amide and dimethyl diallyl ammonium chloride, and the novel copolymer was denoted as MCBF. The effect of MCBF used as coagulant aid with titanium tetrachloride ($TiCl_4$) was investigated for both high and low molecule weight natural organic matter (NOM) removal. Floc characteristics were studied using a laser diffraction particle sizing device. Results indicated that the monomers were successfully grafted onto the CBF, and the molecule weight and zeta potential of CBF were greatly improved. The MCBF with $TiCl_4$ exhibited synergistic effect by promoting NOM removal, especially at low $TiCl_4$ doses. Additionally, using MCBF as coagulant aid with $TiCl_4$ can significantly increase the floc growth rate, size, strength and broken-floc recoverability. The effect of MCBF on fractal dimension of flocs generated by $TiCl_4$ depended on NOM properties. Both coagulation performance and floc properties were significantly affected by dosing sequence.

Keywords: Titanium tetrachloride; Compound bioflocculant; Floc strength; Floc regrowth; Fractal dimension

Introduction

Natural organic matter (NOM) is a diverse mixture of organic compounds with varying molecule weight and chemical nature including fulvic acid (FA) with low molecule weight and humic acid (HA) with relatively high molecule weight (Kabsch-Korbutowicz, 2005). They cause odor, taste, color and bacterial regrowth in potable water, and have potential to form carcinogenic disinfection-byproducts (DBPs)

(Hu, Liu, Qu, Wang and Ru, 2006). Effective removal of NOM in water has become increasingly important in modern water treatment. Coagulation-flocculation has been the most common process to remove NOM and particles in drinking water, seawater and wastewater (Jarvis, Jefferson and Parsons, 2005). Recently, titanium tetrachloride ($TiCl_4$) receives wide attention, because it is not only can be used as an effective coagulant, but also the flocculated sludge could be recycled to produce valuable by-product named titanium dioxide (TiO_2) by calcination (Shon, Vigneswaran, Kandasamy, Zareie, Kim, Cho and Kim, 2009, Shon, Vigneswaran, Kim, Cho, Kim, Kim and Kim, 2007). Therefore, using $TiCl_4$ as a coagulant offers a novel solution to sludge disposal associated with production of TiO_2 with a wide range of environmental applications. Bioflocculant also has drawn great attention, due to its significant advantages over traditional flocculant, such as biodegradability, safety to human beings and minimum second contamination, for future coagulant applications in water treatment (Salehizadeh and Shojaosadati, 2001). It is expected to become an alternative for conventional coagulants.

However, there are disadvantages with both $TiCl_4$ and CBF. The pH value of the supernatant after optimum $TiCl_4$ coagulation was much lower (pH 3.25-5) than those of conventional Al and Fe salts coagulation (Shon, Vigneswaran, Kim, Cho, Kim, Kim and Kim, 2007, Zhao, Gao, Shon, Cao and Kim, 2011). The effluent reuse was negatively affected by the low pH. For the bioflocculants, none of them has been used into practical applications until now because of the low flocculating capacity, low yields and high production cost. To overcome these limitations, numerous researchers have carried out screening of highly efficient strains and optimization of the bioflocculant culture conditions (He, Li, Chen and Lun, 2002). Meanwhile, dual coagulants e.g., bioflocculant used in combination with inorganic coagulants, are investigated as a cost reduction method. They not only reduce the dosage of bioflocculant, but also enhance the coagulation performance. Moreover, the risk raised from the chemical flocculants can be reduced due to relatively less dosage added. Zhao et al., (Zhao, Gao, Shon, Wang, Kim, Yue and Bo, 2012) have investigated the coagulation of compound bioflocculant (CBF) used as coagulant aid with $TiCl_4$, with the results indicating that coagulation performance could be improved with reduced $TiCl_4$ and CBF doses. However, CBF addition significantly decreased the floc size and floc growth rate because of its high negative charge. Thus, changing the surface charge of CBF to facilitate the coagulation performance will be promising. Graft copolymerization is a technique for modifying the chemical and physical properties of natural and synthetic polymers. Many workers have carried out grafting reactions of acrylic amide (AM) or dimethyl diallyl ammonium chloride (DMDAAC) onto starch, sodium alginate etc. (Tripathy, Pandey, Karmakar, Bhagat and Singh, 1999, Zhang, 2010), but the grafting of AM and DMDAAAC onto CBF is rarely reported.

The aims of this study were to i) modify CBF using AM and DMDAAC (define the copolymer as MCBF), ii) evaluate the coagulation performance of MCBF used as coagulant aid with $TiCl_4$ for both high and low molecule weight NOM removal, and iii) investigate the effect of MCBF on floc properties in terms of floc size, floc growth rate, floc strength, recoverability and the fractal dimension. Coagulation performance and floc characteristics of $TiCl_4$ and MCBF were analyzed for comparison. The coagulation mechanisms were also discussed in detail based on coagulation performance, floc properties and floc zeta potential measurement.

Experimental

Materials

$TiCl_4$ stock solution (20%, density = 1.150 g/ml) was obtained from Photo & Environment Technology Co. Ltd (South Korea). CBF was obtained from State Key Lab of Urban Water Resource and Environment, Harbin Institute of Technology, China. The CBF used in this study is mainly composed of polysaccharide (90.6%) and protein (9.3%) (Wang, Ma, Yue and Wang, 2008). Zeta potential of CBF was ca. -46.0 mV. CBF contains carboxyl, which is determined by Infrared spectra. Distributing of molecular weight of purified CBF is from 10^5 to 10^6, which is determined by gelatin chromatogram (Ma, Zhang, Yuan, Wang, Wang and Wang, 2005).

Modification of CBF

The CBF (1.0 g), together with 30 mL deionized water, was added into a four-necked flash, equipped with a stirring apparatus. The solution was stirred constantly with a slow stream of nitrogen on for about 15 min under water bath condition of 50 ℃. Then, various amounts of $K_2S_2O_8$ and Na_2SO_3 dispersed in moderate amount of deionized water were added into the solution to initiate the modification reaction with nitrogen on for further 15 min. The predetermined amount of AM and DMDAAC were added later. Finally, after 3 h of reaction, the resulting product was dewatered with alcohol after cooling to room temperature. The precipitates was filtered and dried at 50 ℃ for 5 h in a vacuum drying oven, and the product was MCBF. In this study, taking into account of AM and DMDAAC cost together with coagulation performance of MCBF, the mass ratio of CBF, AM and DMDAAC was set as 1:2:1 and the mole ratio of $K_2S_2O_8$ and Na_2SO_3 was 1:1. The mass of $K_2S_2O_8$ accounted for 0.6% of monomer mass.

Characterization of MCBF

MCBF was characterized in terms of Fourier transform infrared (FTIR) spectrum, zeta potential and molecule weight. FTIR spectrum was obtained on a NEXUS-470 series FTIR spectrometer (Thermo nicolet, NEXUS). The samples were taken into KBr pellets. Zeta potential and molecule weight of MCBF was respectively obtained by waters 1515 gel chromatography apparatus (Waters, US) and Zetasizer 3000HSa (Malvern, UK). MCBF solutions (about 1.0 mg/L) must be filtered through 0.22 μm filter membrane before molecule weight analysis, while zeta potential was directly measured without any pretreatment. CBF was also characterized for reference.

Test water and jar-test

Coagulation experiments were performed using i) humic acid (HA) simulated water containing HA as model NOM, and ii) fluvic acid (FA) simulated water containing FA as model NOM. Standard jar tests were conducted using a programmable jar-tester. Details about the experimental procedures and characteristics of the water samples are described in S1 of the Supplementary Data.

Floc growth, breakage and regrowth

The dynamic change of floc size was measured using Malvern Mastersizer 2000, UK. The floc size is expressed as an equivalent volumetric diameter d_{50}, which refers to the 50 % floc size was selected as the representative floc size.

The slope of rapid growth region was used to evaluate the floc growth rate during floc growth phase (Xiao, Yi, Pan, Zhang and Lee, 2010):

$$\text{Growth rate} = \frac{\Delta size}{\Delta time} \tag{1}$$

After 10 min of floc growth phase (40 rpm), the aggregated flocs were exposed to shear force (200 rpm) for 5 min, and then slow mixing (40 rpm) was reintroduced for a further 10 min. Floc strength factor (S_f) and recovery factor (R_f) are used to compare the relative breakage and regrowth of flocs in different flocculated systems and are calculated as follows (Jarvis, Jefferson and Parsons, 2005, Yukselen and Gregory, 2004):

$$S_f = \frac{d_2}{d_1} \times 100 \tag{2}$$

$$R_f = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \tag{3}$$

where d_1 is the average floc size of the plateau before breakage, d_2 is the floc size after floc breakage period, and d_3 is the floc size after regrowth to the new plateau. The larger values indicate the existence of the stronger flocs, and the flocs with larger recovery factors show better recoverability after high shear force.

Floc fractal dimension

Details in the theory of the mass fractal dimension have been reported in a few literatures (McCurdy, Carlson and Gregory, 2004, Guan, Waite and Amal, 1998). The light scattering technique involves measurement of light intensity I as a function of the scatter vector Q. The vector is defined as the difference between the incident and scattered wave vectors of the radiation beam in the medium (Guan, Waite and Amal, 1998):

$$Q = \frac{4n\pi \sin(\theta/2)}{\lambda} \tag{4}$$

where n, θ, and λ are the refractive index of the medium, the scattered angle, and the wavelength of radiation in vacuum, respectively

For independently scattering aggregates, the relationship among I, Q and the fractal dimension D_f can be represented by Eq. (5) (Rieker, Hindermann-Bischoff and Ehrburger-Dolle, 2000):

$$I \propto Q^{-Df} \tag{5}$$

D_f is the fractal dimension and can be determined by the slope of a plot of I as a function of Q on a log–log scale. High D_f means the primary particles in an aggregate are arranged compactly, while low D_f results from highly branched and loosely bound structure.

Results and discussion

Characterization of MCBF

FTIR spectroscopic analysis

According to the FTIR spectra of CBF and MCBF as shown in Fig. 1, the adsorption was observed at 3412.08 cm^{-1} and 3383.45 cm^{-1} (hydroxyl stretch influenced by hydrogen bond), 2926.46 cm^{-1} and 2929.39 cm^{-1} (methylene), and, 1081.43 cm^{-1} and 1121.31 cm^{-1} (b-1, 4-glycosidic bond) (Liu, Miao, Wang and Yin, 2009). For MCBF, the stretching vibration adsorption at 3192.79 cm^{-1} for the NH_2 group and at 1350.37

cm^{-1}, 1417.84 cm^{-1} and 1454.78 cm^{-1} for the C-N group can be observed, which did not appear in the FTIR spectrum of CBF. These differences support the grafting of AM and DMDAAC onto CBF and this would be beneficial for the formation of macromolecule, where CBF was the main framework.

Molecular weight and zeta potential

The molecular weight of MCBF was approximately 144k Da and that of CBF was only 1.3k Da, indicating that graft of AM and DMDAAC onto CBF promoted the chain propagation. Additionally, zeta potential of MCBF was +15.0 mV, which was dramatically improved as compared with that of CBF (-46 mV). This result visualized the enormous change of charge on CBF surface by the graft copolymerization of monomers.

Coagulation efficiency by MCBF

Our previous research (Zhao, Gao, Shon, Wang, Kim, Yue and Bo, 2012) showed that particle and NOM removal were barely observed when CBF was used alone, which could be ascribed to the particle repulsion among particles since both NOM and HA were negatively charged. The CBF molecule bridging ability also presented no beneficial effect on NOM removal due to the low molecular weight of CBF. After graft copolymerization, the MCBF coagulant was expected to be effective for water purification since both the molecular weight and zeta potential were significantly improved as aforesaid.

Standard jar tests were conducted to investigate the performance of coagulation by MCBF for both HA and FA simulated water treatment and the results are shown in S2 of the Supplementary Data. In case of HA removal, residual turbidity increased gradually with the increasing MCBF dose, which was accompanied by the increase in both UV_{254} and DOC removal, reaching the plateau value of 75.5±1.0% and 49.0±2%, respectively. Floc zeta potential increased from -15.0 mV to -3.8 mV within the dose range investigated, indicating that charge neutralization played an important role for HA removal. Similar trend was observed for FA removal, while MCBF was less effective for low molecular weight NOM removal as reflected by lower UV_{278} and DOC removal (30% and 5%, respectively) than in case of HA removal. Sweep flocculation was assumed to be the predominant mechanism for FA removal as indicated by slight increase in floc zeta potential with increasing MCBF dose.

As aforementioned, both HA and FA can be removed by MCBF but with low removal efficiency. Moreover, the residual turbidity increased with the increasing MCBF dose, which may be attributed to the fine flocs (data not shown) formed during coagulation process. The cost of MCBF production was another reason to limit the wide application of MCBF as coagulant. Using MCBF as coagulant aid would be a promising way for its further application, since previous research reported that better coagulation performance can be achieved when a polymer coagulant aid is used in combination with a commonly-used coagulant (Chang, Chiang, Tang, Chao and Hsing, 2005). Meanwhile, the MCBF production cost can be reduced due to relatively less dosage added. Details about the application of MCBF as coagulant aid will be discussed in the following sections.

Coagulation efficiency with $TiCl_4$ aided by MCBF

The effect of MCBF on coagulation efficiency

Fig. 2 and 3 present the effect of MCBF used as coagulant aid with $TiCl_4$ for both HA and FA removal. Coagulation performance was significantly influenced by both MCBF dose and dosing sequence of the dual-coagulants.

In case of HA simulated water treatment, MCBF of 1.0 mg/L favored turbidity removal at low $TiCl_4$ doses for $TiCl_4$-MCBF dual-coagulants, while it was not the case for MCBF-$TiCl_4$ dual-coagulants and residual turbidity showed obvious increase by the addition of 1.0 mg/L MCBF (Fig. 2 (a)). The UV_{254} removal was enhanced by MCBF addition as shown in Fig. 2 (b), especially at low $TiCl_4$ doses. However, DOC removal decreased to different degrees with MCBF addition except at the $TiCl_4$ dose of 5 mg/L, where it was improved to different degrees by MCBF addition. In case of the $TiCl_4$-MCBF dual-coagulants, MCBF of 1.0 mg/L improved the UV_{254} removal from 35.3% and 74.0% to 76.6% and 87.5%, respectively at $TiCl_4$ dose of 5 and 8 mg/L. The DOC removal was decreased by 2%~7% within the $TiCl_4$ dose range studied.

In case of FA simulated water treatment, the dual-coagulants had no superior advantage over $TiCl_4$ alone in terms of turbidity removal. The response of UV_{278} removal to MCBF addition was similar as that of UV_{254} in case of HA removal and the UV_{278} removal was more enhanced by MCBF at low $TiCl_4$ doses than at higher ones. As shown in Fig. 3 (c), MCBF of 1.0 mg/L improved the DOC removal regardless of the dosing sequence, while MCBF of 2.0 mg/L decreased the DOC removal, especially with MCBF-$TiCl_4$ dual-coagulants.

Both HA and FA removal can be improved by MCBF addition, however the dose of MCBF as coagulant aid should be optimized as high or low doses from the optimum dose would deteriorate the coagulation efficiency. Low MCBF dose meant no strong enough charge neutralization ability to destabilize the pollutants and no enough molecules to adsorb and then bridge the aggregates. High MCBF dose may result in the decrease of DOC removal, since MCBF is essentially a kind of organic matter. This may be the considerable reason for the decrease in DOC removal when CBF was overdosed. Same observation was previously reported in the flocculation of kaolin particles by bioflocculants (Wang, Tang and Gregory, 2002).

The effect of MCBF on floc zeta potential

Fig. 2 (d) and Fig. 3 (d) show the variation of floc zeta potential as a function of coagulant dose with different coagulants for HA and FA simulated water treatment. Changes in floc zeta potential are generally regarded as an effective tool to investigate coagulation mechanism, which is often expressed in terms of charge neutralization and sweep flocculation (Gregory and Duan, 2001). When charge neutralization is the only mechanism involved during coagulation process, the floc zeta potential should be in excellent correlation with coagulant dose and the optimum coagulation efficiency should be achieved when floc zeta potential was close to zero (Pefferkorn, 2006). The $TiCl_4$ coagulant only gave slight increase in floc zeta potential with coagulant dose, and the floc zeta potential was still negative within the dose range investigated, implying that charge neutralization was very weak for $TiCl_4$ and thus sweep flocculation was possible dominant mechanism for $TiCl_4$ coagulation. This is consistent with previous studies by Zhao et al. (Zhao, Gao, Shon, Cao and Kim, 2011, Zhao, Gao, Cao, Yang, Yue, Shon and Kim, 2011).

In case of dual-coagulants, the floc zeta potential after $TiCl_4$-MCBF coagulation showed significant increase with increasing $TiCl_4$ dose and CBF dose, while MCBF-$TiCl_4$ gave nearly similar floc zeta potential as $TiCl_4$. Additionally, zeta potential of flocs after $TiCl_4$-MCBF coagulation was higher than that after MCBF-$TiCl_4$ coagulation. When $TiCl_4$ was dosed firstly, the negatively charged HA and FA molecules reacted with the hydrolyzates of $TiCl_4$, producing the negatively charged $Ti(OH)_x^{(4-x)+}$-HA/FA complex (XU, GONG and QIN, 2009, Zhao, Gao, Rong, Shon, Kim, Yue and Wang, 2011). When positively charged MCBF was dosed, charge neutralize occurred between the $Ti(OH)_x^{(4-x)+}$-HA/FA complex and MCBF, which resulted in the high zeta potential of flocs formed by $TiCl_4$-MCBF coagulants. For HA simulated water treatment, the floc zeta potential increased sharply with $TiCl_4$ dose when 1.0 mg/L MCBF was used as coagulant aid, reaching nearly the isoelectric point at $TiCl_4$ dose of 20 mg/L. Similar phenomenon was observed for FA simulated water treatment, where the floc zeta potential reached isoelectric point at $TiCl_4$ dose of 35 mg/L when 2.0 mg/L of MCBF was used as coagulant aid. Charge neutralization was therefore concluded to be the predominant coagulation mechanism for $TiCl_4$-MCBF coagulation. When MCBF was dosed firstly, similar floc zeta potential was observed as compared with that by $TiCl_4$, from which it can be concluded that the later $TiCl_4$ addition had slight influence on the surface charge of the microflocs formed by MCBF. The negatively charged HA or FA may be partly neutralized by MCBF firstly, and then as the addition of $TiCl_4$, the HA or FA may be further removed by two ways: one is neutralization between the hydrolyzed Ti species and the residual HA or FA molecules; another is adsorption and bridging between $TiCl_4$ hydrolyzates and MCBF-HA/FA flocs or HA/FA molecules. For both HA and FA simulated water treatment, the flocs formed by MCBF-$TiCl_4$ were negatively charged, indicating that HA and FA was mainly removed by sweep flocculation rather than charge neutralization.

MCBF effect on floc characterization

The MCBF concentration of 1.0 mg/L was selected as coagulant aid with $TiCl_4$ to investigate the effect of MCBF on floc characteristics for both HA and FA simulated water treatment. Floc growth, breakage and re-formation with different coagulants were in-line monitored by using Mastersizer 2000 and the flocs were characterized in terms of floc growth rate, size, strength, recoverability and fractal dimension.

Floc growth rate and floc size

Fig. 4 shows the variation of floc growth rate as a function of coagulant dose with different coagulants for both HA and FA simulated water treatment. In general, the floc growth rate increased with the increasing coagulant dose and was significantly influenced by dosing sequence of the dual-coagulants. Irrespective of HA or FA simulated water treatment, the $TiCl_4$-MCBF coagulants improved the floc growth rate as compared with the $TiCl_4$ alone. The MCBF-$TiCl_4$ coagulants yielded comparable floc growth rate with $TiCl_4$ alone in case of FA simulated water treatment, while the increase or decrease in floc growth rate depended on coagulant dose in case of HA simulated water treatment.

Fig. 5 presents the change in floc size vs. coagulant dose with different coagulants before floc breakage, after breakage and regrowth. In case of HA simulated water treatment, the floc size was greatly improved by the addition of MCBF and was significantly affected by dosing sequence of the dual-coagulants (Fig. 5 (a)). The floc size d_1, d_2 and d_3 all followed the order of $TiCl_4$-MCBF > MCBF-$TiCl_4$ > $TiCl_4$ except the condition at $TiCl_4$ dose of 5 mg/L, where d_2 and d_3 were in the order of MCBF-$TiCl_4$ > $TiCl_4$-MCBF > $TiCl_4$. For MCBF-$TiCl_4$, the positively charged MCBF reacted with the negatively charged HA molecules completely through charge neutralization, forming the HA-MCBF microflocs. At the low $TiCl_4$ dose of 5 mg/L, the hydrolyzates were supposed to react with the HA-MCBF microflocs through complete charge neutralization. For $TiCl_4$-MCBF, the negatively charged HA molecules reacted with the positively charged hydrolyzates of $TiCl_4$ first, and then, the formed microflocs aggregated to form larger flocs through sweep flocculation of MCBF due to its chain structure. Since the flocs formed by charge neutralization are inclined to be more stable and have better recoverability after floc breakage, the flocs formed at $TiCl_4$ dose of 5 mg/L have larger d_2 and d_3 size (Yu, Li, Xu and Yang, 2009). With the increasing $TiCl_4$ dose, the hydrolyzates of $TiCl_4$ are assumed to be composed of polymers with high sweep flocculation ability. This may be the main reason that the floc size d_2 and d_3 followed the order of $TiCl_4$-MCBF > MCBF-$TiCl_4$. In case of FA simulated water treatment, the $TiCl_4$-MCBF coagulants had superior advantage over $TiCl_4$ in terms of floc size d_1, d_2 and d_3, while size of the flocs formed by

MCBF-$TiCl_4$ was improved or decreased to different degrees depending on $TiCl_4$ dose (Fig. 5 (b)).

The variation of floc growth rate and floc size with different coagulants was traditionally explained in terms of different coagulation mechanisms. In this study, both HA and FA removal were obtained while the resultant flocs were still negatively charged regardless of the coagulant used, indicating that sweep flocculation played vital role for coagulation. However, for both HA and FA simulated water treatment, the $TiCl_4$-MCBF coagulants had higher charge neutralization ability compared to $TiCl_4$ and MCBF-$TiCl_4$, as reflected by the higher floc zeta potential (Fig. 2 (d) and Fig. 3 (d)). This may be the reason for higher floc growth rate with larger floc size by $TiCl_4$-MCBF due to the relatively weak repulsion between the negatively charged flocs, since the absolute values of floc zeta potentials by $TiCl_4$-MCBF were lower than those by $TiCl_4$ and MCBF-$TiCl_4$. In case of $TiCl_4$-MCBF, when $TiCl_4$ was dosed firstly, it hydrolyzed instantaneously to form various hydrolyzates, followed by reaction with HA or FA to form the negatively charged $Ti(OH)_x^{(4-x)+}$-HA/FA complex or part of $TiCl_4$ may hydrolyze to form $Ti(OH)_4$ flocs. The $Ti(OH)_x^{(4-x)+}$-HA/FA complex and $Ti(OH)_4$ flocs therefore constituted the microflocs in the initial stage of rapid mixing. When positively charged MCBF was dosed, it quickly adsorbed on the surface of the microflocs and large flocs gradually formed due to the chain structure of MCBF. In case of MCBF-$TiCl_4$, the negatively charged MCBF-HA/FA complex was probably the initially formed microflocs. The increase in floc size under certain $TiCl_4$ dose conditions could presumably be attributed to the effective adsorption and entrapment of $TiCl_4$ hydrolyzates when $TiCl_4$ was dosed as coagulant aid. The bridging ability of MCBF molecules was another reason for the increase in floc size as compared with $TiCl_4$ alone.

Floc strength factor, S_f and floc recovery factor, R_f

After the initial floc growth phase, the floc size immediately decreased once the high shear at 200 rpm was applied, followed by floc re-formation when the original slow stir speed of 40 rpm was reintroduced. The aggregates formed by different coagulants varied over a wide range in floc size after floc growth, breakage and regrowth as shown in Fig. 5. To investigate the floc variation in detail, the floc strength factor (S_f) and recovery factor (R_f) were calculated according to Eqs. (2) and (3), respectively to interpret the floc strength and recoverability.

Fig. 6 presents the change in S_f and R_f vs. coagulant dose with different coagulants for both HA and FA simulated water treatment. Regardless of HA and FA simulated water treatment, $TiCl_4$-MCBF and MCBF-$TiCl_4$ coagulants improved floc strength to different degrees within the $TiCl_4$ dose range investigated, which may be ascribed to the adsorption and bridging ability of MCBF leading to the aggregation of microflocs. After floc breakage, the MCBF with the electrostatic attraction and Van der Waals on newly exposed microflocs surface may bond the floc fragments together, resulting in the good recoverability of the flocs formed by $TiCl_4$-MCBF and MCBF-$TiCl_4$. However, MCBF-$TiCl_4$ yielded the flocs with comparable floc R_f values as $TiCl_4$ within the $TiCl_4$ dose range from 20 to 35 mg/L in case of FA simulated water treatment. Thus, raw water characteristics and coagulant dose were also key parameters influencing the MCBF effect on floc properties. Floc R_f was barely influenced by dosing sequence of the dual-coagulants in case of HA simulated water treatment, as reflected by the comparable floc R_f values obtained by $TiCl_4$-MCBF and MCBF-$TiCl_4$, while $TiCl_4$-MCBF had superior advantage over $TiCl_4$ and MCBF-$TiCl_4$ in improving floc R_f in case of FA simulated water treatment.

Additionally, the floc R_f showed a significant drop at low $TiCl_4$ doses, followed by a gradual decline trend as further increased $TiCl_4$ dose no matter which kind of coagulant was used. At low $TiCl_4$ doses, $Ti(OH)^{3+}$, $Ti(OH)_2^{2+}$, and $Ti(OH)_3^{+}$ might be the dominate hydrolysis products of $TiCl_4$ (XU, GONG and QIN, 2009). The HA and FA removal may be achieved by the reaction with the positively charged $TiCl_4$ hydrolyzates through charge neutralization. As the increase in $TiCl_4$ concentration, the coagulation condition became favorable for hydroxide precipitation and the coagulation mechanism transformed to sweep flocculation. Previous studies have shown that the flocs formed by charge neutralization can fully reform, while the sweep flocs are irreversible after breakage (Yu, Li, Xu and Yang, 2009). This may be the main reason why the flocs formed at low $TiCl_4$ doses had better recoverability as compared with those at high doses. In case of HA simulated water treatment, $TiCl_4$ and MCBF-$TiCl_4$ coagulants gave the floc R_f value of ca. 143.0±1.0% at $TiCl_4$ dose of 5 mg/L, while the floc R_f was 123.8% and 114.3%, respectively with $TiCl_4$-MCBF and MCBF-$TiCl_4$ at $TiCl_4$ dose of 10 mg/L in case of FA simulated water treatment. The floc recoverability was reported to give some indication of floc internal bonding structure (Yang, Gao, Yue and Wang, 2010). The irreversible floc breakage at high

$TiCl_4$ doses was seen as evidence that the flocs formed were held together by chemical bonds rather than physical bonds alone.

Floc fractal dimension, D_f

The floc fractal dimension (D_f) was investigated to identify the effect of MCBF on floc compactness under different shearing patterns conditions in the coagulation system (Table 1). The $TiCl_4$ doses of 8 and 17 mg/L were selected for investigation in case of HA simulated water treatment. At low $TiCl_4$ doses of 8 mg/L, the UV_{254} removal was obviously increased due to MCBF addition while at high $TiCl_4$ dose of 17 mg/L, the dual-coagulants achieved comparable UV_{254} removal as $TiCl_4$ alone. Similarly, $TiCl_4$ doses of 15 and 30 mg/L were chosen for investigation in case of FA simulated water treatment**.**

The floc compactness was seen to increase by floc breakage at 200 rpm, as reflected by the substantial increase in floc D_f value for all of the flocs when intensive shear force was applied. A higher D_f indicates that the aggregates have densely packed structure while lower D_f results from the highly branched and loosely bounded structures. The flocs became more compact after exposure to high shear force as the internal bonds of the flocs were broken under strong shear conditions and the resultant fragments rearranged at more favorable points into more stable structure (Selomulya, Amal, Bushell and Waite, 2001, Yukselen and Gregory, 2002). The floc D_f values after floc regrowth period were comparable with those after breakage, indicating that the floc compactness were barely influenced by floc regrowth even the original mixing speed was reintroduced.

Considerable difference in floc D_f was observed with different coagulants. In case of HA simulated water treatment at $TiCl_4$ dose of 8 mg/L, $TiCl_4$-MCBF and $TiCl_4$ yielded the flocs with comparable D_f value of 2.39, higher than the value of 2.32 by MCBF-$TiCl_4$, while the D_f values varied apparently in the order of $TiCl_4$ > MCBF-$TiCl_4$ > $TiCl_4$-MCBF during floc breakage and regrowth processes. That is, the dual-coagulants reduced the floc compactness, especially during floc breakage and regrowth periods. However, the floc D_f followed the order of MCBF-$TiCl_4$ > $TiCl_4$ > $TiCl_4$-MCBF at $TiCl_4$ dose of 17 mg/L, indicating that the effect of MCBF on floc D_f was greatly influenced by coagulant dose. In case of FA simulated water treatment, dosing sequence of the dual-coagulants has minor effect of floc D_f, as reflected by the little variation of floc D_f values by $TiCl_4$-MCBF and MCBF-$TiCl_4$, while comparatively, for HA simulated water treatment, the floc D_f varied in a larger scale between $TiCl_4$-MCBF and MCBF-$TiCl_4$. That is, D_f was more influenced by dosing sequence in case of HA than that in case of FA. However, the $TiCl_4$ coagulant gave the flocs with the most compact structure given the highest D_f values seen in Table 1 regardless of floc growth, breakage and regrowth periods. Lower floc D_f values by the dual-coagulants indicated that the resultant fractal aggregates may spread out over a larger space than those by $TiCl_4$ alone due to the chain structure of MCBF.

Conclusions

Results showed that, acrylic amide and dimethyl diallyl ammonium chloride were successfully grafted onto the CBF and the molecule weight and zeta potential was improved from 1.3 kDa and -46 mV to 144 kDa and +15.0 mV, respectively. Using

MCBF as coagulant aid is a promising way for its application since both HA and FA removal with $TiCl_4$ can be improved by MCBF addition at low $TiCl_4$ doses. Also, the floc growth rate, size, strength and recoverability were significantly improved by MCBF. Both coagulation performance and floc characteristics were greatly influenced by dosing sequence of the dual-coagulants.

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