The effect of second coagulant dose on the regrowth of flocs formed by charge neutralization and sweep coagulation using titanium tetrachloride (TiCl$_4$)

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A B S T R A C T

Characteristics of flocs formed by charge neutralization and sweep coagulation using titanium tetrachloride (TiCl$_4$) were investigated with humic acid–kaolin suspension by continuous optical monitoring. This paper focused on the regrowth ability of broken flocs after addition of second TiCl$_4$ dose. Variation of floc size and the fractal dimension of flocs versus second TiCl$_4$ dose after regrowth were investigated. Second TiCl$_4$ dose was added during the floc breakage period, and addition time of second TiCl$_4$ dose was also investigated. The results showed that, when coagulated by charge neutralization at pH 6, an appropriate second TiCl$_4$ dose improved regrowth ability of broken flocs at low initial TiCl$_4$ doses. While for high initial TiCl$_4$ doses, second TiCl$_4$ dose lowered floc re-growth ability. When coagulated by sweep coagulation at pH 10, second TiCl$_4$ dose made regrown flocs larger than those without second TiCl$_4$ dose. Floc structure analysis showed that it was determined by not only the fractal dimension of flocs, but also the chemical characteristics of floc surface. Addition time of second TiCl$_4$ dose had a great effect on floc regrowth ability, suggesting that the broken flocs had better regrowth when second TiCl$_4$ dose was added at the end of the breakage period.

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1. Introduction

Coagulation is a widely applied unit process for the removal of particles and organic matter present in water treatment works (WTW) [1]. Hydrolyzing salts such as aluminum sulfate (Al$_2$(SO$_4$)$_3$), ferric chloride (FeCl$_3$), polyferric sulfate (PFS) and polyaluminum chloride (PACl) are commonly used as coagulants [2]. However, two major problems are involved in the flocculation process. One problem is toxicity of the coagulant. Stauber et al. [3] have reported that there were increasing public concern over the connection between residual aluminum coagulant and Alzheimer's disease. Another problem is production of solid waste after flocculation. The flocculation process using Al- and Fe-salt coagulants produces a large amount of sludge. Most of the sludge is solid waste from which nothing can be recovered or reused, and thus requires further treatment such as incineration and landfill. To resolve the sludge disposal problem, titanium tetrachloride (TiCl$_4$) is used as a coagulant, the most significant advantage of which is the possibility of recovering the sludge to produce a valuable by-product namely titanium dioxide (TiO$_2$) [4,5]. The possibility of using titanium compounds as a coagulant in water treatment was first investigated by

Upton and Buswell in 1937 [6]. They found that titanium sulfate (Ti(SO$_4$)$_2$) was better in removing fluoride due to a quadrivalent cation than the trivalent aluminum or iron ions. They also noted that ilmenite extract gave much better coagulation in the colored water than aluminum or ferric sulfates. Since then, the effectiveness of Ti-salts has been proven in terms of removal of organic matter, turbidity, nutrients and flocs. Shon et al. [4] recently reported that removal of organic matter of different molecular sizes by Ti-salt flocculation was similar to that of the most widely used Fe- and Al-salt flocculation. The research used TiCl$_4$ instead of more commonly used salts of FeCl$_3$ and Al$_2$(SO$_4$)$_3$ to remove particulate and dissolved organic matter from wastewater in sewage treatment plants (STPs). TiCl$_4$ successfully removed organic matter to the same extent as Fe and Al salts. The mean size of Ti-, Fe- and Al-salt flocs was 47.5 μm, 42.5 μm and 16.9 μm, respectively. The settleability of flocs by Ti-salt coagulant was better than that by FeCl$_3$ coagulant and Al$_2$(SO$_4$)$_3$. The settling of Ti sludge was faster, which made the subsequent separation process easier. After Ti-salt coagulation, the settled flocs (sludge) could be calcined to produce functional TiO$_2$ nanomaterials, which had similar photocatalytic activity as the commercial TiO$_2$. Thus, the use of Ti-salts instead of Fe or Al salts in coagulation processes was regarded as a promising alternative, which was more efficient and allow the production of 450 kg TiO$_2$/day from a medium size STP of 25 ML/day. Lokshin and Belikov [7] also investigated Ti-salt flocculation. Waste

water could be efficiently purified to remove fluoride ions with titanium compounds, especially with hydrated oxotitanium sulfate with [F⁻] concentration achieved of 0.5–0.6 mg/L. They found that the concentration of the sulfate ions in purified water after $Ti(SO_4)_2$ flocculation did not exceed the permissible limit at the optimum doses of wastewater purification. Moreover, based on *D. magna* and *V. fischeri* bioassays, the toxicities of supernatant after $TiCl_4$ coagulation and recovered titania nanoparticles from the sludge had very low acute toxicity in aqueous conditions [8–10]. Recently, Zhao et al. [11] found that $TiCl_4$ flocculation achieved higher removal of UV_{254} (98%), dissolved organic carbon (DOC) (84%) and turbidity (93%) than conventional coagulants, and the aggregated flocs formed by $TiCl_4$ showed the largest floc size (801 μm) with the fastest growth rate compared to the conventional coagulants. They also found that TiO_2 produced from sludge was to be anatase phase and could remove the majority of the dye after 2 h photocatalytic reaction [12]. TiO_2 is the most widely used metal oxide in pigments, paper, solar cells and environmental applications for the degradation of waste and for hydrogen generation by photocatalytic water-splitting [13,14]. Therefore, $TiCl_4$ has been widely used in the industrial process as an intermediate in the production of titanium rutile, titanium oxide, and titanium pigments. In addition, the cost of $TiCl_4$ is comparable to $FeCl_3$ or $Al_2(SO_4)_3$ so the flocculation processes followed by sludge incineration offer an efficient and economical method for the removal of organic matter and sludge recovery. Protocols for the safe handling and use of bulk $TiCl_4$ have been well documented due to its existing industrial uses [15].

Characteristics of flocs after flocculation have a critical effect on solid/liquid separation process. One property that may have a significant impact on WTW is the potential of flocs for regrowth after being broken. Unit processes at WTW are generally prevalent with high shear regions, such as areas around the impeller zone of flocculating tanks and transfer over weirs and ledges. Although unit processes at WTW are generally designed to minimize floc breakage; however, this is not the case in practice, with regions of high shear being prevalent [16]. Flocs tend to break when they are subjected to an increasing shear rate and several recent investigations have dealt with the reversibility of floc breakage. The poor re-growth ability of flocs is undesirable because the resulted small particles will pose a challenge to the solid/liquid separation processes [17]. So floc regrowth ability is an important parameter to assess the coagulation process. Furthermore, type and concentration of coagulants, applied shear and variables such as concentration and size of particles will influence floc regrowth. Nearly all of the results show that there is a distinct irreversibility of floc breakage, but there is no adequate model to explain these findings [18]. Floc fractal dimension (D_f) of flocs is another particularly important operational parameter influencing the separation processes encountered in conventional treatment. Fractal theories for particle aggregates provide a new quantitative method to describe the structure of particles aggregates in various water systems. High D_f means the primary particles in an aggregate are arranged compactly, while low D_f results from large, highly branched and loosely bound structures. Measurement of fractal dimension is used to assess the compactness of precipitates. In water and wastewater treatment, the mechanisms involved in the formation, breakage and regrowth of flocs formed with $TiCl_4$ are not yet well understood. Also, the effect of second low coagulant dose, added during floc breakage period, on the regrowth of flocs formed by $TiCl_4$ has barely been reported.

Normally, charge neutralization and physical entrapment of colloids within coagulant precipitates and adsorption were the dominant mechanisms at optimal dose of $TiCl_4$, and it was difficult for broken flocs to fully re-grow to their initial size before breakage [11,12]. This work aimed to evaluate the regrowth ability of flocs when coagulation was carried out by $TiCl_4$ in the charge neutralization zone and sweep flocculation zone. The effect of breakage period on floc regrowth ability under different coagulation mechanisms was investigated in this study. The effect of second $TiCl_4$ dose (added during floc breakage period) on floc regrowth ability was investigated in terms of floc characteristics, including floc size and fractal dimension before and after regrowth. Moreover, addition time of second $TiCl_4$ dose was also investigated. The results are of practical interest, since floc breakage is inevitable in most WTW. It would be very valuable to investigate the factors affecting the recoverability of broken flocs and the effect of floc breakage and regrowth on practical separation processes.

2. Materials and methods

2.1. Synthetic water and coagulant

The commercial HA (biochemical reagent) was used in the preparation of HA–kaolin synthetic water, and was purchased from the Jufeng Chemical Technology Co. Ltd., Shanghai, China. Synthetic water was prepared using HA and kaolin. Stock solution of HA was prepared by dissolving 1.0 g of HA in 0.01 mol/L NaOH solution with continuous stirring for 30 min. Coagulation experiments were performed with synthetic water containing 10 mg/L of HA prepared in tap water. The initial turbidity was adjusted to about 15 ± 0.2 NTU by adding kaolin. Kaolin was purchased from the Kermel Chemical Technology Co. Ltd., Tianjin, China.

$TiCl_4$ stock solution (20%, density = 1.148 g/ml) was obtained from Photo & Environment Technology Co. Ltd. (South Korea), and was used as received without any further purification.

2.2. Jar-test

Coagulation was conducted using a jar tester (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) at different initial pHs. The test solution pH was controlled at 6 or 10 by previous addition of an appropriate amount of dilute (0.1 mol/L) HCl and NaOH. A two-stage mixing process, including rapid (1.5-min stage at 200 rpm) and slow mixing (10-min stage at 40 rpm) was followed by a 10-min breakage period, after which the speed was reduced to 40 rpm for 20 min. The zeta potential of coagulated samples (collected using a syringe from about 2 cm below the water surface) after 1 min of rapid mixing were measured with a Zetasizer 3000HSa (Malvern Instruments, UK). Each experiment was repeated three times and the average zeta potential for every sample was determined based on the three measurements. The zeta potential of flocs after 10-min breakage by high stirring speed was also measured. In addition, zeta potential of the test water before coagulation process was measured to evaluate the zeta potential difference under different pH conditions.

2.3. On line monitoring of floc sizes

Experiments on the kinetics of formation, breakage and subsequent regrowth of flocs were performed on laser diffraction Mastersizer 2000 (Malvern, UK) as coagulation and flocculation proceeded. The suspension was monitored through optical unit of Mastersizer and transferred back into the jar by a peristaltic pump (LEAD-1, Longer Precision Pump, China) on a return tube with a 5 mm internal diameter peristaltic pump tubing. Floc size was measured every 0.5 min for the duration of jar test and the results were automatically recorded. A known amount of $TiCl_4$ was added into the test suspension (1000 ml) and a two-stage mixing process, including rapid (1.5-min stage at 200 rpm) and slow mixing (10-min stage at 40 rpm) was followed by a 1-min or 10-min breakage period (200 rpm) to break the flocs, after which the speed

was reduced to 40 rpm for 10-min or 20-min, so that regrowth of broken flocs could occur. In some cases, second dose of TiCl$_4$ was added into suspension during floc breakage period, mostly at the end of the 10-min period of high-speed stirring.

2.4. Floc strength and recovery factors

Floc strength factor (S_f) and recovery factor (R_f) are well-established parameters for describing floc strength and recoverability and can be calculated as follows [1,2,19]:

$$S_f = \frac{d_2}{d_1} \times 100 \tag{1}$$

$$R_f = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \tag{2}$$

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.

Here, the strength factor is an indication of floc strength, which refers to the ability to resist rupture by a velocity gradient, while the recovery factor indicates recovery ability of the floc. The larger values of strength factor indicate that the flocs are stronger than those with lower factors. Flocs with larger recovery factors show better recovery ability after high shear, that is, better regrowth after breakage. In addition, the size data were expressed as an equivalent volumetric diameter, and d_{50} was selected as representative floc size in this paper [20], which referred to the 50 percentile floc size.

2.5. Floc fractal dimension

Light scattering method is widely used for the determination of aggregate mass fractal dimension. The theory of the mass fractal dimension has been reported in detail in a few literatures [21,22]. 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 [22], which is given by Eq. (3):

$$Q = \frac{4\pi n \, \sin(\theta/2)}{\lambda} \tag{3}$$

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. (4):

$$I \propto Q^{-D_f} \tag{4}$$

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 that the primary particles in an aggregate are arranged compactly, while low D_f results from highly branched and loosely bound structures.

3. Results and discussion

3.1. Zeta potential of flocs before and after breakage

Fig. 1 shows the variation of zeta potentials with different TiCl$_4$ doses before and after breakage under different solution pHs. The zeta potential values of HA particles without TiCl$_4$ addition at pH 6 and 10 were −14.3 and −17.9 mV, respectively. The zeta potential values were higher (less negative) at pH 6 than those at pH 10 within all the TiCl$_4$ doses, which may be due to the more positive nature of Ti hydrolysis products, and also partly to the more positive zeta potential value of HA and kaolin at pH 6. As shown in Fig. 1, the increase in zeta potential with the increasing coagulant dosage was
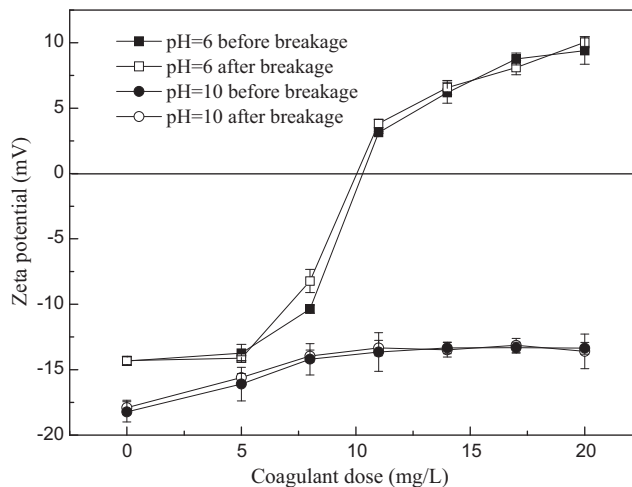

Fig. 1. Variation of zeta potential of flocs with TiCl$_4$ dosage (mg Ti/L) before and after breakage.

quite sharp at pH 6 and the charge became positive at doses higher than about 10 mg/L of Ti. While at pH 10, floc zeta potential showed a slight increase and was negative within the dose investigated.

The zeta potential obtained 1 min after TiCl$_4$ addition was found nearly the same as that obtained after 10 min of floc breakage for both pH values (Fig. 1), which indicated that the reaction between hydrolysis products of TiCl$_4$ and the negatively charged particles occurred during the initial 1 min after TiCl$_4$ addition. Although the average zeta potential of particles (flocs) did not change during the breakage process, the newly exposed surface of aggregates might have a negative, positive or neutral charge [16], which may influence the regrowth of broken flocs.

3.2. The regrowth ability of broken flocs formed by two different coagulation mechanisms with different breakage periods

Zhao et al. [11,12] reported that charge neutralization and sweep coagulation were two primary coagulation mechanisms involved in TiCl$_4$ coagulation process, which depended on TiCl$_4$ dose and solution pH. In this study, different TiCl$_4$ doses and two pH values were fixed in order to let coagulation occur under these two mechanisms. Charge neutralization was the dominant coagulation mechanism when 5 or 8 mg/L of Ti was added and suspension pH was fixed at 6 (Fig. 1). At pH 10, the zeta potential values were negative within the doses investigated, where coagulation was likely more influenced by sweep coagulation and charge effects may be less important.

Variation of floc size d_{50} with time during floc growth, breakage and regrowth with two coagulation mechanisms was shown in Fig. 2. The effect of breakage period (1 min and 10 min) of high shear (200 rpm) on floc breakage and regrowth was also investigated in this section. In all cases, the floc size significantly increased after slow mixing at 40 rpm, implying that the appropriate balance between floc growth and breakage was reached [2,23–26]. Floc sizes formed by TiCl$_4$ at pH 6 were larger than those formed at pH 10, which might be explained as follows: when TiCl$_4$ was dosed, several hydrolysed species formed, e.g. Ti(OH)$^{3+}$ → Ti(OH)$_2$$^{2+}$ → Ti(OH)$_3$$^+$ → Ti(OH)$_4$^{0} → Ti(OH)$_5$$^{1-}$ → Ti(O$_2$)$_2$(OH)$_2$^{2}, and the Ti(OH)$_5$$^{1-}$ and Ti(O$_2$)$_2$(OH)$_2$$^{2-}$ or Ti(O)(O$_2$)(OH)$_2$$^{2-}$ may occur at pH values greater than pH 10 [27]. For pH 6, TiCl$_4$ hydrolyzed to form titanium hydroxide instantaneously which reacted with HA to form the negatively charged Ti(OH)$_x$$^{(4-x)+}$–HA complex. The Ti(OH)$_x$$^{(4-x)+}$–HA complex constituted the microflocs in the initial stage of rapid mixing. Large flocs gradually formed due to the sweep coagulation. For
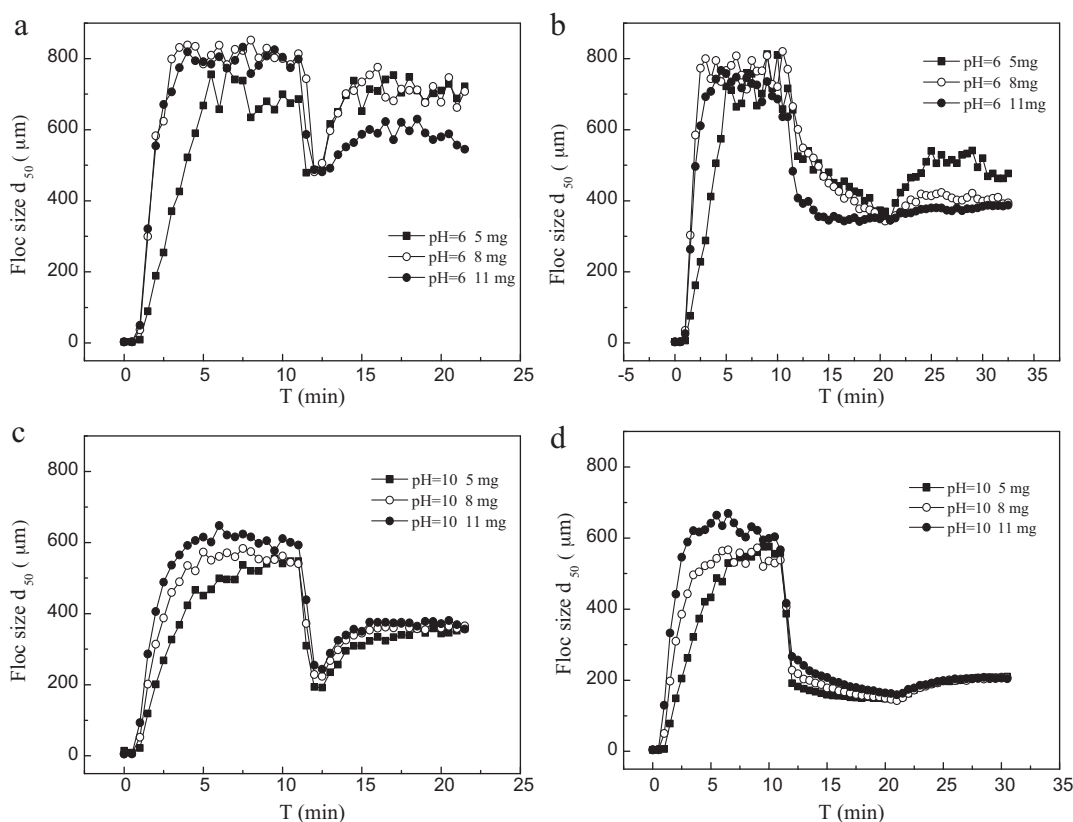
Fig. 2. Variation of floc size d_{50} with time during floc growth, breakage and regrowth with two coagulation mechanisms under different breakage periods: (a) charge neutralization at pH 6 with 1 min of breakage; (b) charge neutralization at pH 6 with 10 min of breakage; (c) precipitation and sweep coagulation at pH 10 with 1 min of breakage; (d) precipitation and sweep coagulation at pH 10 with 10 min of breakage.

pH 10, the $Ti(OH)_5^{1-}$ and $Ti(O_2)_2(OH)_2^{2-}$ or $Ti(O)(O_2)(OH)_2^{2-}$ may occur, or part of $TiCl_4$ hydrolyzed to form $Ti(OH)_4$ flocs, due to high OH^- concentration in test solution. So, adsorption on hydrolysis products was assumed to play an important role in coagulation process at pH 10. The flocs formed were comparatively smaller than those under pH 6, which may be attributed to the repulsion forces between the colloids and the negatively charged $TiCl_4$ hydrolyzates. The floc size immediately decreased with the increasing shear (200 rpm). As the shear was removed, the flocs began to re-grow. However, it was observed that there was a distinct irreversibility of the break-up process except for the flocs formed at pH 6 with 5 mg/L as Ti. Irreversibility of the break-up process was probably caused by the different surface characteristics of broken flocs.

The curves of floc size versus coagulation time were similar for both pH values, while under the same dose condition, the extents of breakage and regrowth of flocs were different. To investigate floc variations in detail, strength and recovery factors calculated using Eq. (1) and (2), were used to interpret the floc breakage and recoverability. As shown in Table 1, the strength factors and the recovery factors of flocs were higher at pH 6 than those at pH 10 regardless of the breakage period of 1 min or 10 min. It is generally accepted that the main removal mechanism of NOM at pH < 6 is dominated by complexation of NOM with soluble metal species into insoluble precipitates; while at pH > 6, NOM is mainly removed by adsorption onto precipitated metal hydroxides. In addition, flocs formed by charge neutralization have total recoverability [28], while sweep flocs have poor re-growth after breakage [29,30]. Based on the discussion above, the dominant NOM removal for $TiCl_4$ at pH 6 was likely the formation of insoluble precipitates and the subsequent charge neutralization. However, at 10, adsorption on hydrolysis

products was assumed to play an important role in coagulation process. Consequently, the flocs showed poor recoverability at high pH value.

The strength and recovery factors for d_{50} under different breakage periods shown in Table 1 indicated that a reduction in the time of exposure to a similar shear caused a significant increase in both floc strength and floc regrowth [19]. This showed that the flocs could resist a certain amount of shear. The extent of floc breakage was much smaller under the reduced shear period of 1 min for both pH 6 and pH 10, with floc strength factors increasing by an additional 13–18 and 8–16, respectively, from the long shear period (Table 1). Different degrees of recovery ability were observed in terms of breakage period. Compared to the short period shear, recovery ability of the flocs declined after long period of shear for both pH values.

Table 1
Variation of S_f and R_f with different coagulant doses.

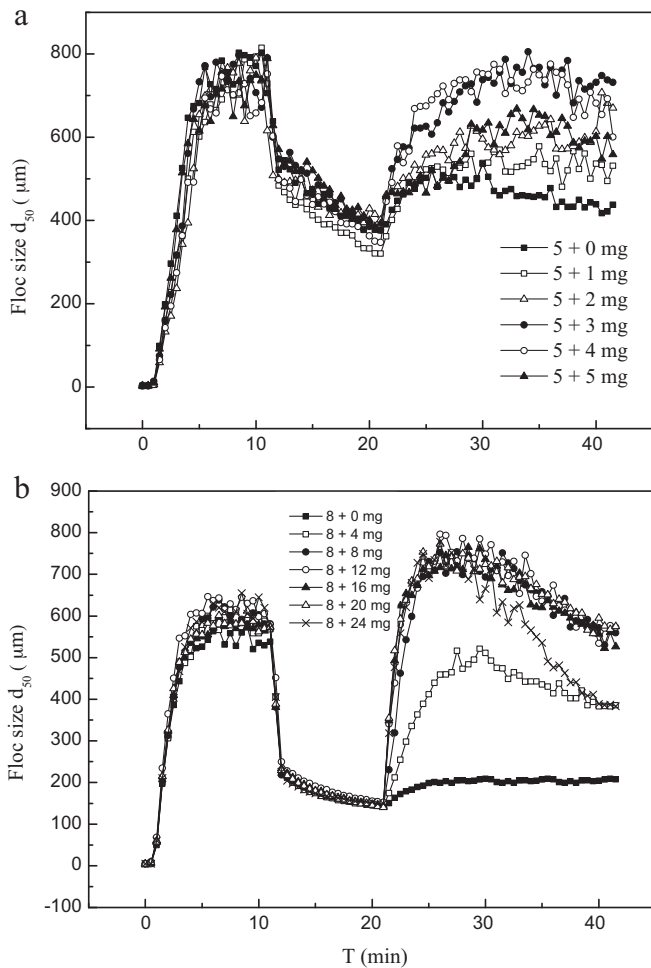| Coagulant dose (mg/L)	pH 6		pH 10	
	1 min	10 min	1 min	10 min
S_f (%)				
5	70	52	35	27
8	61	45	41	27
11	61	48	41	25
R_f (%)				
5	109	38	43	14
8	68	15	41	14
11	34	10	33	8

Fig. 3. Effect of a second dosage of TiCl$_4$ added at the end of the breakage period: (a) pH 6; (b) pH 10. Initial and second dosages (mg Ti/L) were shown in the legends.

3.3. Effect of additional coagulant on the regrowth ability of broken flocs

To investigate the mechanism of floc regrowth, second TiCl$_4$ dose was added to the suspension at the end of floc breakage period (10 min) and the effect of second TiCl$_4$ dose on floc regrowth was shown in Fig. 3. Initial and second doses of TiCl$_4$ were shown in the legends. For initial TiCl$_4$ dose of 5 mg/L at pH 6 and 8 mg/L at pH 10, only limited floc regrowth occurred as before without second coagulant dose (Fig. 2(b) and (d)). However, for both pH 6 and 10, second coagulant dose significantly improved floc regrowth after breakage. For pH 6, with increase of second dose of TiCl$_4$, the floc size first increased and then decreased (Fig. 4(a)), with the maximal floc size of 742.2 μm when second dose of 3 mg Ti/L was added. For pH 10, the flocs showed a continuous regrowth with increasing second dose of TiCl$_4$. TiCl$_4$ achieved the largest mean floc size of 724.8 μm with second dose of 8 mg Ti/L during the first 10 min in the regrowth process, followed by a slight decrease in floc size during the next 10 min. Variation of floc sizes versus coagulation time followed the same way with increasing second dose of TiCl$_4$, and the floc size showed an apparent decrease after 10 min of regrowth when 24 m Ti/L was added.

Besides floc size, fractal dimension of flocs was also an important parameter influencing solid/liquid separation, since it influenced floc density [31]. For pH 6, the average size of flocs was 720.73 μm with D_f of 1.82 after slow stir phase, and the flocs were broken
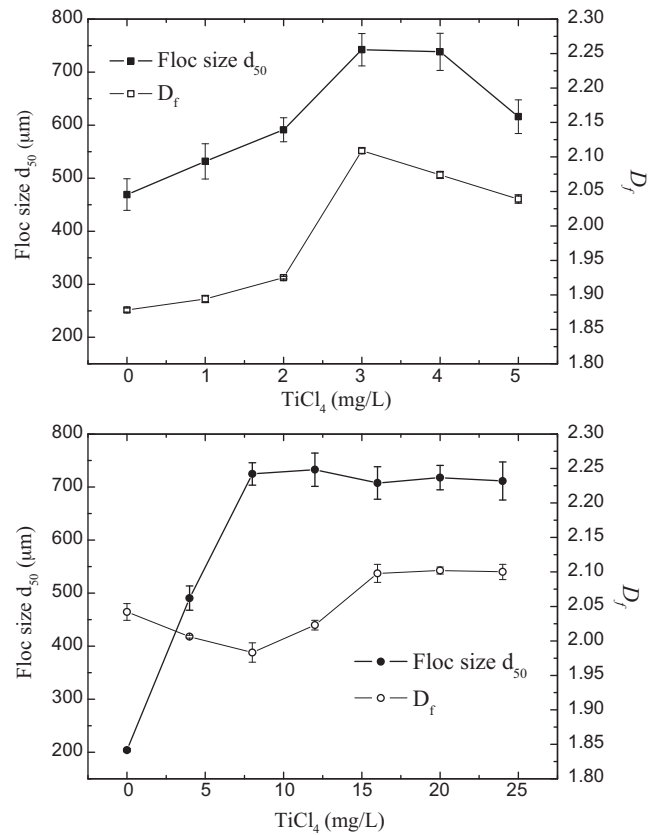

Fig. 4. Variation of size and D_f of flocs with additional dosage of TiCl$_4$ at pH 6 (a) and pH 10 (b).

into small flocs (371.25 μm) with D_f of 1.94 after 10 min of breakage (200 rpm). As the shear was reduced again, the flocs began to regrow. The D_f of flocs after regrowth was 1.878 without second dose of TiCl$_4$. Variation of the D_f of flocs versus second dose of TiCl$_4$, the same as the average floc size, showed a parabolic trend with an inflexion point at which second dose of 3 mg/L of Ti was added. That is, the D_f of flocs increased when second dose of TiCl$_4$ was lower than 3 mg/L and then slightly decreased beyond the point of inflexion. The maximal D_f of flocs was 2.109. For pH 10, the D_f of flocs after the initial growth period and floc breakage was 1.946 and 2.036, respectively, while that of flocs was 2.042 after floc regrowth without second dose of TiCl$_4$. With increasing second dose of TiCl$_4$, the D_f of flocs after floc regrowth showed a decline trend first, followed by an increase (Fig. 4(b)), which was not the case at pH 6.

Changes in the average sizes and D_f of the flocs indicated that the flocs did not retain their original characteristics after breakage and regrowth. Regardless of the flocs formed by charge neutralization or sweep mechanism, a significant drop in floc d_{50} was immediately observed after the introduction of increasing shear at 200 rpm. The broken flocs could not fully aggregate with other flocs at the breakage point and limited reconnection was observed, which might be due to the broken chemical bonds [1]. The D_f of the flocs increased after floc breakage, which may be attributed to the rupture of weak points under high shear force and the more compact flocs were obtained by rearrangement.

For flocs formed by charge neutralization at pH 6, without second TiCl$_4$ dose, the floc size showed certain increase after floc regrowth. However, D_f of the flocs after floc regrowth (1.878) was lower than that after floc breakage (1.939). The floc structure may be slightly loosely arranged due to high shear force. When second TiCl$_4$ dose was added after floc breakage period, the D_f of flocs
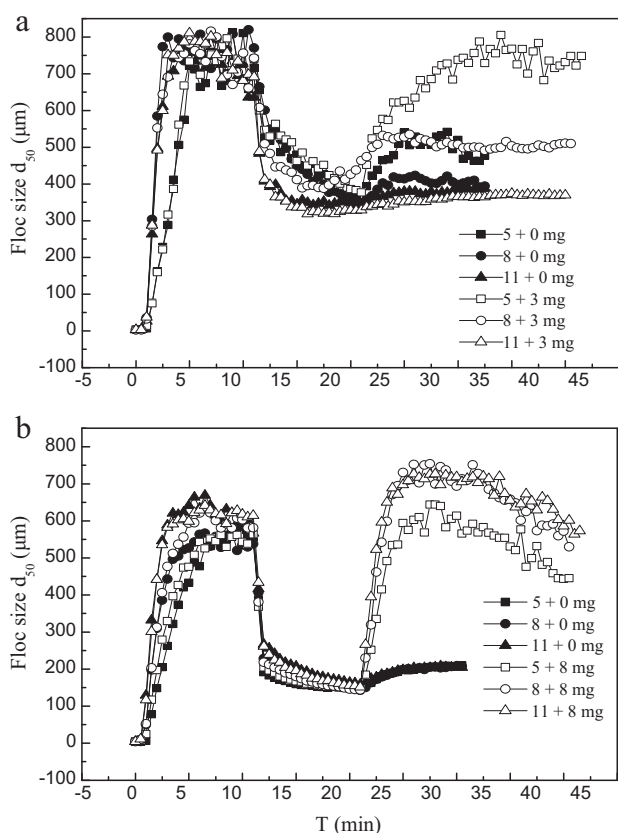
Fig. 5. Effect of initial TiCl$_4$ dosage (shown in legend) on floc regrowth at pH 6 (a) and pH 10 (b) with an additional TiCl$_4$ dosage of 3 mg and 8 mg as Ti, respectively.

the surface of particles resulted in the repulsion among particles, and led to a slight decrease in floc size and D_f.

For flocs formed by sweep mechanism at pH 10, without second dose of TiCl$_4$, the particles formed were negatively charged due to the adsorption of the organic matters (negatively charged) in the surface of the hydrolysis products (TiCl$_4$ coagulant hydrolyzed immediately under alkaline condition (pH = 10) [27]). The flocs were difficult to regrow after breakage due to particle repulsion. With the addition of second TiCl$_4$ dose, the size of flocs increased with increasing second TiCl$_4$ dose, and almost reached the steady value when the second TiCl$_4$ dose was larger than 8.0 mg Ti/L. Second dose of TiCl$_4$ neutralized the negative charges in particle surface, and the increase of floc size may be due to the particle aggregation and adsorption. However, size of the flocs showed apparent decrease when second dose of 24 mg/L was applied, which might be attributed to the particle repulsion with the excess addition of second TiCl$_4$ dose. However, the D_f of flocs firstly showed a slight decline trend with increasing second TiCl$_4$ dose, then showed an increase when second dose of TiCl$_4$ was larger than 8.0 mg/L. That might be explained as follows: when second dose of TiCl$_4$ was less than 8.0 mg/L, the additional TiCl$_4$ reacted with the negatively charged organic matters, and the particles may still adhere to the surface of the hydrolysis products. The loose connection among the particles might result in the decrease of the D_f of flocs. As second dose of TiCl$_4$ further increased, the structure of flocs became more compact, which might be due to the rearrangement of the particles with the change of surface charge. So, fractal dimension of flocs was probably not the only determining parameter for flocs structure, but also the chemical characteristics of floc surface.

3.4. The effect of initial TiCl$_4$ dose on floc regrowth

The effect of initial TiCl$_4$ dose on floc regrowth under different coagulation mechanisms was investigated in this section. Based on the results above, second TiCl$_4$ doses of 3 mg Ti/L and 8 mg Ti/L were selected to investigate the effect of initial TiCl$_4$ dose on floc regrowth, and the results were shown in Fig. 5. Initial TiCl$_4$ doses were shown in the legends and the breakage period was 10 min. In the case of charge neutralization coagulation, second dose of 3 mg Ti/L increased the floc size in the floc regrowth phase at initial 5 and 8 mg Ti/L, while decreased the floc size from 380.00 μm to 366.00 μm at 11 mg Ti/L. The flocs were positively charged when 11 mg Ti/L was added (Fig. 1). When second dose of 3 mg Ti/L was added, particle repulsion decreased the floc size
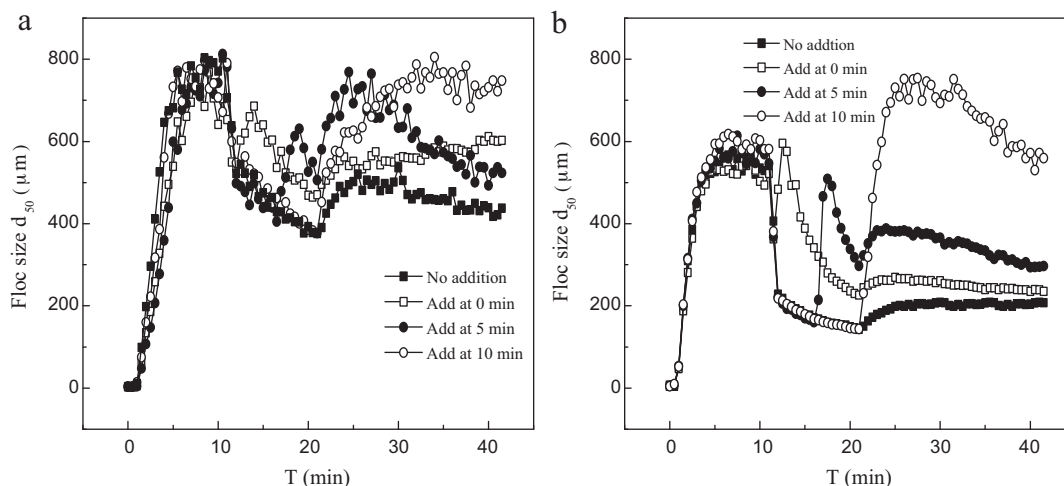
increased with the increase of second TiCl$_4$ dose, which suggested that the floc structure became more compact with increasing second TiCl$_4$ dose during floc regrowth period. The possible reason is: (i) floc structure became more compact and stable by rearrangement [32]; (ii) the rupture of weak points under prolonged mixing and shear conditions contributed to the formation of a homogenous and dense floc structure [33]. The D_f of flocs showed a gradual decrease when second TiCl$_4$ dose was larger than 3 mg/L as Ti. It might be explained as follows: positive charge adsorbed on

Fig. 6. Effect of time of second TiCl$_4$ addition during breakage period on floc regrowth at pH 6 (a) and pH 10 (b). Initial TiCl$_4$ doses were 5 mg and 8 mg Ti, second TiCl$_4$ doses were 3 mg and 8 mg Ti, respectively.

during floc regrowth period. In the case of sweep coagulation, second $TiCl_4$ dose caused significant floc regrowth with the floc size increasing from about 200.00 μm to 600.85 μm, 725.56 μm and 712.42 μm, respectively, for initial $TiCl_4$ dose of 5, 8 and 11 mg Ti/L.

3.5. Effect of addition time of second coagulant dose

Addition time of second $TiCl_4$ dose had a major influence on floc regrowth, with the results shown in Fig. 6. In these experiments, floc breakage at 200 rpm continued for 10 min, and the second $TiCl_4$ dose was added at 0 min, 5 min and 10 min, respectively, of the breakage period. The floc regrowth without second $TiCl_4$ dose was presented for comparison. In all the cases, regrowth of flocs was improved to varying extents compared to the case of no second coagulant. When the second dose was added at the start or 5 min after the start of the breakage period, an initial rise in floc size followed by a decline was observed. That could be explained as follows: the results of preliminary experiments (Fig. 2) indicated that exposure of the flocs to high shear played an important role in the loss of the floc regrowth potential, suggesting that repeated floc breakage may lead to progressive loss of floc regrowth ability. For broken flocs, there must be regions of the surface that previously attached to other flocs. The flocs were less able to attach at previous breakage sites as repeated breakage occurred. In this study, initial $TiCl_4$ doses were 5 mg and 8 mg Ti, respectively. From Fig. 1, it can be seen that the broken flocs were negatively charged. With the addition of second $TiCl_4$ dose, increase of floc size may be due to reaction between the negatively charged broken flocs and $TiCl_4$ hydrolyzates. Then, the flocs formed were broken again with increasing breakage period, and breakage reduced the chance of the attachment between floc fragments, which resulted in the decrease of floc size. Thus, the flocs could not regrow to the original size before floc breakage. It was only a hypothesis and needed to be further investigated. However, when second $TiCl_4$ dose was added at the end of the breakage period, there was a complete recovery of the floc size regardless of the flocs formed by charge neutralization or sweep coagulation. In this process, with the addition of second $TiCl_4$ dose, the hydrolysates of $TiCl_4$ may form fresh precipitates through the reaction with negatively charge particles or attach to the surface of the broken flocs, leading to floc regrowth during regrowth period.

4. Conclusions

The main conclusions of this work:

1. With no second $TiCl_4$ dose and with 1 min of breakage period, complete regrowth of broken flocs was observed under conditions close to charge neutralization with low $TiCl_4$ doses at pH 6, while only limited regrowth of flocs occurred with higher $TiCl_4$ doses and at pH 10. Compared to short shear period of 1 min, recovery ability of the flocs significantly decayed after long shear period of 10 min for both pH values.
2. A second dose of $TiCl_4$, added during the breakage period of 10 min had significant effect on floc regrowth. The regrowth potential of the broken flocs could be significantly improved with appropriate second $TiCl_4$ dose regardless of the flocs formed by charge neutralization or sweep coagulation. For flocs formed by charge neutralization at pH 6, the D_f of flocs increased with the addition of second $TiCl_4$ dose, which suggested that the floc structure became more compact during floc regrowth period. For flocs formed by sweep mechanism at pH 10, the D_f of flocs showed a slight decline trend followed by an increase with

increasing second dose of $TiCl_4$. It seemed that surface characteristic of flocs as well as D_f of flocs was important in influencing floc regrowth ability.

3. Addition time of second $TiCl_4$ dose had a great effect on floc regrowth, as a result of which, complete regrowth of broken flocs was observed when $TiCl_4$ was added at the end of the breakage period.

References

[1] P. Jarvis, B. Jefferson, S.A. Parsons, Breakage, re-growth, and fractal nature of natural organic matter flocs, Environ. Sci. Technol. 39 (7) (2005) 2307–2314.
[2] R.J. Francois, Strength of aluminium hydroxide flocs, Water Res. 21 (9) (1987) 1023–1030.
[3] J.L. Stauber, T.M. Florence, C.M. Davies, M.S. Adams, J.S. Buchanan, Bioavailability of aluminium in alum-treated drinking water and food, J. Am. Water Works Assoc. 91 (1999) 84–93.
[4] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho, G.J. Kim, J.-B. Kim, J.-H. Kim, Preparation of functional titanium oxide (TiO₂) from sludge produced by titanium tetrachloride (TiCl₄) flocculation of wastewater, Environ. Sci. Technol. 41 (4) (2007) 1372–1377.
[5] H.K. Shon, S. Vigneswaran, J. Kandasamy, M.H. Zareie, J.B. Kim, D.L. Cho, J.-H. Kim, Preparation and characterization of titanium dioxide (TiO₂) from sludge produced by TiCl₄ flocculation with FeCl₃, Al₂(SO₄)₃ and Ca(OH)₂ coagulant aids in wastewater, Sep. Sci. Technol. 44 (7) (2009) 1525–1543.
[6] W.V. Upton, A.M. Buswell, Titanium salts in water purification, Ind. Eng. Chem. 29 (8) (1937) 870–871.
[7] E.P. Lokshin, M.L. Belikov, Water purification with titanium compounds to remove fluoride ions, Russ. J. Appl. Chem. 76 (9) (2003) 1466–1471.
[8] B.C. Lee, S. Kim, H.K. Shon, S. Vigneswaran, S.D. Kim, et al., Aquatic toxicity evaluation of TiO₂ nanoparticle produced from sludge of TiCl₄ flocculation of wastewater and seawater 11 (8) (2009) 2087–2096.
[9] A. Bozzi, M. Dhananjeyan, I. Guasaquillo, S. Parra, C. Pulgarin, C. Weins, J. Kiwi, Evolution of toxicity during melamine photocatalysis with TiO₂ suspensions, J. Photochem. Photobiol. Chem. 162 (1) (2004) 179–185.
[10] S.B. Lovern, R. Klaper, Daphnia magna mortality when exposed to titanium dioxide and fullerene (C60) nanoparticles, Environ. Toxicol. Chem. 25 (4) (2006) 1132–1137.
[11] Y.X. Zhao, B.Y. Gao, H.K. Shon, B.C. Cao, J.-H. Kim, Coagulation characteristics of titanium (Ti) salt coagulant compared with aluminum (Al) and iron (Fe) salts, J. Hazard. Mater. 185 (2011) 1536–1542.
[12] Y.X. Zhao, B.Y. Gao, B.C. Cao, Z.L. Yang, Q.Y. Yue, H.K. Shon, J.-H. Kim, Comparison of coagulation behavior and floc characteristics of titanium tetrachloride (TiCl₄) and polyaluminum chloride (PACl) with surface water treatment, Chem. Eng. J. 166 (2011) 544–550.
[13] T.N. Obee, R.T. Brown, TiO₂ photocatalysis for indoor air applications: effects of humidity and trace contaminant levels on the oxidation rates of formaldehyde, toluene, and 1, 3-butadiene, Environ. Sci. Technol. 29 (5) (1995) 1223–1231.
[14] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1) (1995) 69–96.
[15] T. Kapias, R.F. Griffiths, Accidental releases of titanium tetrachloride (TiCl₄) in the context of major hazards spill behaviour using REACTPOOL, J. Hazard. Mater. 119 (1–3) (2005) 41–52.
[16] K. McCurdy, K. Carlson, D. Gregory, Floc morphology and cyclic shearing recovery: comparison of alum and polyaluminium chloride coagulants, Water Res. 38 (2) (2004) 486–494.
[17] P. Jarvis, B. Jefferson, S.A. Parsons, How the natural organic matter to coagulant ratio impacts on floc structural properties, Environ. Sci. Technol. 39 (2005) 8919–8924.
[18] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100–102 (2003) 475–502.
[19] M.A. Yukselen, J. Gregory, The reversibility of floc breakage, Int. J. Miner. Process. 73 (2–4) (2004) 251–259.
[20] J.C. Wei, B.Y. Gao, Q.Y. Yue, Y. Wang, Strength and regrowth properties of polyferric–polymer dual-coagulant flocs in surface water treatment, J. Hazard. Mater. 175 (1–3) (2010) 949–954.

[21] G.C. Bushell, Y.D. Yan, D. Woodfield, J. Raper, R. Amal, On techniques for the measurement of the mass fractal dimension of aggregates, Adv. Colloid Interface Sci. 95 (1) (2002) 1–50.

[22] J. Guan, T.D. Waite, R. Amal, Rapid structure characterization of bacterial aggregates, Environ. Sci. Technol. 32 (23) (1998) 3735–3742.

[23] C.A. Biggs, P.A. Lant, Activated sludge flocculation: on-line determination of floc size and the effect of shear, Water Res. 34 (2000) 2542–2550.

[24] J.J. Ducoste, M.M. Clark, The influence of tank size and impeller geometry on turbulent flocculation: I. Experimental, Environ. Eng. Sci. 15 (3) (1998) 215–224.

[25] D.S. Parker, W.J. Kaufman, D. Jenkins, Floc breakup in turbulent flocculation processes, J. Sanit. Eng. Div.: Proc. Am. Soc. Civ. Eng. SA1 98 (1) (1972) 79–99.

[26] P.T. Spicer, S.E. Pratsinis, Shear-induced flocculation: the evolution of floc structure and the shape of the size distribution at steady state, Water Res. 30 (1996) 1049–1056.

[27] Jing Xu, Peng Gong, Ximei Qin, Research on hydrolysis of TiCl$_4$ characteristic, Petrol. Chem. Ind. Appl. 28 (2009) 13–15.

[28] V. Chaignon, B.S. Lartiges, A. El Samrani, C. Mustin, Evolution of size distribution and transfer of mineral particles between flocs in activated sludges: an insight into floc exchange dynamics, Water Res. 36 (3) (2002), 676–484.

[29] M.I. Aguilar, J. Saez, M. Llorens, A. Soler, J.F. Ortuno, Microscopic observation of particle reduction in slaughterhouse wastewater by coagulation–flocculation using ferric sulphate as coagulant and different coagulant aids, Water Res. 37 (9) (2003) 2233–2241.

[30] P. Jarvis, B. Jefferson, S.A. Parsons, The duplicity of floc strength, in: Proceedings of the Nano and Micro Particles in Water and Wastewater Treatment Conference, International Water Association, Zurich, Switzerland, 2003, pp. 63–70.

[31] J. Gregory, The role of floc density in solid–liquid separation, Filtr. Sep. 35 (1998) 571–575.

[32] C. Selomulya, R. Amal, G. Bushell, T.D. Waite, Evidence of shear rate dependence on restructuring and breakup of latex aggregates, J. Colloid Interface Sci. 236 (1) (2001) 66–77.

[33] D.C. Hopkins, J.J. Ducoste, Characterizing flocculation under heterogeneous turbulence, J. Colloid Interface Sci. 264 (1) (2003) 184–194.