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Polymeric metal coagulants are increasingly used to improve the coagulation/flocculation process efficiency, yet the research on the development of titanium and particularly polytitanium salts remains very limited. In this study, the performance of recently developed polytitanium tetrachloride (PTC) coagulant was compared with both titanium tetrachloride (TiCl_4) and a commonly used coagulant, ferric chloride (FeCl_3) in terms of water quality parameters and floc properties. Compared with FeCl_3 coagulant, titanium-based coagulants had broader region of good flocculation in terms of pH and coagulant dose. Further, they achieved higher removal of UV_{254} and turbidity but lower dissolved organic carbon (DOC) removal. Charge neutralisation, physical entrapment of colloids within coagulant precipitates and adsorption were found to be the main coagulation mechanisms for TiCl_4 while sweep coagulation and adsorption were found to play a more important role for both FeCl_3 and PTC. The aggregated flocs formed by PTC flocculation had the largest floc size of around $836\text{ }\mu\text{m}$ with the highest floc growth rate. A little distinction of the floc strength factor was found among the coagulants tested (i.e. 44.8%, 44.2% and 38.9% for FeCl_3 , TiCl_4 and PTC respectively) while TiCl_4 coagulant yielded the flocs with the highest floc recovery factor. This study indicates that Ti-based coagulants are effective and promising coagulants for water purification. Besides, the resulted flocculated sludge can be recycled and produce functional TiO_2 photocatalyst which is a significant advantage over conventional coagulants.

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Natural organic matter (NOM) is generally composed of a variety of organic compounds with a wide range of molecular weights [1]. It has been found to be responsible for odour, taste, colour and bacterial regrowth in potable water and has also the potential to form carcinogenic disinfection-by-products (DBPs) [2]. Humic acid (HA) consists of polycyclic aromatic macromolecules with a variety of oxygen-containing functional groups, and accounts for about 50–90% of the total freshwater organic matter [3]. Because HA forms the major component of NOM present in natural freshwater, it has therefore has been recognised as an important generator of DBPs [4,5]. The effective removal of HA present in water has thus become increasingly crucial in modern water treating processes.

Coagulation and flocculation are the most commonly used processes to remove HA and colloidal particles in drinking water, seawater and wastewater [6].

Aluminium (Al) and iron (Fe) salts are widely employed as effective coagulants as they showed good performance for the removal of a broad range of impurities including organic substances such as HA [7]. However, the main drawback of conventional coagulants relies on the large quantity of sludge produced after treatment. In fact, the treatment of sludge after coagulation/flocculation is considered to be one of the most costly and environmentally problematic challenges of all water treatment processes [8,9]. To circumvent the issue of sludge disposal, a novel titanium-based coagulant has been proposed by Shon et al. [10]. Titanium tetrachloride (TiCl_4) was investigated as an alternative coagulant and showed comparable or higher performance than conventional Al and Fe salts [11]. Besides, TiCl_4 coagulant has been shown to produce larger flocs with higher growth rate resulting in

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better settleability. The main advantage of TiCl_4 is that the flocculated sludge can be recycled to produce a valuable by-product via calcination: namely titanium dioxide (TiO_2) [12–15]. TiO_2 is the most widely used metal oxide with wide applications in paints, cosmetics, solar cells, photocatalysts or electronic paper [16,17]. Another advantage of Ti-based coagulants compared to conventional Al and Fe coagulants relies on the reported low toxicity of titanium and relative compounds. In fact, they are rarely included in any water quality guidelines [14,18,19]. Titanium is one of the most abundant elements on the earth and is found in almost all living things, rocks, water bodies, and soils. According to Emsley [20], titanium is non-toxic, even in large doses and does not play any adverse or toxicity role inside the human body. An estimated quantity of 0.8 mg of titanium is ingested by humans each day, but most passes through without being absorbed. Because it is biocompatible (it is non-toxic and is not rejected by the body), titanium is used in a gamut of medical applications including surgical implants and implants, such as hip balls and sockets (joint replacement) that can stay in place for up to 20 years. Titanium has the inherent ability to osseointegrate, enabling use in dental implants that can remain in place for over 30 years.

Finally, the World Health Organization's (WHO) environmental health guidelines call for a Ti concentration in drinking water supplies of 0.5–15 $\mu\text{g/L}$ [18] and results from our previous study [10] showed that only 10 $\mu\text{g/L}$ of Ti salts remained in the supernatant after the TiCl_4 flocculation of wastewater.

However, one of the main drawbacks of titanium salts is related to the charge neutralisation (adsorption–destabilisation) of optimum coagulant efficiency occurring at low pH of 3.0–5.0 after coagulation due to the large quantity of H^+ released during the titanium hydrolysis process [10,11]. Based on earlier studies on inorganic polymeric coagulants [21–23], this issue could be resolved by developing polytitanium salts that might minimise the release of H^+ through prehydrolysed titanium coagulants. Also, similar to other inorganic polymer coagulants, polytitanium salts may perform better than titanium salts in terms of organic matter removal and pH dependence. Besides, the advantage of using prehydrolyzed coagulants is that the hydrolysis ions occurs during the preparation stage of the coagulants, not after their addition to the real water, which consequently results in a better control of the coagulation process [24]. Furthermore, they are useful for reducing the need for pH adjustment through prehydrolysis, less sensitive to low temperature, and showed great performance in removing numerous pollutants [22,25]. Additionally, they are usually cheaper than organic polymeric coagulants [26]. The first study to synthesis and characterise polytitanium salts as coagulants has been recently explored by Zhao et al. [27]. Polytitanium tetrachloride (PTC) solutions with different basicity values B (i.e. OH/Ti molar ratio) were prepared using a slow alkaline titration method. Compared to TiCl_4 , higher or comparable turbidity and organic matter removal efficiency was achieved by PTC with improved floc characteristics in terms of size, growth rate, and structure. Besides, the sludge produced after PTC flocculation can also be recycled to prepare functional TiO_2 photocatalyst which showed similar performance as commercially available P-25 TiO_2 for the photodecomposition of acetaldehyde.

Floc characteristics are key parameters influencing coagulation performance in the solid/liquid separation process [28]. Smaller particles settle more slowly than larger particles of similar density [29]. Thus, small particles generally have lower removal efficiency by coagulation-flocculation than larger particles. The ability of flocs to resist breakage and recoverability after they have been broken has a significant impact on water treatment plants (WTP), since the unit processes in WTP have prevalent regions of high shear [30]. Floc strength and recoverability are therefore consid-

ered as important parameters in understanding coagulation behaviour.

In this study, coagulation performance of PTC and TiCl_4 coagulants was assessed in terms of turbidity, dissolved organic carbon (DOC), and UV_{254} absorbance, zeta potential and floc size and then compared with a commonly used coagulant, namely FeCl_3 . Furthermore, a detailed investigation was also conducted to better understand the growth, breakage and re-growth of flocs formed by all three coagulants.

2. Materials and methods

2.1. Coagulants and test water

TiCl_4 solution ($\geq 99\%$ purity) was obtained from Sigma Aldrich (Australia). Stock solution of TiCl_4 was prepared by slowly adding a predetermined volume (i.e. 46.4 mL) of concentrated TiCl_4 solution to cubes of frozen deionized water drop by drop under continuous stirring to obtain a final 20% w/w TiCl_4 solution (density $\rho = 1.26 \text{ g/mL}$). Stock solution of FeCl_3 was prepared at a concentration of 10 g/L by dissolving 2 g of powder in 200 mL of deionized water. The preparation of PTC coagulant can be found elsewhere [27]. In brief, a predetermined amount (i.e. 63.3 mL) of sodium hydroxide (NaOH) solution (200 g/L) was added to 200 mL of the TiCl_4 (20%) solution using a slow alkaline titration method under intensive agitation. In their study, Zhao et al. [27] found that PTC coagulant with a B value (i.e. OH/Ti ratio) of 1.5 achieved the best performance and this value was therefore chosen for this study. It should be noted that coagulant dose is calculated as mmol Ti/L and mmol Fe/L for titanium coagulants and FeCl_3 , respectively.

A concentrated stock solution of HA (1.0 g/L) was prepared by dissolving 1.0 g of HA (technical grade, Sigma–Aldrich, Australia) directly in deionized water. The synthetic water used for the coagulation experiments was prepared by diluting the HA stock solution with tap water to obtain a final HA concentration of 10 mg/L. The raw water turbidity was increased by adding kaolin to obtain a final turbidity ranging from 15 NTU to 25 NTU. The measured UV_{254} absorbance, DOC, zeta potential and pH of the prepared synthetic water was: $0.257 \text{ cm}^{-1} \pm 0.04 \text{ cm}^{-1}$, 8.04 mg/L $\pm 0.74 \text{ mg/L}$, $-39.1 \text{ mV} \pm 1.3 \text{ mV}$ and 7.7 respectively.

2.2. Jar-test

Standard jar tests were conducted using a programmable jar-tester (PB-900TM, Phipps and Bird, USA). After the coagulant was added to 500 mL of the synthetic water, rapid mixing (i.e. 200 rpm) was applied for 1.5 min followed by slow mixing at 40 rpm for a duration of 20 min which was finally followed by 20 min of quiescent settling. Water samples were collected from 2 cm below water surface for measurements. The water samples were pre-filtered using 0.45 μm membrane syringe filter before testing UV_{254} (absorbance at 254 nm using a UV-754 UV/VIS spectrophotometer) and DOC (measured by a Shimadzu TOC-VCPH analyser). Turbidity and floc zeta potential were directly measured without filtration using a 2100P turbidimeter (Hach, USA) and Zetasizer (Malvern Instruments, UK), respectively.

Coagulation/flocculation experiments under different pH and coagulant dose conditions were conducted during preliminary tests in order to determine the region of good flocculation for each coagulant. For these preliminary experiments, the target coagulation pH value was achieved by adding appropriate quantities of HCl and NaOH solutions (0.1 M).

2.3. Floc characterization

A laser diffraction instrument (Mastersizer 2000, Malvern, UK) was used to measure dynamic floc size as the coagulation and flocculation process proceeded. The schematic diagram of the on-line monitoring system for dynamic floc size is detailed in Fig. 1. The median equivalent diameter, d_{50} , was selected as the representative floc size, although the same trends were observed for d_{10} and d_{90} floc sizes.

To investigate the floc properties (i.e. strength and recoverability), the procedures of coagulation tests were as follows: Following the floc growth phase (i.e. 15 min at 40 rpm), the aggregated flocs were exposed to a shear force of 200 rpm for 1 min, followed by a slow mixing of 40 rpm for 20 min to allow floc regrowth. Floc strength factor (SF) and recovery factor (RF), which are used to evaluate the stability and propensity for formation of the flocs were determined as follows [6,31]:

$$SF = \frac{d_2}{d_1} \times 100 \quad (1)$$

$$RF = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \quad (2)$$

where d_1 is the average aggregate size of the plateau before applying the shear force, d_2 is the average aggregate size after aggregate breakage, and d_3 is the average aggregate size after regrowth to a new plateau.

Greater SF values are indicative of flocs that are better able to resist shear. These flocs are thus considered to be stronger than those in a suspension with a lower SF. Similarly, an increase in the RF value indicates the presence of flocs that have better regrowth after exposure to high shear.

The floc growth rate was also determined by calculating the slope of the rapid growth region [32]:

$$\text{Growth rate} = \frac{\Delta_{\text{size}}}{\Delta_{\text{time}}} \quad (3)$$

Previous studies have determined the fractal dimension (FD) of formed flocs by using Mastersizer 2000 [6,33,34]. The total scattered light intensity I , the scattering vector Q and the FD followed a power law as follow [35]:

$$I \propto Q^{-FD} \quad (4)$$

The scattering vector Q is defined as follow [34]:

$$Q = \frac{4\pi \sin(\frac{\theta}{2})}{\lambda} \quad (5)$$

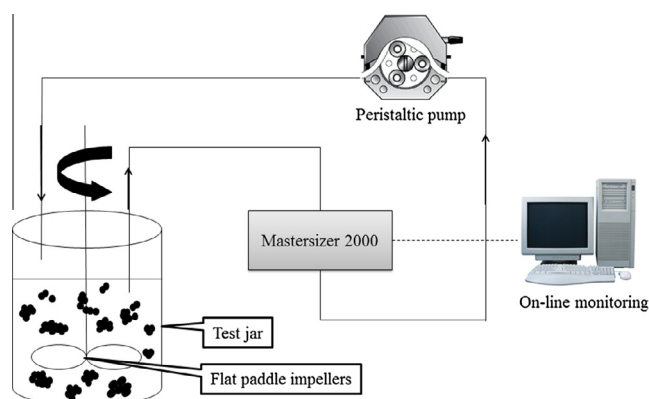


Fig. 1. Schematic diagram of the on-line monitoring system for the dynamic floc sizes.

where n , λ and θ are respectively the refractive index of the medium, the laser light wavelength in vacuum, and the scattering angle.

Densely packed flocs will have higher DF value while low DF values result from high branched and loosely bound structure.

3. Results and discussion

3.1. Determination of flocculation region

Samples of flocculation experiments were classified into three categories to determine the region of good flocculation: (a) no visible flocculation (i.e. either clear liquid samples with no observed hydrolysis or turbid samples with obvious hydrolysis but no visible flocs); (b) unsatisfactory flocculation with turbidity removal efficiency < 90%; (c) good flocculation with turbidity removal efficiency > 90% and (d) optimum flocculation conditions with highest turbidity removal efficiency. The data of category (c) defined the region of good flocculation for each coagulant as shown in Fig. 2.

Fig. 2 shows that the flocculation region of titanium-based coagulants (i.e. PTC and TiCl_4) occurred in a broader pH environment and dosages than FeCl_3 coagulant. For each coagulant tested, pH 7 seemed to be the optimum pH where the highest turbidity removal was achieved. At this pH, PTC flocculated readily at each dosage tested whereas at pH 5, good flocculation was observed at dosages lower than 0.2 mmol Ti/L. These findings are not in good agreement with a previous study on PTC [27] where it was found that pH 9 was the optimum pH before coagulation in the dosage range 8–10 mg Ti/L. TiCl_4 showed very good performance for turbidity removal in the pH range 7–9 which is in accordance with several previous studies by Zhao et al. [11,12] where it was found that TiCl_4 coagulant displayed high and stable turbidity removal under alkaline conditions. In fact, at high pH, TiCl_4 coagulant is gradually hydrolysed, resulting in better turbidity removal. This also indicates that more hydroxide ions are required for TiCl_4 hydrolysis. However, the results obtained in this study also differed from another study on Ti-based coagulants where it was found that the flocculation region of titanium hydroxide was in the pH range 4–6 [19]. It has to be noted that titanium sulphate was used in this study; therefore that presence of SO_4^{2-} as counter ions (instead of Cl^-) may have an effect on the resulted region of good flocculation, especially on the pH range.

3.2. Coagulation performance: floc zeta potential, removal of turbidity, UV_{254} and DOC

Coagulation performance of the tested coagulants was investigated in terms of zeta potential, and removal of turbidity, UV_{254} and DOC, with the results being gathered in both Fig. 3 and Table 1.

Fig. 3 shows the changes in floc zeta potential which is generally used to evaluate the destabilisation ability of coagulants. Changes in floc zeta potential are also often regarded as an effective tool to investigate coagulation mechanism, which is usually explained in terms of charge neutralisation and sweep flocculation [36]. Under the optimum coagulant dose conditions, the floc zeta potential values after coagulation for FeCl_3 , TiCl_4 and PTC were -1.2 mV, -0.4 mV and -2.1 mV, respectively, suggesting that charge neutralisation plays a major role during the flocculation process of all three coagulants. Various studies from Zhao et al. [12,37] already demonstrated that the main coagulation mechanism for TiCl_4 was through charge neutralisation. In the case of FeCl_3 , Cheng [22] reported that the possible coagulation mechanisms arising between FeCl_3 and HA were charge neutralisation and adsorption. It was also stated that the fraction removed by

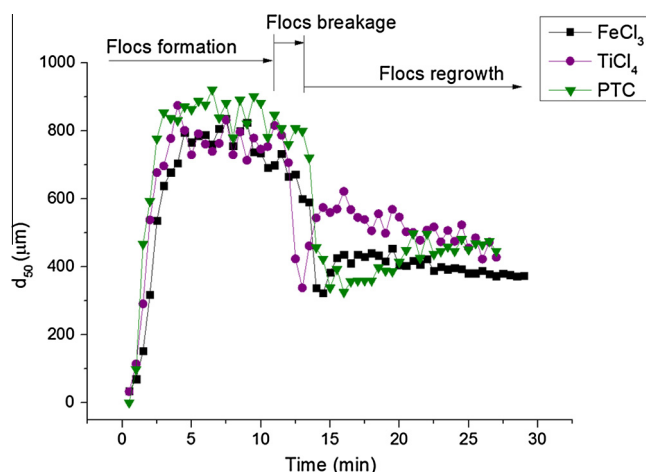


Fig. 4. Growth, breakage and regrowth profile of HA flocs formed by FeCl_3 , TiCl_4 and PTC under optimum dose conditions (the optimum coagulant dose conditions, see Table 1; Initial solution pH condition).

3.3. Dynamic variation of floc size during flocculation

Floc formation, breakage and regrowth process with FeCl_3 , TiCl_4 and PTC under optimum coagulant dose conditions were on-line monitored by using Mastersizer 2000 and the results are displayed in Fig. 4.

As shown in Fig. 4, the floc size gradually increased after the introduction of the slow mixing speed (i.e. 40 rpm) for all coagulants tested, reaching the stable plateau during slow stirring phase, which suggests that appropriate balance between floc growth and breakage was reached. When the shear force was then introduced (i.e. rapid mixing at 200 rpm for 1 min), the floc size immediately decreased, resulting in the flocs being up to 60% smaller than the original value. When the slow mixing speed was reintroduced, the flocs began to regrowth, but none of the flocs formed by all three coagulants recovered to the initial floc size.

Each tested coagulant exhibited different floc sizes and floc growth rates (Table 2). Compared to FeCl_3 , TiCl_4 and PTC had faster floc growth rate with larger floc size, indicating that TiCl_4 and PTC need shorter period to form larger aggregates. Boller and Blaser [29] explained that a short retention time coupled with larger floc size formation will likely lead to smaller and more compact flocculation and sedimentation units as larger particles generally settled down more rapidly than smaller particles of the same density. The floc growth rate during the coagulation process varied in the following order: $\text{PTC} > \text{TiCl}_4 > \text{FeCl}_3$ and the order of floc size d_1 was PTC (836.9 μm) $>$ TiCl_4 (764.3 μm) $>$ FeCl_3 (722.2 μm). These results clearly indicate the advantage of using titanium-based coagulants over Fe-salts since the resultant flocs are with much larger size regardless of floc growth, breakage and regrowth process. Besides, as it is known that fine flocs are more prone to suspend in the supernatant, larger flocs will then achieve better removal efficiency by settling. This may explain the lower turbidity removal efficiency of FeCl_3 compared to Ti-based coagulants.

3.4. Floc breakage and recovery

Floc strength factor (SF) and floc recovery factor (RF) were calculated using Eqs. (1) and (2) to investigate the floc strength and recoverability. Results are gathered in Table 2 and show that the SF of FeCl_3 , TiCl_4 and PTC were 44.8, 44.2 and 38.9 while the RF were 20.4, 42.0 and 20.5 respectively. Breakage and reformation of flocs are generally partly controlled by the characteristics of different coagulants. The FeCl_3 coagulants showed the highest SF but with no significant difference from that of TiCl_4 and PTC. The flocs formed by TiCl_4 showed the highest RF while FeCl_3 and PTC showed the lower but similar RF values. Previous studies have already reported that the flocs formed by sweep flocculation (i.e. FeCl_3 and PTC in this study) had weaker recoverability after breakage than those by charge neutralisation (i.e. TiCl_4 in this study) [38,39]. However, even though TiCl_4 showed the highest RF value, the flocs did not regrow to their initial size before breakage, suggesting that charge neutralisation is not the only coagulation mechanisms responsible for TiCl_4 coagulation. Gregor et al. [40] stated that the main removal route of HA via coagulation varies depending on the pH conditions as follow: precipitation by forming insoluble complexes at $\text{pH} < 6$, and adsorption of HA onto hydroxide solid at $\text{pH} > 6$. As the optimum coagulation pH for TiCl_4 was 7.0, adsorption of HA onto hydroxide solid might be the dominant removal mechanism. Zhao et al. [11] explained that the floc growth process for TiCl_4 coagulant could be interpreted as follow: During the first minutes, the floc size sharply increased due to charge neutralisation between negatively charged HA present in water and Ti^{4+} . As the coagulation process continued, the flocs aggregated to form even larger flocs (i.e. $d_{50} > 800 \mu\text{m}$) possibly resulted from the physical enmeshment of the colloids within the coagulant precipitates combined with chemical sorption. Then, the floc size slowly decreased (i.e. $d_{50} \sim 700 \mu\text{m}$) possibly due to the disturbance on the aggregated flocs on extended mixing.

Fig. 5 presents the particle size distribution (PSD) of the three coagulants before breakage, after breakage and after regrowth. Analysis of PSD showed that, for all tested coagulants, the size of the flocs after breakage is under half the original value. After regrowth, there is an obvious shift to larger sizes indicating the floc reformation after the breakage period. Compared to TiCl_4 , fewer changes were observed between the PSD before breakage and after floc regrowth for FeCl_3 and PTC which implies the poor floc regrowth after breakage and which is confirmed by the lower RF obtained for these two coagulants.

3.5. Floc structural analysis

The floc fractal dimension (FD) of all three coagulants was calculated based on Eqs. (4) and (5) to compare the floc compaction degree. Floc FD is another important parameter which influences floc density and thus affects solid/liquid separation process [41]. Results are presented in Table 2 and showed that the floc FD values followed the order of $\text{FeCl}_3 > \text{TiCl}_4 > \text{PTC}$. This is in accordance with a previous study [21] which demonstrated that the larger the floc size, the smaller the fractal dimension. Besides, it can be seen that the FD followed the same trend as the SF which indicates that flocs

Table 2

Summary of floc size before breakage (d_1), after breakage (d_2) and after regrowth (d_3), floc growth rate, strength and recovery factors and fractal dimension (FD) of the formed flocs for each coagulant tested.

Coagulants	d_1 (μm)	d_2 (μm)	d_3 (μm)	Floc growth rate ($\mu\text{m}/\text{min}$)	SF (%)	RF (%)	FD
FeCl_3	722.2	323.2	404.6	162.90	44.8	20.4	2.51
TiCl_4	764.3	338.3	517.1	248.50	44.2	42.0	2.48
PTC	836.9	325.7	430.6	278.90	38.9	20.5	2.40

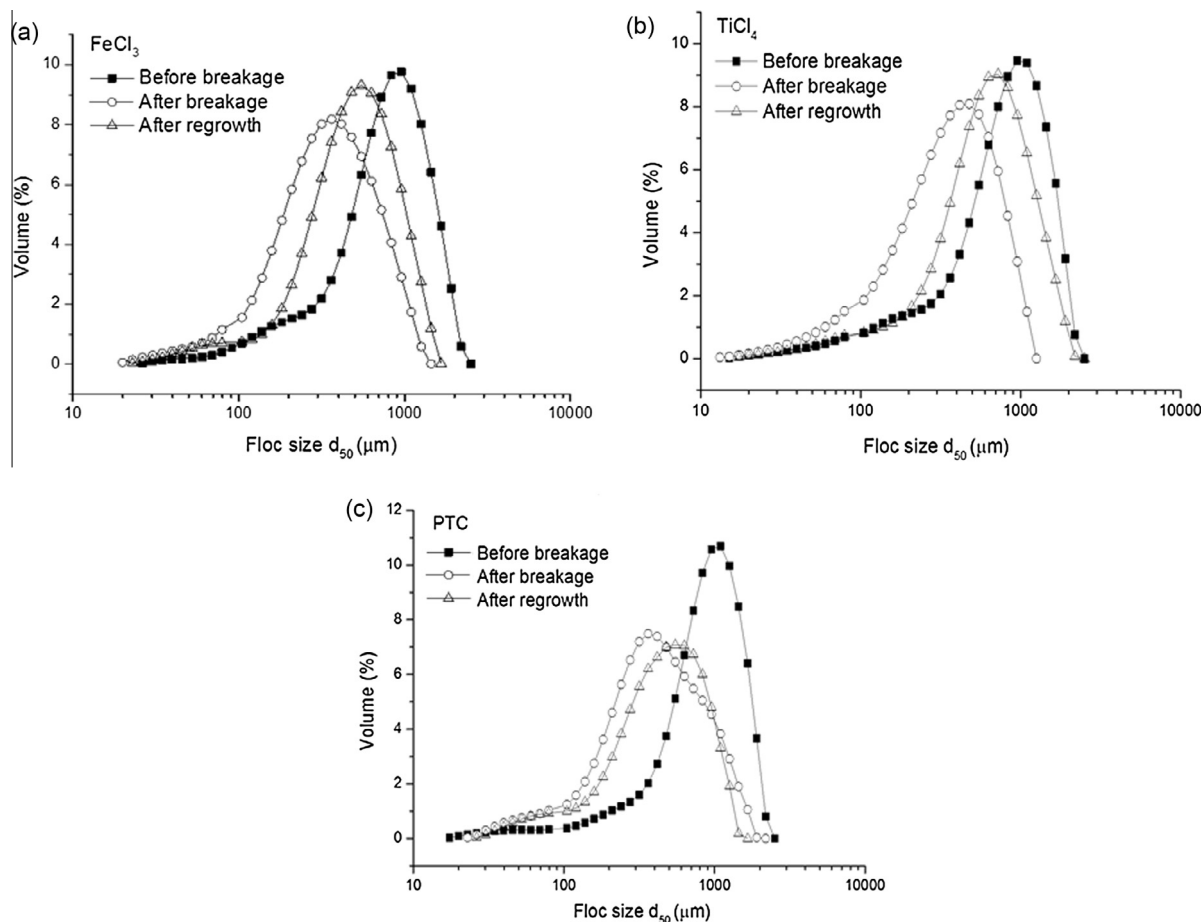


Fig. 5. Floc size distribution before breakage, after breakage and after regrowth of (a) FeCl_3 , (b) TiCl_4 and (c) PTC under optimum coagulant dose conditions (the optimum coagulant dose condition, see Table 1; initial solution pH condition).

having high SF will also present a high degree of compactness. This was also demonstrated in a previous study by Wang et al. [42] where they found a tight relationship between floc structure and floc strength.

4. Conclusions

The performance of recently developed PTC coagulant was investigated for synthetic wastewater treatment compared with TiCl_4 and conventional FeCl_3 in terms of water quality parameters, coagulation mechanisms and flocs characteristics. The following conclusions are drawn from the present study:

1. PTC and TiCl_4 presented a broader flocculation region in terms of pH and coagulant dose for turbidity removal and can thus potentially be applied over a wider range of pH than FeCl_3 . Besides, PTC and TiCl_4 achieved higher turbidity and UV_{254} removal.
2. During the initial floc growth period, PTC showed the fastest growth rate (i.e. $278.9 \mu\text{m}/\text{min}$) with the largest floc size of $836 \mu\text{m}$, which suggests significant advantages in terms of compact mixing and sedimentation tanks.
3. The strength factor and fractal dimension of all three coagulants were quite similar and followed the same order: $\text{FeCl}_3 > \text{TiCl}_4 > \text{PTC}$; suggesting a close relationship between floc strength and structure. However, PTC and FeCl_3 showed similar but lower values of recovery factors, proposing that PTC flocs require more careful handling during the separation process.

4. Charge neutralisation combined with physical entrapment of colloids within floc precipitates and adsorption were the main mechanisms involved in TiCl_4 coagulation. Sweep coagulation and adsorption were found to be the primary mechanisms for both PTC and FeCl_3 .

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