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 (TiCl₄) 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 TiCl₄ exhibited synergistic effect by promoting NOM removal, especially at low TiCl₄ doses. Additionally, using MCBF as coagulant aid with TiCl₄ can significantly increase the floc growth rate, size, strength and broken-floc recoverability. The effect of MCBF on fractal dimension of flocs generated by TiCl₄ 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 (TiCl₄) 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 (TiO₂) by calcination (Shon, Vigneswaran, Kandasamy, Zareie, Kim, Cho and Kim, 2009, Shon, Vigneswaran, Kim, Cho, Kim, Kim and Kim, 2007). Therefore, using TiCl₄ as a coagulant offers a novel solution to sludge disposal associated with production of TiO₂ 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 TiCl₄ and CBF. The pH value of the supernatant after optimum TiCl₄ 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 TiCl₄, with the results indicating that coagulation performance could be improved with reduced TiCl₄ 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 DMDAAC 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 TiCl₄ 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 °C. Then, various amounts of K$_2$S$_2$O$_8$ and Na$_2$SO$_3$ 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 K₂S₂O₈ and Na₂SO₃ was 1:1. The mass of K₂S₂O₈ 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):

\[
\text{Growth rate} = \frac{\Delta \text{size}}{\Delta \text{time}}
\]

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):

\[
S_f = \frac{d_2}{d_1} \times 100
\]

\[
R_f = \frac{d_3-d_2}{d_3-d_1} \times 100
\]

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):

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

(4)

where $n$, $\theta$, and $\lambda$ 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):

$$I \propto Q^{-D_f}$$

(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 TiCl₄ 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 TiCl₄ doses for TiCl₄-MCBF dual-coagulants, while it was not the case for MCBF-TiCl₄ dual-coagulants and residual turbidity showed obvious increase by the addition of 1.0 mg/L MCBF (Fig. 2 (a)). The UV₂₅₄ removal was enhanced by MCBF addition as shown in Fig. 2 (b), especially at low TiCl₄ doses. However, DOC removal decreased to different degrees with MCBF addition except at the TiCl₄ dose of 5 mg/L, where it was improved to different degrees by MCBF addition. In case of the TiCl₄-MCBF dual-coagulants, MCBF of 1.0 mg/L improved the UV₂₅₄ removal from 35.3% and 74.0% to 76.6% and 87.5%, respectively at TiCl₄ dose of 5 and 8 mg/L. The DOC removal was decreased by 2%~7% within the TiCl₄ dose range studied.

In case of FA simulated water treatment, the dual-coagulants had no superior advantage over TiCl₄ alone in terms of turbidity removal. The response of UV₂₇₈ removal to MCBF addition was similar as that of UV₂₅₄ in case of HA removal and the UV₂₇₈ removal was more enhanced by MCBF at low TiCl₄ 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-TiCl₄ 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 TiCl₄ 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 TiCl₄ and thus sweep flocculation was possible dominant mechanism for TiCl₄ 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 TiCl₄, 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 TiCl₄ hydrolyzates and MCBF-HA/FA flocs or HA/FA molecules. For both HA and FA simulated water treatment, the flocs formed by MCBF-TiCl₄ 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 TiCl₄ 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 TiCl₄-MCBF coagulants improved the floc growth rate as compared with the TiCl₄ alone. The MCBF-TiCl₄ coagulants yielded comparable floc growth rate with TiCl₄ 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-TiCl₄ was improved or decreased to different degrees depending on TiCl₄ 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 TiCl₄-MCBF coagulants had higher charge neutralization ability compared to TiCl₄ and MCBF-TiCl₄, 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 TiCl₄-MCBF due to the relatively weak repulsion between the negatively charged flocs, since the absolute values of floc zeta potentials by TiCl₄-MCBF were lower than those by TiCl₄ and MCBF-TiCl₄. In case of TiCl₄-MCBF, when TiCl₄ 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⁺-HA/FA complex or part of TiCl₄ may hydrolyze to form Ti(OH)₄ flocs. The Ti(OH)ₓ⁺⁻⁴⁺-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-TiCl₄, the negatively charged MCBF-HA/FA complex was probably the initially formed microflocs. The increase in floc size under certain TiCl₄ dose conditions could presumably be attributed to the effective adsorption and
entrapped of TiCl₄ hydrolyzates when TiCl₄ was dosed as coagulant aid. The bridging ability of MCBF molecules was another reason for the increase in floc size as compared with TiCl₄ alone.

**Floc strength factor, S₇ and floc recovery factor, R₇**

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 (S₇) and recovery factor (R₇) were calculated according to Eqs. (2) and (3), respectively to interpret the floc strength and recoverability.

Fig. 6 presents the change in S₇ and R₇ vs. coagulant dose with different coagulants for both HA and FA simulated water treatment. Regardless of HA and FA simulated water treatment, TiCl₄-MCBF and MCBF-TiCl₄ coagulants improved floc strength to different degrees within the TiCl₄ 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 TiCl₄-MCBF and MCBF-TiCl₄. However, MCBF-TiCl₄ yielded the flocs with comparable floc R₇ values as TiCl₄ within the TiCl₄ 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
coaugulant was used. At low TiCl$_4$ doses, Ti(OH)$_{3+}$, Ti(OH)$_{2+}$, 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
coaugulation condition became favorable for hydroxide precipitation and the
coaugulation 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 TiCl₄ can be improved by MCBF addition at low TiCl₄ 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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