Coagulation performance and floc characteristics of polytitanium tetrachloride (PTC) compared with titanium tetrachloride ($TiCl_4$) and ferric chloride ($FeCl_3$) in algal turbid water

L. Chekli, [a, #] C. Eripret, [a, #] S.H. Park, [b, *] S.A.A. Tabatabai, [c] O. Vronska, [d] B. Tamburic, [d] J.H. Kim [e] and H.K. Shon [a, *]

[a] School of Civil and Environmental Engineering, University of Technology, Sydney, Post Box 129, Broadway, NSW 2007, Australia.

[b] Korea Institute of Industrial Technology (KIITECH), 89 Yangdaegiro-gil, Ipjang-myeon, Seobuk-gu, Cheonan-si, Chungcheongnam-do, 331-822, Republic of Korea.

[c] Water Desalination and Reuse Center (WDRC), 4700 King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

[d] Plant Functional Biology and Climate Change Cluster (C3), Faculty of Science, University of Technology Sydney (UTS), Sydney, NSW 2007, Australia.

[e] School of Applied Chemical Engineering and the Institute for Catalysis Research, Chonnam National University, Gwangju 500-757, Korea.

[*]Corresponding authors: Email: Hokyong.Shon-1@uts.edu.au; Phone: (+61) 02 9514 2629.
Email: shpark08@kitech.re.kr; Phone: (+82) 10 84273775

[#] L.C. and C.E. equally contributed to this work.

Abstract:

Seasonal green algae blooms in freshwaters have raised attention on the need to develop novel effective treatment processes for the removal of algae in water. In the present study, the performance of newly developed polytitanium tetrachloride (PTC) coagulant for the removal of freshwater microalga *Chlorella vulgaris* has been investigated and compared with titanium tetrachloride ($TiCl_4$) coagulant and the conventional ferric chloride ($FeCl_3$) coagulant. The main benefit of using titanium-based coagulants is that the sludge produced after flocculation may be recycled into a valuable product: titanium dioxide photocatalyst. Both titanium-based coagulants achieved good flocculation over a broader pH range and coagulant dose compared to conventional $FeCl_3$ coagulant. All three coagulants achieved comparable performance in terms of turbidity removal (i.e. turbidity removal efficiency > 97%); although $TiCl_4$ performed slightly better at the lower tested dose (i.e. < 9 mg/L). Zeta potential measurements indicated that charge neutralisation may not be the sole mechanism involved in the coagulation of algae for all three coagulants. Analysis of the dynamic floc size variation during floc breakage showed no regrowth after floc breakage for the three coagulants. The flocs formed by both Ti-based coagulants were larger than those formed by $FeCl_3$ and also grew at a faster rate. This study indicates that Ti-based coagulants are effective and promising coagulants for algae removal in water.

Keywords: Coagulation, Algae, Polytitanium tetrachloride, Titanium tetrachloride, Floc size, Floc strength.

1 Introduction

The occurrence of seasonal algal blooms (including microalgae and cyanobacteria) in surface waters such as lakes, artificial reservoirs and rivers has raised concerns for water treatment process disruption and maintenance, as well as final drinking water quality. Recent green algae blooms in South Korea's four major rivers have posed a major problem for the quality of drinking water in the country. Cyanobacteria blooms in the Han, Nakdong, Geum and Yeongsan rivers have been attributed to a controversial flood prevention project in the four major rivers [1, 2]. Completed in 2011, the project consisted of dredging of more than 500 million m^3 of mud from the rivers and the construction of 16 dams. Quiescent water, as a result of dam construction, together with environmental factors such as high temperature and nutrient concentration have been identified as the main factors contributing to cyanobacteria proliferation [2]. Therefore, effective treatment processes to remove algae are required for safe drinking water supply and a healthy ecological system.

To date, several methods have been employed to remove or reduce algae growth, including chemical processes such as coagulation/flocculation [3, 4] and chlorination [5]; physical processes such as air flotation [6], media filtration [7] and membrane technologies [8]; and finally electromagnetic radiation such as ultraviolet (UV) light [9] and ultrasonic irradiation [10]. Electromagnetic radiation processes suffer from high capital and maintenance costs [11] while physical processes (e.g. membrane technologies) may impose high cost due to the energy requirement in these systems. Besides, the use of oxidizing agents (e.g. chlorine) in some chemical processes may cause algal cell wall damage, increasing the potential release of taste and odour causing compounds and intracellular organic matter [12]. Finding a low-cost treatment process that can remove algae or limit their growth without causing cell damage would be the optimum solution.

Coagulation/flocculation is by far one of the most economical water treatment processes for the removal of algae [13, 14]. Algal cells have a negative surface charge that can be neutralized by the positive charge of cationic ions such as ferric or aluminium and thus destabilized the algae cells to form clusters or flocs, which can then be removed by sedimentation or flotation. However, the main issue related to the use of conventional coagulants is the production of sludge after treatment. In countries with stringent environmental legislation, coagulant-rich sludge requires extensive treatment and handling prior to disposal, all of which contribute to overall cost and complexity of the treatment process [15]. In fact, this has been recognised as one of the most environmentally problematic and costly challenges of water treatment processes [16, 17].

An alternative titanium-based coagulant (i.e. titanium tetrachloride - $TiCl_4$) has been proposed by Shon et al. [18] to resolve the sludge disposal issue associated with conventional Fe and Al salts. The

key advantage of titanium-based coagulants is that the sludge can be easily recycled (i.e. sludge dewatering through simple filtration, drying at 100 °C and finally calcination at 600 °C) to produce a valuable by-product [19-23]: titanium dioxide (TiO_2). TiO_2 is a widely used metal oxide with applications in cosmetics, paints, photocatalysts, solar cells or electronic paper [24, 25]. In addition, $TiCl_4$ has shown comparable or superior performance to conventional coagulants (e.g. $Al_2(SO_4)_3$, $FeCl_3$, polyaluminum chloride and polyferric sulfate) during surface water treatment [26]. Besides, the flocs produced by $TiCl_4$ coagulation were, in most cases, larger and grew faster, resulting in better settleability. Finally, the low toxicity of titanium salts and related compounds (i.e. salicylate, peroxide, oxides, tannate) compared to Al salts has already been reported [27]. In fact, titanium-related compounds are often not reported in any water quality guidelines [21, 28, 29]. Our previous study [18] demonstrated that the concentration of Ti salts remaining in the supernatant after flocculation of wastewater by $TiCl_4$ was about 10 μg/L. In contrast, titanium concentration usually encountered in drinking water supplies is in the range of 0.5-15 μg/L [28]. Application of $TiCl_4$ thus provides a cost-effective alternative to dispose of coagulation sludge since the produced sludge can be recycled into a valuable commercial photocatalyst. In fact, the early study by Shon et al. [18] demonstrated that a medium size (i.e. 25,000 m^3/d) wastewater treatment plant could produce an average of 446.5 kg/day of photocatalyst.

However, it was observed that the optimum coagulation efficiency of $TiCl_4$ (at a dose of 20 mgTi/L) occurred at low pH (i.e. pH 3.0 to 5.0), which was attributed to the release of large amounts of H^+ during titanium hydrolysis [18, 26]. Thus, new methods were developed to address this issue so as to reduce the need for pH adjustment over a wider range of coagulant dose. A recent study focused on the development of polytitanium salts, which minimizes the release of H^+ through prehydrolysis of titanium salt [23]. In this study, polytitanium tetrachloride (PTC) was synthesized by a slow alkaline titration method at different basicity values (i.e. at different OH/Ti molar ratios in PTC solution) and tested as an alternative Ti-coagulant to $TiCl_4$ [23]. Results showed higher or comparable (i.e. based on the parameter being measured) treatment performance of PTC compared to $TiCl_4$ in terms of removal efficiency for turbidity and organic matter. Additionally, improved floc characteristics such as floc size, growth rate and structure were also observed when using PTC.

In this study, coagulation performance of PTC and $TiCl_4$ coagulants was assessed for the first time for the treatment of algal turbid water in terms of turbidity, zeta potential and floc size and then compared with a commonly used coagulant, namely $FeCl_3$. Furthermore, a detailed comparative study was also conducted to understand the growth and breakage of flocs formed by all three coagulants. This study uses biomass derived from the model freshwater microalga *Chlorella vulgaris* for coagulation/flocculation experiments. In addition to carrying out photosynthesis and primary

production, *Chlorella* also undergoes rapid growth under mixotrophic conditions in the presence of a favourable organic carbon source [30]. Consequently, algal blooms involving *Chlorella* species are frequently observed during freshwater eutrophication events [31].

2 Materials and methods

2.1 Coagulants

A stock solution of $TiCl_4$ (20% w/w) was prepared by slowly adding a predetermined volume (46.4 mL) of a concentrated $TiCl_4$ solution (>99% purity, density ρ = 1.26 g/mL; Sigma Aldrich, Australia) to frozen cubes of deionized water (initial volume of 400 mL). The concentrated solution was added drop by drop under continuous stirring to reach a final concentration of 20% w/w. The concentration of the final solution was systematically checked using a microwave plasma-atomic emission spectrometer (4100 MP-AES, Agilent Technologies, US) and adjusted to the desired concentration as necessary. Stock solution of $FeCl_3$ (10 g/L) was obtained by dissolving 2 g of powder in 200 mL of deionized water. The preparation of PTC coagulant has been detailed in a previous study [23]. In brief, a fixed volume (63.3 mL) of sodium hydroxide (200 g/L) was added to 200 mL of the $TiCl_4$ solution (20% w/w) using slow alkaline titration under intensive agitation to avoid formation of precipitate. PTC was prepared with a basicity value (i.e. OH/Ti ratio) of 1.5; this was previously determined to produce the best coagulation performance [23]. Coagulant dose was defined in units of g-Ti/L and g-Fe/L for Ti-coagulants and $FeCl_3$, respectively.

2.2 Algae culture and algal turbid water

C. vulgaris is a well-studied species commonly found in eutrophic surface water and was thus selected for this study as a model freshwater microalga. The unicellular chlorophyte microalga *C. vulgaris* (CS-42, ANACC, CSIRO) was grown as a suspended culture in MLA medium [32, 33]. 1 L glass conical flasks containing *C. vulgaris* were stored at 21.5°C in an incubator (Labec Pty Ltd, Australia) with fluorescent illumination at a 12h/12h light/dark cycle and a photon flux density of 40 µmol.photon/m^2.s^2.

A volume of 1 L of approximately 3 weeks old stock culture was used as inoculum to grow 10 L of *C. vulgaris* (i.e. diluted in 9 L of fresh MLA medium) in a 15 L modified transparent carboy. Aeration was provided using an air pump (Aqua One 12000 Precision Air Pump) via an air diffuser placed at the bottom of the carboy. An exhaust tube attached to the lid of the carboy was inserted into a vessel with seawater to prevent overflow and distribution of the airborne microalgal cells. The culture was subjected to 12h/12h light/dark cycles and a photon flux density of 100-200 µmol.photon/m^2.s^2 under

LED illumination (Aqua Illumination Hydra 52 HD). The setup was located in a constant temperature room maintained at 22°C.

Microalgal growth was monitored by measuring the cell density, dry weight and chlorophyll *a* concentration based on the protocols described by Borowitzka and Moheimani [34]. In brief, the cell density was determined by fixing a sample of *C. vulgaris* with 1% glutaraldehyde and performing microscopic cell counts with a haemocytometer (Neubauer, Germany). For the determination of the dry weight, a 47 mm GF/C filter (Whatman plc, GE Healthcare, Australia) was pre-dried at 100°C in an oven (Labec Pty Ltd, Australia), cooled in a desiccator and weighted. Then, a known volume of microalgal sample was filtered and washed with 0.65M ammonium formate solution to remove salts. This algal filter was heated at 100°C overnight, cooled and re-weighted to calculate the algal dry mass. Chlorophyll *a* was extracted by filtering a microalgal sample (GF/C filter) and incubating the filter in 100% methanol at 4°C in the dark, followed by sonicating and centrifuging at 4000 rpm (Rotanta 460R centrifuge). The absorbance at 666 nm was measured, and the chlorophyll *a* concentration was calculated according to a method described elsewhere [35]. The approximate optical density in the carboy was also determined as an absorbance at a wavelength of 750 nm (Spectronic 200 spectrophotometer). After each of these measurements, the culture was diluted back to approximately 10 L with fresh MLA medium [33].

Before each coagulation experiment, the live algal suspensions were diluted with tap water [36] to prepare stable algal turbid waters with initial turbidity of 20 NTU, typically found in South Korea's rivers during algal bloom [37, 38]. The detailed characteristics of the algal turbid water used in this study are shown in Table 1.

Table 1

2.3 Jar-test

Standard jar-tests were carried out using a programmable jar-tester (PB-900TM, Phipps and Bird, USA). The coagulant was added to 300 mL of algal turbid water (i.e. initial turbidity of 20 NTU). The turbidity of the algal turbid water was systematically checked before each experiment with a turbidity meter (2100P turbidity meter, Hach, USA) and adjusted to 20 NTU by either diluting with tap water or by adding more algae solution as necessary. Rapid mixing was first applied for 1.5 min (i.e. 200 rpm), followed by slow mixing for 20 min at 40 rpm to promote particle collision and thus floc growth, and finally 20 min of quiescent settling. Water samples were collected from 2 cm below the water surface for further measurements. Residual turbidity and zeta potential were directly measured using a turbidity meter and Zetasizer (Malvern Instruments, UK), respectively. Turbidity and zeta

potential measurements were run in triplicate using three independent samples. Data presented in this study are the average value with standard error.

Jar tests were conducted to define the optimum coagulation parameters (i.e. pH and coagulant dose). Several jar tests were performed at various coagulant dose and pH values, and coagulation performance was determined based on turbidity removal efficiency. For these experiments, the target pH value was reached by titrating with appropriate volumes of either HCl or NaOH solutions (0.1M).

2.4 Floc characterization

Throughout the coagulation/flocculation process, the dynamic floc size was continuously measured by a laser diffraction instrument (Mastersizer 2000, Malvern, UK). The representative floc size was highlighted by the median equivalent diameter d_{50}, although similar trends for d_{10} and d_{90} floc sizes were also observed (data not shown). The schematic diagram of the on-line monitoring system for dynamic floc size is detailed in a previous study [39].

This set of experiments was conducted under the optimum conditions determined during the jar tests. The investigation of floc properties (i.e. strength and regrowth capacity) was carried out in the following stages: initial growth phase, floc breakage and regrowth cycle of the floc. These stages were achieved by applying different mixing conditions: 15 min at 40 rpm (i.e. growth phase), 1 min at 200 rpm (aggregated flocs exposed to high shear force to induce breakage) and finally 20 min at 40 rpm (slow mixing to allow potential floc regrowth). These experiments were run in duplicate for each tested coagulant and the data presented are the average value with standard error.

To evaluate the strength and regrowth capacity of the flocs, the strength factor (SF) and recovery factor (RF) were calculated as follow [40, 41]:

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

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

where d_1 is the steady-state floc size at the plateau before breakage, d_2 is the average floc size after breakage, and d_3 is the average floc size after regrowth to a new plateau.

The higher the SF value, the more resistant the flocs are to breakage due to shear. Flocs with high SF are thus considered to be stronger than those remaining in the suspension. Similarly, the higher the RF value, the better is the floc ability to regrow after exposure to high shear force.

The floc growth rate was also assessed by determining the slope of the rapid growth period, assuming linear growth [42]:

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

3 Results and discussion

3.1 Determination of flocculation region

The combined effect of pH and coagulant dose was used to define a 2D region of good flocculation. Flocculation results, in terms of turbidity removal efficiency, were classified into four categories: (i) optimum flocculation conditions with the lowest residual turbidity after flocculation (limit of detection of 0.01 NTU); (ii) good flocculation when the residual turbidity after flocculation was below 1 NTU (or turbidity removal efficiency ≥ 95%); (iii) insufficient flocculation when the residual turbidity after flocculation was above 1 NTU and (iv) no visible flocculation or residual turbidity after flocculation above 10 NTU.

Results in Figure 1 show that the region of good flocculation for both titanium-based coagulants (i.e. $TiCl_4$ and PTC) is broader compared to the $FeCl_3$ coagulant. This might be attributed to the formation of reactive hydrolysis species over a broader pH range for these two coagulants. For all three coagulants, pH 7 appears to be the optimum coagulation pH where the lowest residual turbidity was found. This pH falls into the typical pH range found in the main South Korea's rivers [43]. This result is in accordance with our previous study where it was found that, at pH 7, all three coagulants achieved the highest turbidity removal efficiency (i.e. in this study, turbidity was due to the addition of kaolin in synthetic wastewater) [39]. In fact, at this pH, positively charged amorphous hydroxide precipitates are present in high concentrations whereas dissolved cationic hydrolysis species are present at low concentrations. This is in contrast to what occurs at pH 5. *Chlorella vulgaris* has been shown to have a relatively high charge density (i.e. $1.1x10^{-5}$ neq/cell) [44] and therefore requires a high coagulant demand for complete charge neutralization. As can be seen from the data presented in this study (Table 2), at the coagulant doses tested, charge neutralization of the algal turbid water was not achieved. Therefore, at pH 7, there is not only charge neutralization mechanism but also sweep flocculation, which allows for enmeshment and adsorption of the foulants into and onto the hydroxide precipitates allowing for better turbidity removal at relatively lower dose.

For each tested coagulant, insufficient flocculation was observed at dosage lower than 9 mg/L (except for $TiCl_4$ at pH 5) which differs from previous studies where the optimum coagulant dose for these

three coagulants were in the range 8-10 mg/L for the treatment of wastewater containing various concentration of organic compounds and inorganic colloids [23, 39, 45]. This can be attributed to the living algae cells influencing the surface charge by ion transfer across the cell membrane to maintain a negative surface charge, thus remaining stable in suspension [46, 47]. Therefore, high coagulant dosages are necessary to overcome the ion transfer mechanism, leading to more efficient destabilisation. Besides, as discussed in the previous paragraph, the relatively high charge density of *Chlorella vulgaris* requires a high coagulant demand for complete destabilization. These results again suggest that sweep flocculation (i.e. physical entrapment of the algae cells within metal coagulant precipitates formed at high coagulant dose) is involved for the removal of algae from suspension.

Figure 1

Both $TiCl_4$ and PTC were flocculated readily at any pH with a sufficiently high flocculation dose, in the range 12-20 mg-Ti/L. These results contrast with a previous study on PTC [23] where it was found that pH 9 was the optimum pH in the dosage range 8-10 mg-Ti/L. However, this study focused on the performance of PTC for the removal of humic acid (HA) in synthetic water and thus coagulation mechanisms were most likely different from the ones in the present study. Similarly, it was found in previous studies on $TiCl_4$ [19, 26] that this coagulant displayed high turbidity removal efficiency under alkaline conditions (i.e. in the pH range 7-9) where $TiCl_4$ is gradually hydrolysed resulting in better turbidity removal, mainly via charge neutralisation mechanisms. In the present study, the coagulant dose, rather than the pH, seems to play a more important role in the coagulation efficiency.

3.2 Coagulation performance: Turbidity removal efficiency and zeta potential

The performance of all three coagulants was assessed and compared in terms of turbidity removal efficiency and zeta potential. Results are presented in Figure 2 and Table 2 and show that all tested coagulants achieved very high and similar turbidity removal efficiency (i.e. > 97%) at higher dosage (i.e. > 9 mg/L) suggesting that the coagulant type does not influence removal of algal cells at higher doses. It is interesting to note that $TiCl_4$ performed better at lower doses (i.e. removal efficiency higher than 70% at each tested dose) as compared to the other two coagulants.

Figure 2

Table 2

Zeta potential measurements are often carried out to assess the changes in floc surface charge to evaluate the ability of a coagulant in destabilizing the constituents in feed water. The changes in floc zeta potential are also generally used to determine which coagulation mechanism is involved (i.e. in terms of charge neutralization or sweep flocculation) [48]. Table 2 shows that, under the optimum

conditions defined in section 3.1, the floc zeta potential values after coagulation were -9.5 mV, -12.3 mV and -8.3 mV for $FeCl_3$, $TiCl_4$ and PTC, respectively. These results suggest that, for the coagulant doses studied, charge neutralisation is unlikely to be the sole mechanism involved in the flocculation of algae for all three coagulants otherwise zeta potential values would have been close to zero after flocculation. These results differ from previous studies on titanium coagulants [19, 23, 26, 49-53] where it was found that the predominant coagulation mechanism for both $TiCl_4$ and PTC was through charge neutralisation. However, most of these studies were targeting the removal of organic macromolecules during wastewater treatment. The high coagulant dose needed in this study may suggest that sweep flocculation (i.e. adsorption and enmeshment in metal hydroxide precipitates) was also involved in the coagulation of algal cells. In fact, Henderson et al [44] demonstrated that the total charge density of the algae (and associated OM) in water is a better indicator of coagulant demand than other parameters such as density, cell size, cell area, etc. *C. vulgaris* has a relatively high charge density and consequently a high coagulant dose is required to neutralize the charge of the system. The highest removal rate for all three coagulants was observed at pH 7 and relatively high dose (in comparison with previous studies). Under these conditions large concentrations of cationic amorphous hydroxide precipitates are present in the water that can cause sweep flocculation and provide adsorption sites for negatively charged contaminants. The high removal rates at relatively high negative zeta potential values (-8.3 to -12.3) are a consequence of not only charge neutralization but also sweep flocculation mechanisms.

3.3 Dynamic variation of floc size, floc breakage and recovery

The variation of flocs size for the three coagulants ($TiCl_4$, $FeCl_3$ and PTC) was monitored on-line by using a Mastersizer 2000 (Malvern, UK). Results are shown in Figure 3 and Table 3. For the three coagulants, the median equivalent diameter (d_{50}) was measured every 30 seconds. As shown in Figure 3, the floc size gradually increased for all three coagulants during the slow mixing phase (i.e. 40 rpm) up to a steady-state size after 7-10 minutes. When a shear force (i.e. increasing the mixing speed up to 200 rpm for 1 minute) was introduced, the floc size sharply decreased, resulting in an average floc size of up to 70% smaller than the value at steady-state. When the slow mixing speed was re-established, the floc size remained quite stable and no regrowth was observed for all three coagulants. This confirms that sweep flocculation could be the main mechanism involved in the coagulation of algae since it was demonstrated in previous studies that flocs formed by sweep flocculation had a reduced recovery rate than flocs formed by charge neutralisation [54, 55]. This was previously explained by the differences in the internal bonding structure of flocs [40]. Irreversible breakage was seen as evidence that the flocs formed by sweep flocculation were held together by chemical rather than physical bonds suggesting that chemical bonds (e.g. with carboxyl and phenol groups of organic molecules) do not have the capacity to reform after breakage.

Figure 3

Table 3 shows the floc sizes before and after breakage, the floc growth rate as well as the strength factor (i.e. calculated based on equation (1)) for each tested coagulant. It is clear that both titanium-based coagulants had faster growth rate with larger floc sizes compared to the conventional $FeCl_3$ coagulant (see also Figure 3) which suggests that $TiCl_4$ and PTC can form larger aggregates in a shorter period of time. The larger floc size obtained with both titanium-based coagulants might be attributed to the larger hydrated radius of titanium compared to iron [56] as well as the fact that titanium has a higher valence in $TiCl_4$ (i.e. 4 instead of 3 for iron in $FeCl_3$), resulting in the formation of larger metal precipitates and thus larger flocs. Besides, previous studies (e.g. [39]) also found that flocs formed by Ti-salts are not only larger but also more compact; resulting in better settling performance. This is highly advantageous in terms of capital cost and footprint since a shorter retention time combined with larger and more compact flocs will result in smaller and more compact flocculation and sedimentation units [57]. The floc size at steady-state (i.e. d_1) among all three coagulants varied in the following order: PTC (1310 μm) > $TiCl_4$ (1195 μm) > $FeCl_3$ (820 μm), which is slightly larger than the floc size obtained in previous studies with these three coagulants [39, 45]. This result is not surprising considering that the size of algae cells is significantly larger than the organic macromolecules (e.g. humic acid) used in previous studies [39, 45]. Besides, the higher coagulant dose used in this study (i.e. compared to previous studies on titanium-based coagulants) may lead to the formation of metal hydroxide precipitates (e.g. $Fe(OH)_3$ or $Ti(OH)_4$) which lead to the formation of large aggregates. Finally, it was also demonstrated in previous studies that polysaccharide exudates from the algae may play an important role in their flocculation by bridging together the algal cells and hydroxide precipitates to form large flocs [58].

The floc growth rates obtained in this study also diverged from previous studies and are comparatively slower; suggesting that algal cells may need more time to flocculate than other particles. This finding corroborates with a previous study [58] where the flocculation of green algae *C. vulgaris* was compared with both kaolin and natural organic matter (NOM) and it was found that the steady-state floc size was achieved after 4, 6 and 25 minutes for kaolin, NOM and algae, respectively. The difference in floc growth rate can be attributed to steric interactions between loosely bound extracellular organic matter (EOM) which can interfere with the coagulation process [59].

Table 3

Floc strength factor (SF) was calculated using equation (1) to investigate the floc ability to withstand an applied shear force (i.e. increasing the mixing speed to 200 rpm). Results gathered in Table 3 show that the SF of all three coagulants was quite similar with values following the order: $FeCl_3$ (33.1) > $TiCl_4$ (27.4) > PTC (27.1). These values are lower than those obtained in previous studies focusing on the removal of organic macromolecules [39, 45] but corroborate with another study which found that

algal flocs are much weaker compared to NOM flocs on exposure to increased shear (i.e. > 40 rpm) [58]. These results can also be supported by the larger floc size obtained in this study. In fact, it was demonstrated in previous studies [57, 60] that the larger the flocs, the more they are exposed to microscale energy-dissipating eddies, increasing their breakage potential and leading to smaller SF.

Figure 4 shows the particle size distribution (PSD) of the three tested coagulants before and after floc breakage. Analysis of the PSD indicates that the floc size after breakage was 3-3.5 times lower than the original value for all three coagulants. Results also show that the flocs formed by $FeCl_3$ are polydispersed in size with the presence of finer flocs (i.e. presence of 2 additional main peaks with smaller volume at about 100 and 300 μm). The flocs formed by both PTC and $TiCl_4$ display a much narrower size distribution but also present peaks with small volume (i.e. less than 2.5%) at smaller sizes (i.e. presence of peaks at about 300 μm and 700 μm for both Ti-coagulants). The presence of fine flocs is not desirable in this process since they tend to remain in suspension after flocculation, which ultimately leads to lower turbidity removal efficiency. In this context, Ti-based coagulants are preferable since the floc size at steady-state presents a much narrower PSD.

The analysis of the breakage profile of algal flocs can also provide information on the breakup mechanisms. According to Jarvis et al. [61], there are two mechanisms of floc breakup: surface erosion (slow) and large-scale fragmentation (rapid). Flocs with weak and loose structure will preferentially breakup via fragmentation mechanism whereby flocs split into pieces of comparable size. It is clear from Figure 4 that large-scale fragmentation was the main breakup mechanism since the flocs size was reduced to 200-300 μm with the complete disappearance of the main peak before breakage. These results are supported by the low SF values (i.e. ratio of flocs size before and after breakage) obtained in this study. Finally, it was found that this floc breakage pattern was very similar to the one obtained with NOM + polymer flocs suggesting that EOM, and more specifically polymeric algal EOM, play a significant role in algal flocculation [40].

Figure 4

Conclusions

In the present study, the performance of Ti-based coagulants (PTC and $TiCl_4$) was tested and compared with conventional $FeCl_3$ coagulant for the removal of freshwater algae. The performance was assessed in terms of turbidity removal efficiency, coagulation mechanisms and floc characteristics. The following findings have been drawn from this study:

1. Both Ti-based coagulants had a broader region of good flocculation in terms of pH and coagulant dose compared to $FeCl_3$. All three coagulants had to be operated at higher dose in comparison with previous studies based on the removal of organic macromolecules during wastewater treatment.

2. Zeta potential measurements combined with analysis of the dynamic floc size variation upon exposure to shear force showed a negative surface charge after flocculation and no regrowth of the floc after breakage suggesting that charge neutralisation may not be the sole coagulation mechanism.
3. Ti-based coagulants produced the largest floc size with the fastest growth rate, which is highly advantageous in terms of compact mixing and sedimentation tanks. The flocs formed by all three coagulants were larger than those formed by the coagulation of organic macromolecules; suggesting that EOM may play a role in the coagulation of algae through bridging mechanisms.

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