Effect of shear force, solution pH and breakage period on characteristics of flocs formed by Titanium tetrachloride (TiCl$_4$) and Polyaluminum chloride (PACl) with surface water treatment

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ABSTRACT

The growth, breakage and regrowth nature of flocs formed by Titanium tetrachloride (TiCl$_4$) and polyaluminum chloride (PACl) was comparatively evaluated with surface water treatment. A series of jar experiments were conducted to investigate the impacts of different operating parameters such as shear force, solution pH and a breakage period on floc strength and re-aggregation potential. Results indicated that the responses of flocs to different operating parameters depend on the coagulant used. The ability of floc to resist breakage decreased with the increase of shear force and breakage period. Floc strength properties were also measured in response to increasing shear force, with the results suggesting that the order of floc strength was TiCl$_4$ > PACl. Floc regrowth of the two coagulants after exposure to high shear was limited, and flocs formed by TiCl$_4$ displayed weaker recoverability. The flocs generated in acid conditions were more recoverable than those generated in alkaline conditions no matter which coagulant was used.

1. Introduction

Coagulation is a widely applied unit process for the removal of particles and organic matter present in water treatment works (WTW) [1]. 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 [2]. One property that may have a significant impact at water treatment works is the potential for flocs to regrow after being broken. Characteristics of flocs after flocculation also cause a critical effect on solid/liquid separation process [3]. Therefore, flocs formed are strong enough to resist rupture under exposure to shear force and have a good recovery capacity.

Floc growth is a process between the balance of floc formation and breakage [4–8]. Boller and Blaser [9] reported that small particles generally had lower removal efficiency by flocculation, since smaller particles generally settled down more slowly than larger particles of similar density. Li et al. [10] also found that broken flocs were difficult to regrow. Reduced floc size slows down the sedimentation rate and change particle transport mechanisms [11,12].

Some researchers found that regrowth of chalk aggregates could be reversible after high shear force was applied [13]. Chaignon et al. reported that the flocs formed by charge neutrality had complete recoverability [14]. Therefore, floc strength and recoverability are considered as an important parameter to provide valuable information in understanding the performance of a novel coagulant. Floc aggregation depends on not only characteristics of water source and coagulants, but also various water quality parameters, such as applied shear force, solution pH, breakage period, etc. [15,16].

Due to the effectiveness in treating a wide range of waters at a relatively low lost, researches on polyaluminum chloride (PACl) have rapidly developed [17,18]. However, aluminum salts are suspected to be harmful to human and living things [19]. In addition, the main drawback of the flocculation process using aluminum salt coagulants is a large amount of sludge produced, which still needs to be disposed of either into landfills or dumped into the ocean. To resolve the problem of sludge disposal, Shon et al. used TiCl$_4$ as a coagulant and the Ti-salt flocculated sludge was recycled to produce valuable by-product namely TiO$_2$ [20,21]. TiO$_2$ was the most widely used metal oxide for environmental applications as photocatalyst, cosmetics, paints, electronic paper, and solar cells [20,22,23]. Therefore, recycling of Ti-flocculated sludge offers a novel solution to sludge disposal from water and wastewater treatment plants associated

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with production of TiO_2 with a wide range of environmental applications.

While the major coagulation performance, as well as removal mechanisms of the pollutants by $TiCl_4$, was studied recently, few researchers have focused on the breakage and regrowth nature of flocs coagulated by $TiCl_4$. In this study, breakage and regrowth properties of flocs formed by $TiCl_4$ and PACl under different conditions in terms of various shear force, solution pH and breakage period were comparatively investigated. The relationship between floc strength and coagulation mechanisms was also discussed.

2. Experimental

2.1. Water used in this study

The water sample used in this study was withdrawn from Queshan Reservoir, an important drinking water source in Jinan, China. The water was collected in winter season, January 2010 and the water temperature was at 4–8 °C. The turbidity, UV_{254} absorbance, (dissolved organic carbon) DOC, chemical oxidation demand (COD_{Mn}), zeta potential and pH was 1.05 ± 0.03 NTU, 0.05 ± 0.002 cm^{-1}, 1.686 ± 0.05 mg/L, 2.50 ± 0.20 mg/L, -12.7 to -11.5 mV and 8.34–8.53, respectively.

2.2. Preparation and characteristics of coagulants

$TiCl_4$ stock solution (20%, density = 1.148 g/mL) was obtained from Photo & Environment Technology Co. Ltd. (South Korea).

PACl with a basicity value (B, OH/Al molar ratio) of 2.0 was synthesized. The procedures of PACl preparation are described as follows [24]: predetermined amount of $AlCl_3 \cdot 6H_2O$ and Na_2CO_3 powder was fully mixed and then slowly added into deionized water at constant speed for 30 min while stirring at 70–80 °C to obtain the desired basicity value of PACl. The mixture was stirred until no bubbles were formed and the solution became transparent. The product was allowed to keep more than 24 h before the properties of the coagulant were examined. Here the aluminum content was measured by ethylenediaminetetraacetic acid (EDTA) complexometric titration [25]. All the reagents used in the preparation of PACl were of analytical pure grade and deionized water was used for the preparation of all the solutions.

2.3. Jar-test

Coagulation was conducted using a jar tester (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) at different coagulant dosages and different initial pH. A two-stage mixing process, including rapid (1.5 min stage at 200 rpm) and slow mixing (20 min stage at 40 rpm) was followed by a 20 min settling period, after which the supernatant samples were collected using a syringe from about 2 cm below the water surface for the measurements of turbidity, UV_{254} absorbance, zeta potential and DOC. The samples were prefiltered through a 0.45 μm fiber membrane before testing for UV_{254} (absorbance at 254 nm using a UV-754 UV/VIS spectrophotometer) and DOC (measured by a Shimadzu TOC-VCPH analyzer), while the turbidity was measured without microfiltration using a 2100P turbidimeter (Hach, USA) and zeta potential was analyzed with a Zetasizer 3000HSa (Malvern Instruments, UK). Coagulation experiments at different initial pH were conducted after optimal coagulant dosages were determined. HCl and NaOH solutions were added to adjust the initial pH.

2.4. Floc formation, breakage and regrowth

Flocs were formed by performing a series of jar tests. However, after 20 min of slow growth phase, the effect of increasing shear force was investigated by increasing mixing speed to 75, 100, 150, 200, 300 rpm on the jar tester for 5 min, followed by another slow mixing at 40 rpm for 20 min for flocs to reform. The dynamic floc sizes were measured using laser diffraction Mastersizer 2000 (Malvern, UK) as coagulation and flocculation processes proceeded. The suspension was monitored through optical unit of Mastersizer and 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.

While the rate at which a floc size decays on exposure to shear is an indication of the floc strength, the relationship between the applied shear and broken floc size has been used by many researchers to evaluate the floc strength [5,26–30]:

$$\log d = \log C - \gamma \log \mathrm{rpm} \tag{1}$$

Where d is the broken floc diameter (μm), C is floc strength, γ is stable floc size exponent, rpm is the imposed shear speed.

Then, the broken floc size d after 5 min shear was plotted against rpm on a log–log scale, and the slope of the line ($-\gamma$) indicated the rate of the degradation. γ represented the floc strength. A larger γ was an indication of the flocs that are more prone to break into smaller sizes with the increase of shear force.

In order to investigate the effect of solution pH on floc breakage and regrowth for PACl and $TiCl_4$, the pH was adjusted to 5, 6, 8 and 10. The procedures of coagulation tests were a rapid mixing at 200 rpm for 1.5 min, followed by a slow mixing phase at 40 rpm for 20 min. Flocs were then exposed to an increased shear of 200 rpm for 5 min followed by a restoration of the 40 rpm slow mixing phase for 20 min.

In addition, a series of jar tests were conducted to investigate the effect of breakage period on floc strength and recovery ability. Coagulation experiments were carried out as follows: a rapid mixing at 200 rpm for 1.5 min, followed by a slow period at 40 rpm for 20 min, followed by the breakage phase at fixed 200 rpm. Two separate breakage periods were investigated: (i) a long breakage period of 10 min and (ii) a short breakage period of 1 min. When the breakage phase was completed, slow mixing at 40 rpm was reintroduced for further 20 min.

2.5. Floc strength and recovery factors

Floc strength factor (S_f) and recovery factor (R_f) are well-established parameters of describing floc strength and recoverability and can be calculated as follows [1,5,15]:

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

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

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.

Here the strength factor is an indicative 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 is expressed as an equivalent volumetric diameter, and d_{50} was selected as representative floc size in this paper [31], which refers to the 50 percentile floc size.
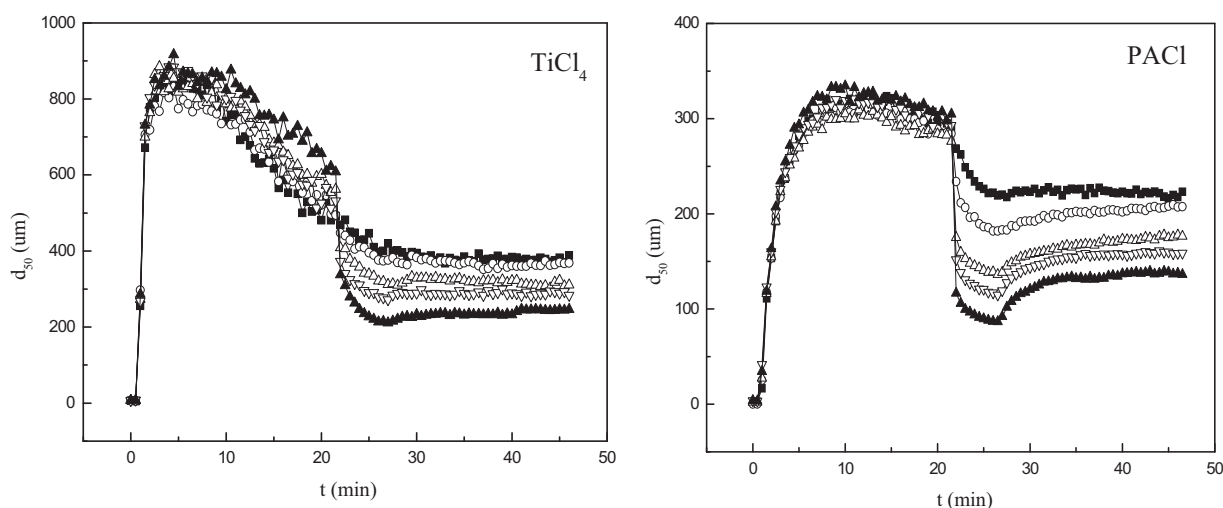
Fig. 1. Effect of different shear forces on breakage and regrowth of different coagulant flocs (d_{50}) (■ 75 rpm, ○ 100 rpm, △ 150 rpm, ▽ 200 rpm, ▲ 300 rpm).

3. Results and discussion

3.1. Coagulant dose optimization

Through standardized jar testing procedures, it showed that the optimum dosage for TiCl$_4$ was 35 mg/L as Ti, which yielded an optimum UV$_{254}$, COD$_{Mn}$ and DOC removal efficiency of 71.1%, 50.8% and 77.9%, respectively. While the corresponding values for PACl were 36.0%, 21.3% and 40.3%, respectively, at dosage of 12 mg/L as Al. Zeta potential under optimum dosage was +4.2 mV for PACl and −3.23 mV for TiCl$_4$, which indicated that (i) adsorption of (natural organic matter) NOM and NOM-complexes (insoluble charge neutral or charged products because of charge neutralization and adsorption between cationic metal species and anionic NOM) on amorphous Al(OH)$_3$ (s) was an important mechanism involved in NOM removal besides charge neutralization. Similar results were found by Gregor et al. [32]. They reported that a combination of charge neutralization and entrapment/adsorption of NOM onto metal precipitates was the major floc formation mechanism for PACl; (ii) physical entrapment of colloids within coagulant precipitates and adsorption played an important role in the process of flocculation with TiCl$_4$ besides charge neutralization.

3.2. Effect of shear force on floc

The growth phase of flocs throughout the TiCl$_4$ coagulation indicated a rapid growth during the first 3 min, giving the mean floc size of 837.4 μm, followed by 7 min stable stage of floc size. A slight decrease in floc size during the subsequent 11.5 min was then observed. The rapid growth of floc size in the first 3 min was likely due to the aggregation of particles. The extended mixing resulted in the breakage of the aggregated flocs during the subsequent 11.5 min. Due to the floc breakage in the slow stir phase, floc size at the end of the slow stir period was selected to calculate the floc strength and recovery factors later. In contrast, the floc size after PACl coagulation was more stable than that of TiCl$_4$. The breakage of flocs seldom appeared during the growth period.

To investigate the effect of high shear on floc breakage and regrowth, the suspension was exposed to the increasing shear force from 75 rpm to 300 rpm after a slow mixing phase. Fig. 1 shows the change of breakage and regrowth of different coagulant flocs (d_{50}) after exposure to different shear force for duration of 5 min. The responses of floc d_{50} to the increasing shear force were similar for both TiCl$_4$ and PACl. For both TiCl$_4$ and PACl, the d_{50} decreased with the increasing shear force. At the slow mixing speed (75 and 100 rpm), there was a comparatively gradual decline of floc size. However, a significant drop in floc d_{50} was immediately found after the introduction of the increasing shear at 150 rpm and above. After the stirring rate was reduced to 40 rpm, the regrowth of flocs occurred. However, the flocs had variable regrowth depending on the intensity of breakage shear and did not regrow to their original floc sizes before breakage. Therefore, floc breakage and regrowth were intensively affected by the shear force. After 20 min of the regrowth, no further significant growth in floc size was observed. The flocs were aggregated to a new steady state of floc size. For different shear forces, the shear did not break the flocs to the same degree (Fig. 1).

Table 1 shows the strength and recovery factors calculated by Eqs. (1) and (2). The strength factors decreased with the increasing shear force. Except the shear force, breakage and reformation of flocs were also controlled by the characteristics of coagulants. Flocs formed by TiCl$_4$ had better ability to resist shear with a higher S_f than those by PACl under the same conditions, which would not correspond with the general conception that smaller flocs tend to have greater strength than larger flocs [33]. While, flocs formed by TiCl$_4$ presented significantly weak recovery ability as reflected by lower R_f (Table 1). Compared with the flocs formed by PACl, the regrowth of flocs formed by TiCl$_4$ was barely observed after the breakage period.

To quantitatively compare the difference of TiCl$_4$ and PACl in the response of floc d_{50} to increased shear, the d_{50} of the broken flocs after 5 min shear was plotted against the rpm on a log–log scale (Fig. 2). It can be found that a straight line could be drawn through the data ($R^2 > 0.999$). As mentioned above, the slope (γ) of the line indicated the degradation rate of floc size. The larger the slope (γ) was, the weaker the floc was. As was shown in Fig. 2, TiCl$_4$ gave more gentle decrease in floc size than PACl, as reflected by the

Table 1
Strength and recovery factors of flocs (d_{50}) after 5 min of breakage followed by regrowth for 20 min under different shear force.

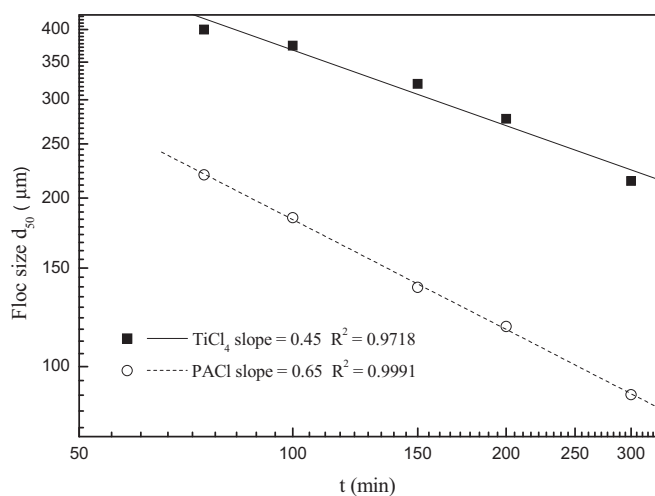| Coagulant	G/RPM				
	75	100	150	200	300
Strength factor (%)					
PAC	70.5	61.4	47.2	38.3	27.9
TiCl$_4$	81.4	75.7	56.9	52.1	35.3
Recovery factor (%)					
PACl	2.9	17.0	20.9	20.6	20.0
TiCl$_4$	0.0	0.0	0.0	4.7	7.7

Fig. 2. Floc breakage rates of TiCl$_4$ and PAC coagulants.

lower value of γ (0.45). PACl gave more rapid drop in floc size and a higher γ value. Thus, the flocs formed by TiCl$_4$ were much stronger while those formed by PACl were more prone to be broken with increasing shear force. The results correspond well with the results obtained via the analysis of strength factor.

The coagulation mechanism had a considerable impact on floc strength and regrowth potential. For PACl, a combination of charge neutralization and entrapment/adsorption of NOM onto metal precipitates was likely to be the primary route of floc formation. The lack of bridging bonds holding flocs together might partially explain why the flocs formed by PACl were smaller. In addition, PACl contains a range of preformed Al (III) hydrolysis species [34], which can be divided into three kinds of species by using ^{27}Al nuclear magnetic resonance (NMR) spectroscopy methods: the monomeric and dimetric aluminum species (denoted as Al$_m$), Al$_{13}$O$_4$(OH)$_{24}$$^{7+}$ (Al$_{13}$ for short) and large polymer aluminum species and solid phase Al(OH)$_3$ [35]. Generally, the Al$_m$ species in PACl can complex with humic and fulvic acids in NOM to form coordinated complexes, which are considered too strong to be broken easily. Then, the complexation would join to the large flocs by charge neutralization. In the case of TiCl$_4$, the flocs with loose and branchy structure might be formed by sweeping mechanism. Therefore, the regrowth of flocs was not relatively apparent after floc breakage, which was consistent with the view that adsorption and sweep flocs showed limited regrowth after breakage, while the flocs formed by charge neutralization have complete recovery ability [11,14]. Large flocs formed by TiCl$_4$ might be due to physical forces such as van der Waals force, rather than intra-molecular bond strength or there was not such a low ability to recover the floc size.

3.3. Effect of initial pH on floc

Fig. 3 shows the variations of floc sizes versus coagulation time at different pH. During the growth period, the average d_{50} size of flocs formed by PACl increased from 416.8 μm to 482.7 μm as pH increased from 5 to 6, but decreased to 279.6 μm at pH 8 and to 404.6 μm at pH 10. Floc sizes formed by TiCl$_4$ at pH 5, 6, 8 and 10 were 314.0 μm, 347.9 μm, 560.4 μm and 417.4 μm, respectively. In all cases, floc sizes immediately decreased with the increase of shear and the flocs began to reform when the shear was reduced. However, the flocs after being broken could not regrow to their original floc size regardless of any coagulant. The curves of floc size versus coagulation time were similar for both TiCl$_4$ and PACl while at the same pH condition, the extents of breakage and regrowth of flocs were different.

Table 2 shows the floc strength and recovery factors for TiCl$_4$ and PACl at different pH. In the case of TiCl$_4$, the strength factors with the variation of pH showed the following order: pH 5 < pH 6 < pH 8 < pH 10, while those of PACl indicated a reverse trend. Within the pH range investigated, the recovery factors decreased with the increasing pH regardless of what coagulant was used. It is worthwhile to note that the recovery factors of the flocs formed by TiCl$_4$ were much smaller than those by PACl. 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 [32]. In addition, flocs formed by charge neutralization have complete recovery ability, while the adsorption and sweep flocs show limited regrowth after breakage [11,14]. Based on the discussion above, the dominate NOM removal for TiCl$_4$ and PACl coagulants is likely to be the formation of insoluble precipitates and the subsequent charge neutralization at pH 5 and 6. However, at pH 8 and 10, adsorption on hydrolysis products was assumed to play an important role in coagulation process. Consequently, the flocs showed poor recoverability at high pH values.

The rate of floc formation with TiCl$_4$ coagulation increased with the increasing pH and the flocs rapidly grew to 745.5 μm in 2.5 min at pH 8 (298.2 μm/min). This might be attributed to (a) charge neutralization of negatively charged NOM followed by aggregation of the destabilized particles and (b) formation of flocs composed of metal hydroxide precipitates accompanied or followed by sweep flocculation of colloidal particles. In the case of PACl, the maximum floc size was obtained at pH 6 (482.7 μm, much smaller than that of TiCl$_4$), while the maximum growth rate was observed at pH 10 (115.6 μm/min), only less than a half of that of TiCl$_4$. The maximum NOM removal and the largest floc (482.7 μm) formed at pH 6 could be attributed to the combined mechanism: Al$_m$ species reacted with NOM and neutralized or substantially reduced the negative charges on the NOM, promoting their adsorption onto Al(OH)$_3$ (s) [36].

3.4. Effect of breakage period on floc

The effect of breakage period (1 min and 10 min) of high shear (200 rpm) on floc breakage and regrowth was investigated in this section (Figs. 4 and 5). In all cases, the floc size immediately reduced with the increasing shear. In the shear period of 10 min (Fig. 5(a)), d_{50} size of flocs after the exposure to shear was about 243 μm for TiCl$_4$ while the flocs formed by PACl were broken into smaller flocs with 111 μm size. As the shear was reduced again, the flocs began to regrow. However, irreversible breakage was usually observed. The initial floc sizes were not recovered after breakage. Flocs formed by TiCl$_4$ regrew up to 244 μm size, while the flocs by PACl increased in equivalent diameter (140 μm). Compared with the long period shear, the flocs were able to resist short period shear with the floc size of 346 μm for TiCl$_4$ and 142 μm for PACl after the breakage period. The corresponding floc sizes after the regrowth period was 383 μm (TiCl$_4$) and 189 μm (PACl), respectively (Fig. 4(a)). Floc par-

Table 2
Strength and recovery factors of flocs (d_{50}) after 5 min of breakage followed by regrowth for 20 min under different pH.

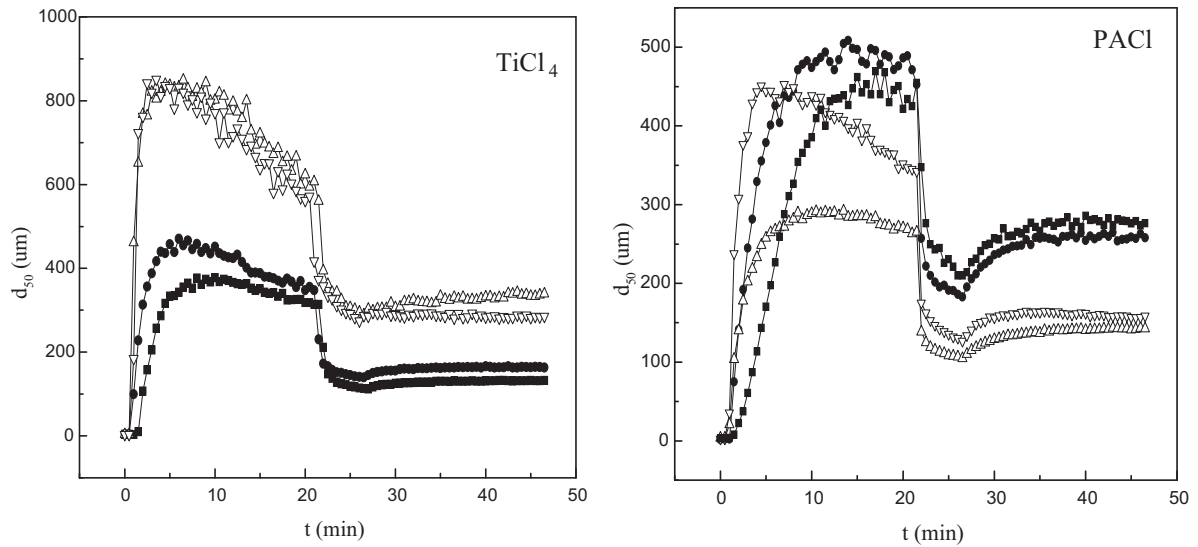| Coagulant	pH			
	5	6	8	10
Strength factor (%)				
PACl	50.4	37.8	37.5	31.3
TiCl$_4$	36.5	41.0	53.1	67.6
Recovery factor (%)				
PACl	32.2	25.1	21.6	11.5
TiCl$_4$	10.6	10.0	8.2	4.0

Fig. 3. Effect of initial pH changes on breakage and regrowth of different coagulant flocs (d_{50}).

ticle size distribution (PSD) was also analyzed in this section, and was shown in Fig. 4(b) and Fig. 5(b). In terms of short breakage period, analysis of the floc PSD shows that (i) an apparent shift in the major peak after breakage to under half the original value was

observed for PACl, while, comparatively, small extent of shift in the major peak was found; (ii) there was obvious increase in the smaller floc size between 10 and 100 μm for PACl after breakage. But for TiCl$_4$, minor change was observed; (iii) after the regrowth
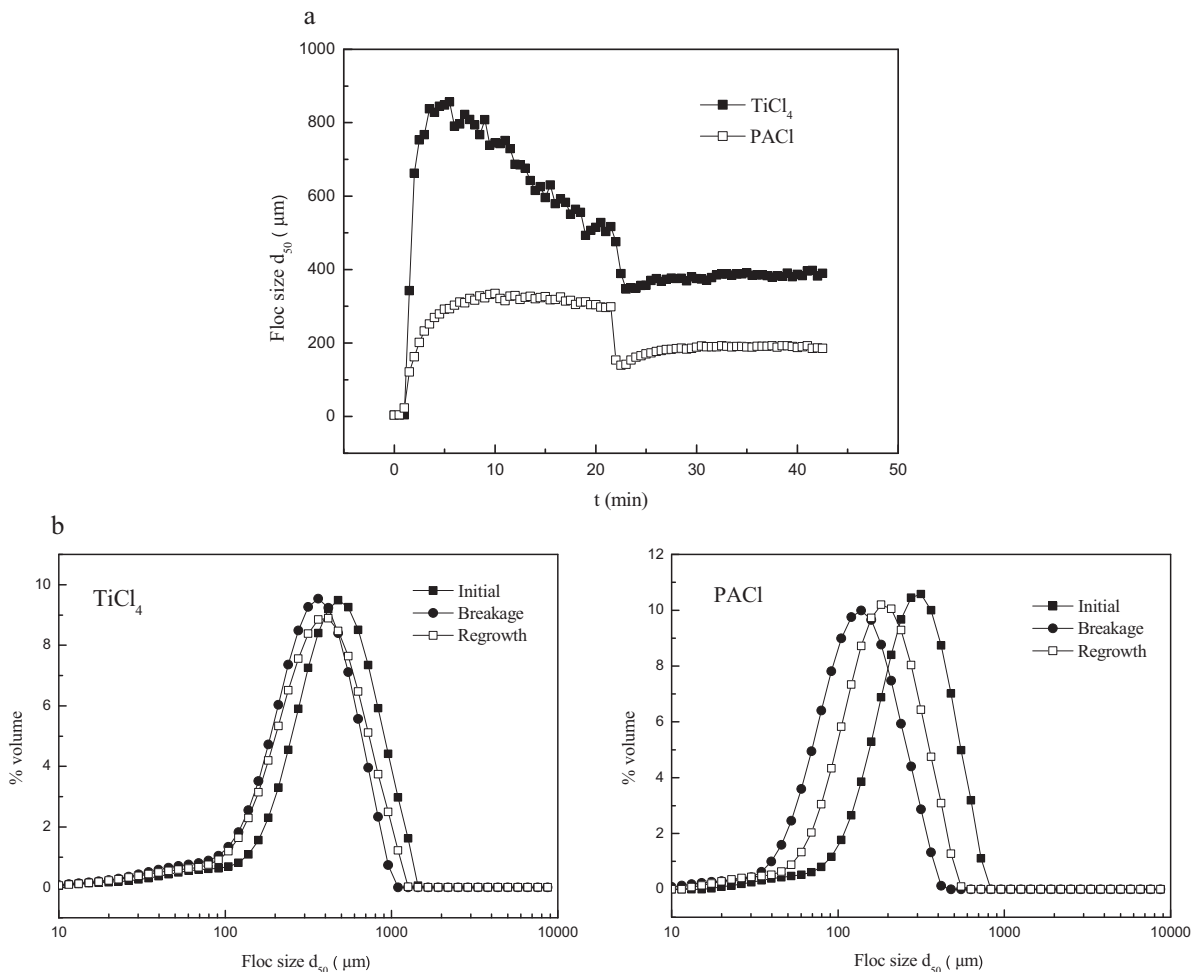

Fig. 4. Short shear period: (a) Breakage and regrowth profile of the NOM flocs formed by TiCl$_4$ and PACl; (b) particle size distributions of the NOM flocs after growth, breakage and regrowth after 1 min high shear time.
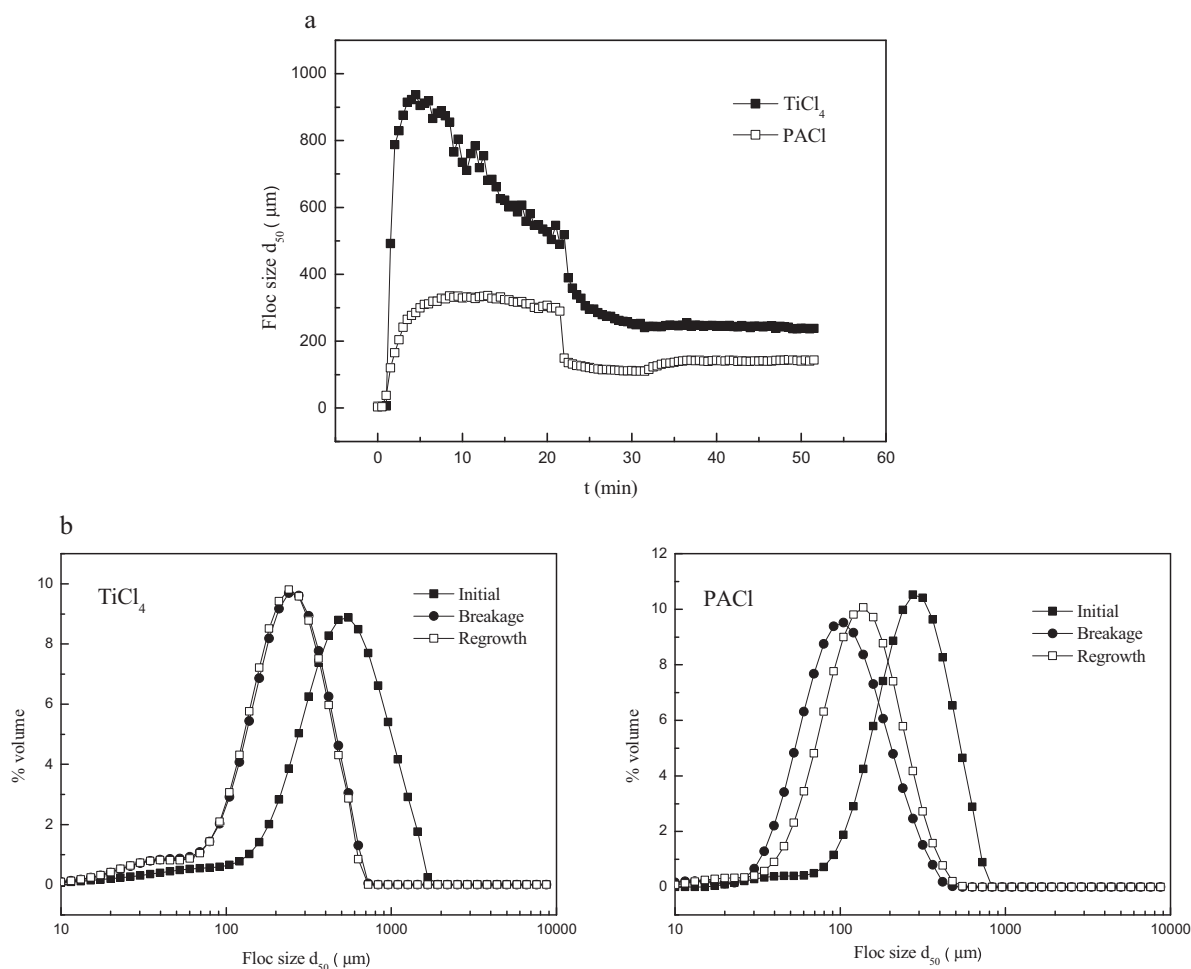
Fig. 5. Long shear period: (a) Breakage and regrowth profile of the NOM flocs formed by TiCl$_4$ and PACl; (b) particle size distributions of the NOM flocs after growth, breakage and regrowth after 10 min high shear time.

phase, for PACl, this small peak was reduced with a comparatively apparent shift to the right of the major peak compared with TiCl$_4$. In terms of long breakage period, similar conclusions were drawn as to PACl. While, for TiCl$_4$, few change is observed between the floc PSD before and after regrowth. That is in accordance with the conclusions obtained above, that is, flocs formed by TiCl$_4$ showed very weak recovery ability after long breakage period.

The strength and recovery factors for d$_{50}$ under different breakage periods are shown in Table 3. A reduction in the time exposed to a similar shear showed both a significant decrease in floc breakage and an increase in floc regrowth [15]. This shows that the flocs could resist a certain amount of shear. The extent of floc breakage was much less at the reduced shear period of 1 min for both TiCl$_4$ and PACl, with floc strength factors increasing by an additional 17–26 from the long shear period (Table 3). Different degrees of recovery ability were observed in terms of both the coagulant and breakage period. Compared with the short period shear, recovery ability of the flocs decayed after long period shear for both coagulants. How-

ever, the recovery factor of flocs formed by PACl was larger than that by TiCl$_4$. In the case of 10 min shear period, the regrowth of flocs formed by TiCl$_4$ was poor with a recovery factor of 0.3, which was considerably lower than the value of 14.4 for the flocs formed by PACl. Consequently, the floc aggregation was also affected by the breakage period besides shear force and solution pH as mentioned above. Recovery ability of flocs provided some indication of internal bonding structure of the floc. The irreversible flocs formed by PACl and TiCl$_4$ after breakage were seen as an evidence that the flocs not only were formed by charge neutralization mechanism and but also might be held together by a chemical bonding rather than the physical bond.

4. Conclusions

The growth, breakage and regrowth nature of aggregated flocs formed by TiCl$_4$ and PACl was comparatively investigated with Queshan reservoir water under different operating parameters such as shear force, solution pH and breakage period. Relationship between floc characteristics and coagulation mechanisms were also discussed. For the given optimum coagulation dosage, the flocs formed by TiCl$_4$ showed larger floc strength than those by PACl and with larger average size during growth period, while flocs formed by PACl presented a better recovery ability. Floc strength decreased with the increase of shear force and breakage period. For both TiCl$_4$ and PACl, the flocs formed in acid conditions were more recoverable than those formed in alkaline conditions. Regardless of TiCl$_4$

Table 3
Strength and recovery factors of flocs (d_{50}) after different breakage periods[a].

Coagulant	Strength factor (%)		Recovery factor (%)	
	long	short	long	short
PACl	29.8	48.2	14.4	27.4
TiCl$_4$	46.9	74.0	0.3	24.2

[a] Short breakage = 1 min; long breakage = 10 min.

or PACl, limited regrowth of the flocs after breakage suggested that the flocs not only were formed by charge neutralization mechanism and but also might be held together by a chemical bonding rather than the physical bond.

Acknowledgements

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