Performance of titanium salts compared to conventional $FeCl_3$ for the removal of algal organic matter (AOM) in synthetic seawater: Coagulation performance, organic fraction removal and floc characteristics.

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Abstract:

During algal bloom periods, operation of seawater reverse osmosis (SWRO) pretreatment processes (e.g. ultrafiltration (UF)) has been hindered due to the high concentration of algal cells and algal organic matter (AOM). The present study evaluated for the first time the performance of titanium salts (i.e. titanium tetrachloride ($TiCl_4$) and polytitanium tetrachloride (PTC)) for the removal of AOM in seawater and results were compared with the conventional $FeCl_3$ coagulant. Previous studies already demonstrated that titanium salts not only provide a cost-effective alternative to conventional coagulants by producing a valuable by-product but also minimise the environmental impact of sludge production. Results from this study showed that both $TiCl_4$ and PTC achieved better performance than $FeCl_3$ in terms of turbidity, UV_{254} and dissolved organic carbon (DOC) removal at similar coagulant dose. Liquid chromatography – organic carbon detection (LC-OCD) was used to determine the removal of AOM compounds based on their molecular weight (MW). This investigation revealed that both humic substances and low MW organics were preferentially removed (i.e. up to 93% removal) while all three coagulants showed poorer performance for the removal of high MW biopolymers (i.e. less than 50% removal). The detailed characterisation of flocs indicated that both titanium coagulants can grow faster, reach larger size and present a more compact structure, which is highly advantageous for the design of smaller and more compact mixing and sedimentation tanks. Both titanium coagulants also presented a higher ability to withstand shear force, which was related to the higher amount of DOC adsorbed with the aggregated flocs. Finally, $TiCl_4$ had a better recovery after breakage suggesting that charge neutralization may be the dominant mechanism for this coagulant, while the lower recovery of both PTC and $FeCl_3$ indicated that sweep flocculation is also a contributing mechanism for the coagulation of AOM.

Keywords: Coagulation, Algal organic matter (AOM), Polytitanium tetrachloride, Titanium tetrachloride, Floc characteristics

1 Introduction

The sustainability of water and energy resources is being threatened due to rapid population and industry growth and therefore, developing low-energy separation technologies is crucial to meet the increasing water demand through unconventional sources (Chung et al., 2012; Elimelech and Phillip, 2011; Rasul and Sharma, 2016; Zhao et al., 2012). Nowadays, membrane processes are the most widely used technology to produce clean water and, among them, reverse osmosis (RO) is currently the most employed separation technology for desalination (up to 70% of installed desalination plants) (Lee et al., 2011). One of the major obstacles for cost-effective operation of seawater RO (SWRO) is membrane fouling, which significantly reduces the process efficiency in terms of quality and quantity of produced water (Matin et al., 2011). Therefore, pretreatment processes such as micro- or ultra-filtration (MF/UF) are generally required to mitigate this issue. UF has gained increased popularity as an alternative pretreatment process to SWRO (Basha et al., 2013; Brehant et al., 2002). In fact, UF systems have lower footprint, better permeate quality and lower overall chemical consumption compared with conventional pretreatment process (e.g. dual media filtration) (Wilf and Schierach, 2001). However, similar to RO, membrane fouling remains one of the major challenges impeding the high production capacity of this membrane system (Pearce, 2009). During seawater desalination, membrane fouling in UF pretreatment systems is largely associated with algal bloom events and it has been recently shown that algal cells and more specifically algal organic matter (AOM) were responsible for the severe permeability decline (Li et al., 2016; Merle et al., 2016; Pivokonsky et al., 2016; Villacorte, 2014).

AOM released by bloom-forming algal species mainly comprises extracellular biopolymers (i.e. high molecular weight, hydrophilic, anionic compounds such as polysaccharides and glycoproteins) but the composition of AOM varies from one species to another, and changes over the course of an algal bloom (Fogg, 1983). These high molecular weight (MW) biopolymers are also known as transparent exopolymer particles (TEP) and have been found to play a key role in the aggregation of algae during bloom events (Myklestad, 1995). Previous studies have demonstrated that AOM can deposit on the membrane surface and/or within the pores, which increases the resistance to permeate flow but also reduces the effectiveness of hydraulic cleaning (i.e. backwashing) (Qu et al., 2012; Schurer et al., 2013; Villacorte et al., 2010). Besides, if a fraction of the AOM passes through the UF membranes, it affects the downstream RO membranes by increasing the fouling and biofouling potential of the feed water.

Coagulation using conventional metal salts (i.e. aluminium and iron) has been effective in controlling and reducing membrane fouling in UF systems (Busch et al., 2010; Choi and Dempsey, 2004), including in the context of AOM removal during algal bloom events (e.g. (Schurer et al., 2012; Schurer et al., 2013; Tabatabai et al., 2014)). Coagulation can reduce UF membrane fouling by AOM via several mechanisms (which depends on the coagulant dose) including partial complexation of algal biopolymers and formation of biopolymer-colloidal metal complexes (e.g., for low coagulant dose < 1 mgFe/L) and adsorption and enmeshment of biopolymers in metal hydroxide precipitates at higher coagulant dose (Tabatabai et al., 2014; Yan et al., 2017). These mechanisms have been found to be quite different from the coagulation of natural organic matter and are still relatively poorly understood (Tabatabai et al., 2014). To date, ferric salts, and more specifically ferric chloride ($FeCl_3$), are the most commonly used coagulants in seawater desalination mainly because of their lower solubility compared to aluminium salts, resulting in lower dissolved metal concentration and thus lower scaling potential in the treated water (Edzwald and Haarhoff, 2011). However, the coagulation/flocculation process performed by ferric salts generates a large volume of chemical sludge which has to be disposed, creating an environmentally-challenging burden.

To overcome the issue of sludge disposal, titanium salts can be used as alternative coagulants since the sludge generated after titanium salt flocculation can be recycled to produce an economically valuable by-product via calcination: titanium dioxide (TiO_2) (Lee et al., 2009; Okour et al., 2010; Shon et al., 2009; Zhao et al., 2011a). Therefore, the use of titanium-based coagulants offers a more attractive and cost-effective solution to the sludge disposal approach. In fact, an early study on $TiCl_4$ (Shon et al., 2007) showed that a medium size wastewater treatment plant (i.e. treatment capacity of 25,000 m^3/day) could produce an average of 446.5 kg of TiO_2 photocatalyst per day, which is quite significant considering the increasing market demand for TiO_2. Besides, the performance of recycled TiO_2 (i.e. photocatalytic activity and surface area) was found to be higher than the commercially available TiO_2 (Shon et al., 2007). Finally, another study (Okour et al., 2009), focusing on the application of $TiCl_4$ and $Ti(SO_4)_2$ as pretreatment for SWRO, found that the residual Ti after flocculation caused significantly less fouling compared to the residual Fe after conventional $FeCl_3$ flocculation.

Floc characteristics (i.e. floc size, floc growth rate, strength and recovery factors and floc structure) are crucial factors to assess for the design and the performance evaluation of a coagulation process. For instance, large flocs with high degree of compaction will settle more rapidly than smaller flocs with large open pore structure. This will lead to not only higher removal efficiency, but also faster settling time resulting in reduced sedimentation tank size requirement. The ability of flocs to resist a shear force and to recover after breakage is also important to evaluate since it will have significant impact on the process design and its capital and operational costs (McCurdy et al., 2004).

The objective of this study was therefore to investigate, for the first time, the performance of titanium-based coagulants (i.e. $TiCl_4$ and polytitanium tetrachloride (PTC)) as an alternative to conventional ferric salts for the removal of AOM in seawater. Coagulation performance has been assessed in terms of turbidity, zeta potential, UV_{254} and dissolved organic carbon (DOC) removal and compared with

$FeCl_3$. The coagulation performance of Ti-salts was also investigated for the removal of AOM fractions (i.e. based on MW). Finally, a detailed comparative study was also conducted to understand the growth, breakage and structural parameters of flocs formed by all three coagulants.

2 Materials and methods

2.1 Coagulants

$TiCl_4$ stock solution was obtained by adding continuously drop by drop a concentrated $TiCl_4$ solution (>99% purity, density $\rho = 1.26$ g/mL; Sigma Aldrich, Australia) to frozen cubes of deionized water to obtain a final concentration of 20% w/w. The concentration of the stock solution was checked using a microwave plasma-atomic emission spectrometer (4100 MP-AES, Agilent Technologies, US) and adjusted to the desired concentration as necessary. $FeCl_3$ stock solution (i.e. 10 g/L) was prepared by dissolving 2 g of $FeCl_3$ powder in 200 mL of deionized (DI) water. The preparation of PTC coagulant was developed in a previous study (Zhao et al., 2013). In brief, a predetermined volume (i.e. 63.3 mL) of concentrated sodium hydroxide (i.e. 200 g/L) was added to 200 mL of the $TiCl_4$ stock solution using a slow alkaline titration under intensive agitation. The basicity value (i.e. OH/Ti ratio) was fixed to 1.5 since it was previously found to generate the best coagulation performance (Zhao et al., 2013). Coagulant dose is given in units of g-Ti/L and g-Fe/L for Ti-coagulants and $FeCl_3$, respectively.

2.2 Algae cultivation and AOM harvesting

To simulate seawater bloom conditions, the marine diatom species *Chaetoceros muelleri* was cultivated for laboratory-scale production of AOM. In fact, the diatoms of the genus *Chaetoceros* are a suitable choice since they bloom regularly in coastal waters (Ignatiades, 1969; Lewin and Mackas, 1972; Passow and Alldredge, 1995) and they were found to generate significant volume of extracellular polysaccharides during their growth cycle (Dam and Drapeau, 1995; Myklestad, 1995; Watt, 1969).

An aquaculture strain of the diatom *Chaetoceros muelleri* (Department of Primary Industries, Port Stephens, Australia) was grown in synthetic seawater enhanced with F/2 medium (Cell-hi F2P, Varicon Aqua) and silicate (Guillard and Ryther, 1962). The microalgae were grown in a 10 L transparent carboy bubbled with filtered air, at an incident irradiance of approximately 120 $\mu mol.photon/m^2.s^2$ and a temperature of 25°C.

The algae culture was collected approximately 14 days after inoculation (i.e. during the stationary phase of growth) when the production of extracellular polysaccharides has been found to be maximal (Myklestad, 1974). Samples were collected regularly and the culture was stopped when the biopolymer concentration reached a steady value of 5 mgC/L. The bottle containing the culture was first gently shaken to ensure homogeneity. Then, the sample was filtered through 0.45 μm nylon membrane filters (Whatman) to harvest the AOM and obtain a stock solution which was then used for characterization and preparation of the feed solution. The AOM stock solution therefore includes mainly extracellular organic matter (EOM) but may also contain intracellular organic matter (IOM) if some of the algae cells were broken during the filtration process.

2.3 AOM characterization

The detailed organic fraction of the AOM stock solution (Table 1) and samples before and after flocculation was determined using liquid chromatography with organic carbon detection (LC-OCD) (LC-OCD model 8, DOC Labor, Germany), with organic carbon, organic nitrogen and UV_{254} detectors and two TSK HW-50S (Toso, Japan) chromatographic columns in series (double column setup) (Huber et al., 2011). The longer retention time (240 mins) of the double column setup was used to analyse organic sub-fractions of seawater (Naidu et al., 2015). LC-OCD separates the hydrophilic fraction of the total dissolved organic carbon (DOC) by molecular size per retention time, with an initial peak of high molecular-sized biopolymer followed by humic substance and their related building blocks and finally low MW organics (LMW organics) (Huber et al., 2011; Naidu et al., 2015). The proportion of each organic fraction was calculated by specialised software (ChromCALC DOC-LABOR, Karlsruhe, Germany).

Table 1

The AOM harvested from *Chaetoceros muelleri* (Table 1) mostly comprised of biopolymers (i.e. 38.5% of the total DOC) and a relatively large amount of building blocks and LMW organics. The composition of AOM, and more specifically the MW distribution of the organic compounds, has been found to have significant impact on the coagulation process (Henderson et al., 2010).

2.4 Jar-tests

For coagulation performance studies, the AOM stock solution was diluted with synthetic seawater (TDS: 31.8 g/L; Conductivity: 49.7 mS/cm; pH: 7.7 ± 0.1) following the recipe of Lyman and Fleming (1940) to obtain a biopolymer concentration of 0.5 mgC/L. This concentration corresponds to AOM concentrations during algal bloom events in the North Sea, which resulted in significant biofouling of UF systems (Schurer et al., 2013).

Coagulation experiments were performed using a programmable jar-tester (PB-900TM, Phipps and Bird, USA). The coagulant was added to 500 mL of AOM in synthetic seawater at the beginning of the rapid mixing step. Since metal hydrolysis occurs immediately after coagulant addition, solution pH decreases and, depending on the coagulant dose, needs to be adjusted. Therefore, to maintain pH in the operational range of SWRO plants (i.e. pH 7-8), pH adjustment was necessary, especially for the higher coagulant doses as shown in Table 2.

Table 2

It is worth noting that $TiCl_4$ required a higher NaOH dose for pH adjustment which is likely related to the release of large amount of hydrogen ions during titanium hydrolysis (Shon et al., 2007; Zhao et al., 2011b). This is one of the main reasons behind the development of polytitanium salts through the prehydrolysis of $TiCl_4$ to reduce the need for pH adjustment and thus chemical consumption and cost.

Experimental conditions are summarized as follow: rapid mixing was first applied for 1.5 min (i.e. 200 rpm), followed by slow mixing for 20 min at 40 rpm and finally 20 min of quiescent settling. Water samples were collected from 2 cm below the water surface for subsequent measurements. The water samples were pre-filtered using a 0.45 μm membrane syringe filter before testing UV_{254} (absorbance at 254 nm using a UV-754 UV/VIS spectrophotometer) while residual turbidity and zeta potential were directly measured using a turbidity meter and Zetasizer (Malvern Instruments, UK), respectively. Turbidity, UV_{254} and zeta potential were measured on three independent samples. Data are presented as mean ± standard error.

2.5 Floc characterization

The variation of floc size was continuously monitored via an on-line monitoring system using a static light scattering instrument (Mastersizer 2000, Malvern, UK) with an array of photosensitive detectors, positioned at different angles between 0.01° and 40.6°. The floc size was represented 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 continuous floc size measurement can be found elsewhere (Chekli et al., 2015).

Floc characterization experiments were conducted under the optimum conditions determined during the jar tests (i.e. at optimum coagulant dose and pH 7-8). The floc properties (i.e. growth rate, strength and regrowth capacity) were determined using the following protocol: 15 min at 40 rpm (i.e. initial growth phase followed by steady state phase), 1 min at 200 rpm (high shear force to induce breakage of aggregated flocs) and finally 20 min at 40 rpm (slow mixing to allow floc regrowth). During these different stages, the suspended flocs were sent through the measurement cell and pumped back into the jar using a peristaltic pump. A preliminary study showed that a flow rate of 2.5 L/h was the optimum flow rate for these experiments. In fact, higher flow rates gave rise to floc breakage while lower ones induced flocs settling within the tubing. These experiments were run in duplicate for each tested coagulant and the data presented are the mean ± standard error.

The flocs strength factor (SF) and recovery factor (RF) were calculated using the following equations (Jarvis et al., 2005; Yukselen and Gregory, 2002):

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

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

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

The floc growth rate was evaluated by determining the slope during the growth period (assuming linear growth) (Xiao et al., 2010):

$$\text{Growth rate} = \frac{\Delta_{\mathrm{size}}}{\Delta_{\mathrm{time}}} \tag{3}$$

The highly disordered structure of floc aggregates can be defined by its scaling behaviour which is known as the mass fractal dimension (FD) (Rice and Lin, 1993; Weitz et al., 1985). The FD describes the actual space occupied by the solid and defines the degree of compactness of the floc aggregate structure.

Previous studies have used static light scattering instrument to evaluate the FD of formed flocs (Jarvis et al., 2005; Lin et al., 2008; Wei et al., 2009). The total scattered light intensity I, the scattering vector Q and the FD followed a power law as per the following equation (Rieker et al., 2000):

$$I \propto Q^{-\mathrm{FD}} \tag{4}$$

Besides, the scattering vector Q can be defined as follow (Lin et al., 2008):

$$Q = \frac{4n\pi \sin\left(\frac{\theta}{2}\right)}{\lambda} \tag{5}$$

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

High FD values generally represent densely packed flocs while low FD values characterise highly-branched flocs with loosely-bound structure.

3 Results and discussion

3.1 Coagulation performance: Zeta potential and Turbidity, UV_{254} and DOC removal

Coagulation performance of the three coagulants was assessed in terms of zeta potential and turbidity, UV_{254} and DOC removal efficiencies (Figure 1).

Zeta potential gives a measurement of the apparent surface charge and is therefore very useful to evaluate the ability of a coagulant to destabilize the components in the feed water. In fact, the reduction in magnitude of the negative zeta potential implies a reduction in the repulsive electrostatic forces up to the point of zero charge (PZC) whereby the attractive van der Waals forces overcome the repulsive forces and particles start to agglomerate (Gregory, 2005). Besides, the changes in floc zeta potential have also been commonly used to identify the mechanisms involved in the coagulation process (Gregory and Duan, 2001). Figure 1a shows that the magnitude of the negative zeta potential values first decreased, up to a coagulant dose of 5 mg/L for all three coagulants, and then charge reversal occurs at higher dose (floc zeta potential values become positive). These results suggest that charge neutralization somewhat plays a dominant role in the coagulation of AOM for all three coagulants. However, charge neutralization is unlikely to be the sole mechanism involved since the highest removal efficiencies were achieved at a coagulant dose of 5 mg/L at which the floc zeta potential values after coagulation were slightly negative (i.e. -4.3 mV, -2.03 mV and -4.1 mV for $FeCl_3$, $TiCl_4$ and PTC respectively). These results corroborate with another study (Henderson et al., 2008a) where it was suggested that a zeta potential operational window of -5 to 0 mV would provide optimum removal of AOM. Besides, coagulation experiments were run at a pH between 7 and 8 which has been found to be the optimum pH range where the highest turbidity removal was achieved for all three tested coagulants (Chekli et al., 2015; Zhao et al., 2011a; Zhao et al., 2011b). It is interesting to note that similar removal efficiencies were observed at positive zeta potentials which have been found to be typical of coagulation experiments conducted at pH 7. In fact, at the relatively high dose required to induce charge reversal, removal efficiency is generally attributed to a change in the dominant coagulation mechanism from charge neutralization to sweep flocculation whereby coagulation is enhanced by adsorption to and/or enmeshment in metal hydroxide precipitates (Duan and Gregory, 2003).

The coagulants performance in terms of turbidity (Figure 1b), UV_{254} (Figure 1c) and DOC removal (Figure 1d) shows that both Ti-based coagulants achieved better removal efficiencies than $FeCl_3$ and the optimum coagulant dose was 5 mg/L for all three tested coagulants. This coagulant dose is much lower than those found in previous studies focusing on the removal of organic matter in wastewater (e.g. 8-20 mg/L in (Galloux et al., 2015)). One possible explanation could be that AOM can act as a polymer aid which will decrease the amount of coagulant required (Henderson et al., 2008b). In an earlier study (Zhao et al., 2013), it was found that PTC performed better or similarly to $TiCl_4$ in terms of turbidity, UV_{254} and DOC removal, which is not consistent with the results obtained in the present study. The difference in coagulation performance between $TiCl_4$ and PTC may be explained by the difference in hydrolysed Ti species formed in the AOM feed solution. The dominant hydrolyzates for $TiCl_4$ are most likely $Ti(OH)_2^{2+}$ or $Ti(OH)^{3+}$ which can both form complex with negatively charged AOM compounds (Zhao et al., 2013). For PTC, the lower performance can be due to the formation of $Ti_n(OH)_m^{4n-m}$ complexes with high m value such as $Ti(OH)_3^+$ or $Ti(OH)_4$ which will have lower efficiency for the removal of negatively charged AOM compounds (Zhao et al., 2013) .

Figure 1

3.2 Detailed organic carbon fraction removal

The detailed composition of the AOM feed solution before and after flocculation has been analysed and fractionated (i.e. based on MW) by LC-OCD (Table 3). LC-OCD results can provide further understanding of the mechanisms involved in AOM coagulation. In fact, LMW AOM has been shown to cause inefficient flocculation and therefore demands a high coagulant load because crosslinking of the LMW AOM with metal compounds is necessary to build flocs (Henderson et al., 2010). On the other hand, high MW AOM (e.g. protein-rich AOM) can act as polymer aid and thereby increase the coagulation efficiency (Henderson et al., 2010).

Following dilution with synthetic seawater, the AOM feed solution was mainly composed of building blocks and LMW organics (i.e. 42% and 41%, respectively, of the total DOC) while the fractions of biopolymers and humic substances were relatively low (i.e. less than 10%).

Table 3 shows the removal efficiencies of the different AOM fractions by all three coagulants. It can be seen that the highest removal efficiencies were obtained for humic substances and LMW organics (i.e. up to 90% removal efficiency) while the removal of biopolymers was significantly less efficient (i.e. maximum removal efficiency of 48.1% obtained with $TiCl_4$ at 10 mg-Ti/L). These results are consistent with the high turbidity and UV_{254} removal efficiencies obtained with all three coagulants (Figure 1). In fact, biopolymers are dominated by hydrophilic polysaccharides that do not absorb UV_{254} and since these high MW compounds (also known as TEPs) are transparent, turbidity measurements neither detect their presence nor quantify their concentration (Li et al., 2016; Tabatabai, 2014). Thus, these two parameters are not adequate for the measurement of biopolymers but may provide useful information for the other organic carbon fractions such as UV_{254} for the aromatic organic compounds (i.e. humic substances). It is therefore not surprising that the removal efficiency for humic substances obtained with LC-OCD measurements follows the trend as the UV_{254} removal efficiency shown in Figure 1c. Similarly, the high turbidity removal efficiency obtained in this study reveals that biopolymers were not effectively removed by coagulation, as confirmed by the low biopolymer removal efficiency measured by LC-OCD.

Both Ti-based coagulants, and more specifically $TiCl_4$, performed better than $FeCl_3$ regardless of the AOM fraction, which corroborates with previous studies where $TiCl_4$ performed better than $FeCl_3$ for the removal of different organic carbon fractions in seawater (Jeong et al., 2013; Okour et al., 2009). However, although these studies measured similar removal efficiencies for the LMW organics (i.e. up to 93% at 5 mg-Ti/L), much higher removal efficiencies of biopolymers were obtained at relatively low dose for both $FeCl_3$ and $TiCl_4$ (e.g. complete removal of biopolymers at 5 mg-Ti/L). In another recent study (Tabatabai et al., 2014), $FeCl_3$ achieved a biopolymer removal efficiency of about 80% at 10 mg-Fe/L while in the present study, at the same coagulant dose, only 40% removal efficiency was achieved.

The main difference between these studies and the present one relies on the composition of the feed solution before coagulation. In fact, the fraction of high MW biopolymers was relatively high (i.e. reaching 51% (Tabatabai et al., 2014) and in more balanced proportion in comparison to the other organic carbon fractions, especially the LMW organics. In another recent study by Henderson et al. (using aluminium sulfate as coagulant) (Henderson et al., 2010), the authors demonstrated that some algae species (and related AOM) require a higher coagulant demand due to the presence of LMW AOM compounds while high removal efficiencies were achieved at relatively low coagulant dose for species that have AOM with high MW compounds. Higher removal efficiencies were also obtained with highly charged species (Henderson et al., 2010). The AOM feed solution used in the present study had a high fraction of LMW organics (i.e. about 40% of the total DOC) combined with a relatively low charge (i.e. initial zeta potential of -9.98 mV ± 0.39 mV), which probably caused the lower removal efficiencies at similar coagulant dose.

Table 3

3.3 Dynamic variation of floc size, floc breakage and recovery and floc structural analysis

Initial slow mixing (at 40 rpm) allowed a gradual increase of floc sizes for all three coagulants up to a steady-state floc size plateau after 3 to 5 minutes (Figure 2). When a shear force (200 rpm for 1 minute) was introduced after 15 minutes, the floc size immediately decreased to 73%, 55% and 52% of the average floc size at steady state for $FeCl_3$, $TiCl_4$ and PTC, respectively (d_1 and d_2 –Table 4). Upon reintroduction of slow mixing, the flocs started to regrow; however, none of the flocs formed by any of the three coagulants recovered back to their initial size before breakage (d_1 and d_3 –Table 4). This irreversible breakage of flocs is evidence that the flocs were to some extent formed by sweep flocculation, suggesting that the flocs were held together by chemical bonds (e.g. carboxyl and phenol groups of organic molecules), which do not have the capacity to reform after breakage (Jarvis et al., 2005).

Figure 2

Results in Table 4 also show the calculated floc growth rate, SF and RF based on equations (1), (2) and (3). Both Ti-based coagulants exhibited a faster growth rate and formed larger flocs at each stage (i.e. steady-state, after breakage and after regrowth) compared to the conventional $FeCl_3$ coagulant (Table 4), which corroborates with previous studies comparing the performance of these three coagulants (Chekli et al., 2015; Galloux et al., 2015). The floc sizes obtained at steady state (i.e. d_1 – Table 4) were larger than those obtained in previous studies (Chekli et al., 2015; Galloux et al., 2015). This can be explained by the composition and MW distribution of the organic carbon compounds present in the initial feed solution. In fact, in previous studies, synthetic or coal-mining wastewater were used as feed whereby the DOC concentration was either much lower or mainly composed of humic substances with narrower MW distribution consisting of lower MW compounds. The presence of biopolymers in AOM feed solution, even at low concentration, can enhance the coagulation process by acting as polymer aid resulting in the formation of larger flocs. The larger floc sizes obtained in this study could also be explained by the presence of divalent cations such as Ca^{2+} in the synthetic seawater. In fact, divalent cations can enhance the coagulation performance in the presence of negatively charged organic compounds due to bridging effects resulting in the formation of (Ca-AOM-Metal hydrolyzates) complexes at low coagulant dose and (Ca-AOM-Metal hydroxide precipitates) complexes at high coagulant dose (Zhao et al., 2014).

Floc strength and recovery factors (SF and RF) were calculated to investigate the capacity of the flocs to resist an applied shear force and to regrow after exposure to this force. Both $TiCl_4$ and PTC showed higher SF than $FeCl_3$ (i.e. 47.9% and 45.1 % for PTC and $TiCl_4$ against 27.1% for $FeCl_3$) while $TiCl_4$, alone showed the highest RF (i.e. 70.5%). These results suggest that charge neutralisation could be the main mechanism for $TiCl_4$ while sweep flocculation might have also contribute to a certain degree for both $FeCl_3$ and PTC. In fact, previous studies have reported that flocs formed by sweep flocculation have a weaker recovery after breakage than those formed by charge neutralisation (Aguilar et al., 2003).

Table 4

The floc fractal dimension (FD) was also evaluated for all three coagulants before breakage and after regrowth using equations (4) and (5). Floc FD is an important factor representing the floc density, which impacts greatly on the efficacy of the solid/liquid separation process (Gregory, 1998). Results in Table 4 showed that the floc FD values followed the order of $FeCl_3$ (1.99) < $TiCl_4$ (2.14) ≤ PTC (2.2). The FD values obtained in this study are typical for flocs generated in water treatment processes (i.e. 1.5-2.2) (McCurdy et al., 2004). Results also indicate that the floc FD values follow the same trend as the floc SF values; suggesting that flocs having a better ability to resist a shear force will also present a higher degree of compactness. This can be explained by the strong relationship between the floc breakup mechanism and the floc structure. In fact, there are two main breakup mechanisms: surface erosion (slow) and large-scale fragmentation (fast) (Jarvis et al., 2005). Flocs with low FD will preferentially breakup via a fragmentation mechanism during which floc aggregates will split into pieces of comparable size, leading to a low SF. However, compact flocs with a high FD will breakup via surface erosion where small aggregates are separated from the surface of the main aggregated floc, leading to a higher SF. This result has also been demonstrated in a previous study where a close relationship between floc structure and floc strength was established (Wang et al., 2009). The discernible difference between $FeCl_3$ and Ti-based coagulants could be explained by the amount of AOM adsorbed within the flocs, which is higher for both Ti-based coagulants (i.e. higher DOC removal – Figure 1d). In fact, it has been previously demonstrated for inorganic colloids that the adsorption of organic macromolecules can induce a change in aggregate structure (Baalousha et al., 2008). Christian et al. (2008) also explained that the adsorption of organic macromolecules on aggregate surfaces can occur in two steps. First, the organic macromolecules may cover the surface of the aggregates in a fast adsorption step which could then be followed by a second step whereby slow diffusion of organic macromolecules within the aggregates pores occurs, resulting in the formation of more compact aggregates. Finally, results in Table 4 show that the FD values after regrowth were slightly higher than before breakage. In fact, it has been demonstrated that cyclic breakup and re-aggregation may lead to more compact aggregates through rearrangements at more favourable points resulting in more stable structures (Chakraborti et al., 2003; McCurdy et al., 2004).

Figure 3 displays the floc size distribution of the three coagulants before breakage (i.e. at steady state) and after regrowth. Flocs formed by $FeCl_3$ were polydispersed in size with the presence of smaller flocs (i.e. additional peak with smaller volume at about 700 μm) while the flocs formed by both Ti-based coagulants have a much narrower size distribution with the presence of only one peak at around 1100 μm. The presence of smaller flocs in the case of $FeCl_3$ is not advantageous since they tend to remain in suspension or settle more slowly after flocculation as evidence for the lower turbidity removal efficiency displayed in Figure 1b. After regrowth, a much broader floc size distribution towards lower floc size was obtained for all three coagulants, which corroborates with the lower average floc size obtained after regrowth (i.e. d_3 in Table 4). However, the volume of the main peak (i.e. observed before breakage – Figure 3a) remains relatively high after regrowth for $TiCl_4$ (Figure 3b) which supports the high RF value obtained for this coagulant.

Figure 3

Conclusions

This study investigated the performance of titanium salts as alternative coagulants for the removal of AOM in seawater. The results were systematically compared with those obtained with conventional $FeCl_3$ coagulant. The key findings can be summarised as follow:

- Both titanium salts (i.e. $TiCl_4$ and PTC) performed better in terms of turbidity, UV_{254} and DOC removal than conventional $FeCl_3$ at the same dose. The presence of AOM acting as coagulant aid combined with the presence of divalent cations (e.g. Ca^{2+}) promoting bridging mechanisms resulted in similar performance at low dose for all coagulants tested.
- LC-OCD measurements revealed that both humic substances and LMW organics were preferentially removed by all three coagulants while the removal efficiency for biopolymer was relatively low (i.e. about 15-50% removal efficiency). This was attributed to the presence of high proportion of LMW organics (i.e. 40% of the total DOC) interfering/competing with the flocculation process of other higher MW compounds.
- Detailed analysis of the floc characteristics showed that both $TiCl_4$ and PTC can grow faster and reach larger floc size than $FeCl_3$ while having a better ability to resist shear force (i.e. SF of about 45%, 48% and 27% for $TiCl_4$, PTC and $FeCl_3$, respectively). This is highly advantageous since many water treatment processes (e.g. desalination plants) are non-ideal with many potential zones of high shear forces that could induce floc breakage. The high recovery factor obtained with $TiCl_4$ (i.e. about 70%) is another obvious benefit.
- Finally, the floc FD followed the same trend as the floc SF indicating that flocs that have a better ability to resist shear force are also more compact and will therefore break up via surface erosion rather than large-scale fragmentation. The higher floc FD obtained with both $TiCl_4$ and PTC was related to their higher DOC removal efficiency.

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