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Ti-salt flocculation for dissolved organic matter removal in seawater

Sanghyun Jeong, Yosef Okour, Tien Vinh Nguyen, Ho Kyong Shon, Saravanamuthu Vigneswaran*

Faculty of Engineering and IT, University of Technology, Sydney (UTS), PO Box 123, Broadway, NSW, 2007, Australia
Tel. +61 2 9514 2614; Fax: +61 2 9514 2633; email: s.vigneswaran@uts.edu.au

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ABSTRACT

In this study, the removal of different fractions of organic matter in seawater was investigated using titanium tetrachloride ($TiCl_4$) flocculation and compared with ferric chloride ($FeCl_3$) flocculation. The organic matter fractions were characterised using liquid chromatography–organic carbon detector (LC–OCD). Results showed the hydrophobic compounds removal was dominant by both flocculants. However, the removal of hydrophilic organic compounds, such as humics and low-molecular weight neutral compounds of seawater, was superior by $TiCl_4$ flocculation compared to $FeCl_3$ flocculation and this removal increased considerably with the increase of $TiCl_4$ doses. The flocculated sludge after $TiCl_4$ flocculation was incinerated to produce titanium dioxide (TiO_2) nanoparticle. TiO_2 from seawater sludge characterised by X-ray diffraction (XRD) and scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM/EDS) showed predominant anatase phase with Si as a main dopant.

Keywords: Seawater; Flocculation; Titanium tetrachloride ($TiCl_4$); Ferric chloride ($FeCl_3$); Titanium dioxide (TiO_2) nanoparticle

1. Introduction

Natural organic matter (NOM) is one of the main foulants related to membrane processes that has a potential to form additional fouling by interaction between organic foulant itself or biomass [1,2]. This fouling is due to the adsorption onto the membrane surface or inside the pores. In addition, NOM can aggregate on the membrane surface and consequently form a sticky gel layer presenting high hydraulic resistance [3].

NOM usually have negatively functional groups such as carboxyl (–COOH) and phenolic groups (–OH) [4]. Pre-treatment methods such as Fe-salt and Ti-salt flocculation can remove a portion of NOM through three mechanisms namely charge neutralisation, electrostatic patch and bridging flocculation to reduce membrane fouling [5,6]. In general, flocculation preferentially removes the hydrophobic NOM fraction, whereas the neutral hydrophilic fraction is responsible for much of the irreversible fouling [7].

Coagulation–flocculation is a well-known pre-treatment method that can remove particles and colloids in water and wastewater treatment. The use of $FeCl_3$ as Fe-salt flocculant is considerably increased due to its high DOC removal efficiency with no detrimental effect to the living environment compared to aluminium (Al) salt [8]. However, the application of Ti-salt flocculant in water treatment, which was firstly investigated, by Upton and Buswell [9] has attracted a new

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*Corresponding author.

attention in seawater treatment. Recently, Okour et al. [6] studied the application of Ti-salt flocculant as a pre-treatment for seawater reverse osmosis (SWRO). They reported that flocculation followed by granular activated carbon (GAC) filtration significantly reduced the turbidity, silt density index (SDI_{15}), dissolved organic carbon (DOC), colour and UV absorbance of flocculated seawater. In addition, $TiCl_4$ flocculation as a pre-treatment to SWRO was compared with $FeCl_3$ flocculation with respect to flocculation performance, membrane autopsy of fouled RO and sludge recovery after $TiCl_4$ flocculation. The authors found that the residual Ti salts did not cause any severe membrane fouling compared to Fe salts. Zhao et al. [10] investigated the flocculation mechanism by $TiCl_4$ and they stated that the flocculation was not only processed by charge neutralisation but also might be by a chemical bond. During flocculation, NOM might absorb by hydroxide solid at an optimum pH of 8.0. Floc size by $TiCl_4$ flocculant was larger than that of $FeCl_3$, polyferric sulphate (PES), $Al_2(SO_4)_3$ and polyaluminium chloride (PACl). $TiCl_4$ flocculation has an advantage in application over a wider range of high pH [11]. However, no efforts were made to study the organic matter removal in detail by Ti-salt flocculant.

A significant disadvantage of flocculation is the production of a large amount of sludge. The sludge requires an additional treatment and disposal in ocean and landfills. In recent years, due to serious oceanic contamination and damage of the fragile ecology of the coastal area, disposal of the waste into the ocean has been restricted. Shon et al. [12,13] developed a method to recover multi-functional titanium dioxide (TiO_2) nanoparticles from the $TiCl_4$ sludge. The prices of Ti-salt coagulation are five times higher than those of Al-salt while the sludge recycling and TiO_2 production compensate for the high Ti-salt price and ultimately provide numerous benefits with revenue to promote a water treatment plant [14]. These benefits of adopting Ti-salt coagulation, sludge recycling and by-product production have been proven during the last six years of research studies. Titanium dioxide is used in a number of industries. It is used as white pigment, sunscreen, a thickener in cosmetic and skin-care products and particularly a photocatalyst under ultraviolet (UV) light. Lee et al. [15] evaluated aquatic toxicity of this TiO_2 nanoparticle produced from flocculated sludge of seawater in terms of LC50 and mortality of *Daphnia magna* and EC50 of Microtox® test. They found that $TiCl_4$ coagulant and TiO_2 produced from flocculated seawater sludge had very low toxicity in aqueous condition compared with Degussa TiO_2-P25.

Therefore, the advantages of Ti-salt coagulation are: (1) it is required at lower dosage; (2) it is active at low water temperatures; (3) it facilitates short sedimentation time; (4) it has better removal of organic/inorganic materials; and (5) it generates a valuable by-product. In this study, the flocculation performance of $TiCl_4$ of organic matters in seawater was investigated in terms of NOM fractionations removal. NOM removal of $TiCl_4$ was also compared with that of commonly used $FeCl_3$ flocculant. Finally, TiO_2 recovered from flocculated sludge of seawater was characterised in terms of particle structure and atomic composition to evaluate its use.

2. Materials and methods

2.1. Seawater

Seawater conducted in this study was drawn from Chowder bay, Sydney, Australia. It was withdrawn from 1 m below the surface level of the sea and then filtered through the centrifuge to remove large particles. The range of turbidity, pH and dissolved organic carbon (DOC) values of the seawater during the study period was 0.41–0.42 NTU, 7.98–8.04 and 1.30–1.45 mg/L, respectively.

2.2. Flocculation test

$TiCl_4$ and $FeCl_3$were used as flocculants in this study. $TiCl_4$ was prepared as 10% stock solution and $FeCl_3$ was prepared as 1000 mg/L of stock solution using $FeCl_3 \cdot 6H_2O$. The flocculation tests were carried out using standard jar test as indicated below. The seawater was placed in 1 L beakers and predetermined concentrations of titanium (Ti^{4+}) and ferric (Fe^{3+}) of 1.3–6.3 mg/L and 1.0–5.0 mg/L were added, respectively. The samples were then stirred rapidly for 2 min at 120 rpm, followed by 20 min of slow mixing at 30 rpm and 30 min of settling. The supernatant was filtered through 0.45 μm microfilter and the filtrate was used for further dissolved organic carbon (DOC) analysis.

2.3. Organic fractionation

Total DOC and detailed organic fractions were measured (two replicates) using a liquid chromatography–organic carbon detector (LC–OCD) Model 8 (DOC-Labor, Karlsruhe, Germany), which is an automated size-exclusion chromatography coupled to three detectors, organic carbon (OCD), organic nitrogen (OND) and UV-absorbance (UVD). The measurement procedure has been described in detail elsewhere [20]. In this study, a Toyopearl TSK HW50S column (TOSOH Bioscience GmbH, Stuttgart, Germany) was utilized with phosphate buffer as mobile phase of pH 6.4 ($2.6\,g\,L^{-1}$ KH_2PO_4 and $1.5\,m\,L^{-1}$ Na_2HPO_4) at a flow rate of $1.1\,mL\,min^{-1}$. Injection volumes and retention time were 1000 μL and 120 min, respectively. The chromatographic column was a weak cation exchange column on polymethacrylate basis. In this paper, mean values (from two replicates) of DOC data were used and standard variation was less than 5%.

2.4. TiO_2 recovery

The flocculated sludge of $TiCl_4$ was collected, filtered and dried in the oven at 100°C for three days to remove the water content. Then it was grinded and placed in a furnace at 600°C for 24 h. After incineration, the colour was changed from black to white indicating the formation of TiO_2.

2.5. TiO_2 characterisation

To identify TiO_2 particle structure, X-ray diffraction (XRD) was investigated using MDI Jade 5.0 (Materials Data Inc., USA). The aggregated particle image and composition of TiO_2 were observed using scanning electron microscopy (SEM, Rigaku, Japan).

3. Results and discussion

3.1. Organic matter removal

In this study, $TiCl_4$ was used as Ti-salt flocculant and its performance was compared with that of $FeCl_3$. Table 1 presents the DOC of flocculated effluent after $TiCl_4$ and $FeCl_3$ flocculation.

Organic matter was divided into two parts by LC–OCD. Hydrophobic organic carbon (HOC) was calculated as a difference of dissolved organic carbon (DOC) with chromatographic DOC (CDOC). All organic matter retained in the column was defined as hydrophobic. This could be either dissolved hydrocarbons or microparticulate including humics. CDOC is calculated from the area enclosed by the total chromatogram (Fig. 1).

Although the seawater samples were taken from the same sampling site, they were collected at different times for $TiCl_4$ and $FeCl_3$ flocculation tests. This is the reason why the seawater used in flocculation with $TiCl_4$ had more hydrophobic matters (40.7%) than that with $FeCl_3$ (25.4%).

The results showed that the DOC removal efficiency increased with the increase in flocculant doses. Hydrophobic compound removal was significant by both flocculants. The removal efficiency of hydrophobic compounds by $FeCl_3$ flocculation was much higher than that of hydrophilic compounds. Most hydrophobic compounds (94%) and a part of hydrophilic compounds (49%) were removed at ferric (Fe^{3+}) dosage of 5.0 mg/L.

In case of $TiCl_4$, the difference in hydrophobic and hydrophilic compounds removal was only 12% at a dose of 5.0 mg of Ti^{4+}/L. Interestingly, at all experimental concentrations, around 75% of hydrophobic compounds in seawater were removed by $TiCl_4$ flocculation. On the other hand, the removal of hydrophilic compounds was improved significantly as $TiCl_4$ concentration was increased from 1.3 to 5.0 mg/L.

Table 1
The removal of DOC after flocculation with $TiCl_4$ and $FeCl_3$

	DOC (mg/L)[a]	Removal efficiency (%)[b]	HOC (mg/L)[a] Hydrophobic	Removal efficiency (%)[b]	CDOC (mg/L)[a] Hydrophilic	Removal efficiency (%)[b]
(a) $TiCl_4$ (as mg of Ti^{4+}/L)						
0.0[c]	1.45	–	0.59	–	0.86	–
1.3	0.62	57.2	0.15	74.6	0.47	45.3
2.5	0.57	60.7	0.15	74.6	0.42	51.2
3.8	0.52	64.1	0.15	74.6	0.37	57.0
5.0	0.47	67.6	0.15	74.6	0.32	62.8
(b) $FeCl_3$ (as mg of Fe^{3+}/L)						
0.0[c]	1.30	–	0.33	–	0.97	–
0.5	0.70	46.2	0.05	84.8	0.65	33.0
1.0	0.65	50.0	0.05	84.8	0.60	38.1
3.0	0.60	53.8	0.04	87.9	0.56	42.3
5.0	0.52	60.0	0.02	93.9	0.50	48.5

[a] Concentrations of the different organic fractions in seawater.

[b] Removal efficiencies of different organic fractions in seawater after the pre-treatment.

[c] Seawater with no flocculant.

Similar results were obtained by Okour et al. [6]. They reported that biopolymers, fulvic acids and low-molecular weight compounds with molecular weight of 1200, 950 and less than 650 Dalton were removed by Ti-salt flocculant.

3.2. Detailed natural organic matter (NOM) fraction

Natural organic matter (NOM) in seawater mainly contains biopolymers (BP), humic substances (HS or humics), building blocks (BB) and low-molecular weight neutrals (LN). It was observed that $TiCl_4$ flocculation led to a higher amount of CDOC removal than $FeCl_3$ (Table 2).

3.2.1. Biopolymers (BP)

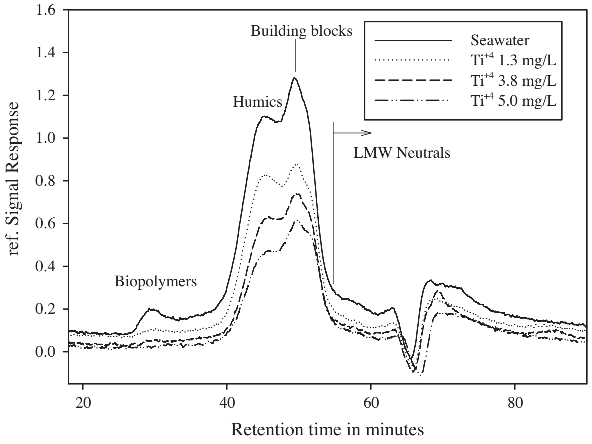
BP have very high molecular weight (20,000–100,000 g/mol) and it represent compounds such as polysaccharides, amino sugars, polypeptides, proteins, "extracellular polymeric substances", hydrophilic fraction and not UV-absorbing. In surface water, BP exist as colloidal transparent exopolymer particles (TEP) and polysaccharide. These fractions were identified as possible fouling active substances [16–18]. BP decreased significantly after flocculation with both flocculants (Fig. 1 and Table 2). The comparison of LC–OCD chromatograms shows that $TiCl_4$ flocculation retained more organic biopolymers than the $FeCl_3$ flocculation. BP removal efficiency increased as $TiCl_4$ doses increased with complete removal occurring at a dose of 5.0 mg of Ti^{4+}/L.

3.2.2. Humic substances (HS)

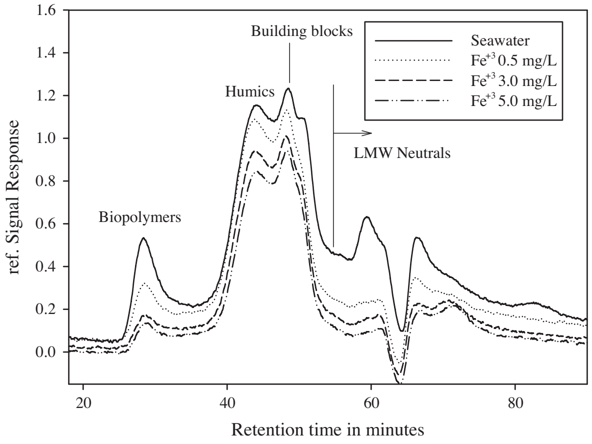
Humic substances (HS) represent compounds with molecular weights approximately 1000 g/mol. Zazouli et al. [19] reported that the flux reduction on NF membrane increased with increasing humics concentration in foulants. As can be seen from Fig. 1 and Table 2, HS removal was marginal by flocculation with $FeCl_3$ (20.6–26.5%). On the other hand, as $TiCl_4$ dose increased from 1.3 to 5.0 mg/L, the HS was removed remarkably from 40.9% to 63.6%.

3.2.3. Building blocks (BB)

Building blocks (BB) are defined as HS-hydrolysates, sub-units of HS with molecular weights between 300 and 450 g/mol. There are mainly weathering and oxidation products of HS. According to Huber et al. [20], BB cannot be removed by typical flocculation processes. Flocculants or coagulants as well as flocculated particles sometimes should be considered as another factor in the formation of BB. In the same manner, in our study also BB did not show high removal (Table 2). BB removal slightly decreased with the increase of flocculant doses. Removal efficiencies of BB by $FeCl_3$ and $TiCl_4$ flocculants at a dose of 5.0 mg of Ti^{4+}/L were below 38.1% and 44.4%, respectively.



(a) $TiCl_4$



(b) $FeCl_3$

Fig. 1. LC–OCD chromatogram of seawater and pretreated seawater using $TiCl_4$ and $FeCl_3$.

3.2.4. Low-molecular weight neutrals (LMW neutrals or LN)

Low-molecular weight neutrals (LMW Neutrals; LN) are the only low-molecular weight weakly charged hydrophilic or slightly hydrophobic "amphiphilic" compounds such as alcohols, aldehydes, ketones and amino acids. Dittmar and Kattner [21] stated that LMW neutrals could be described as amphiphilic dissolved organic matter (DOM) recalcitrant to biodegradation such as metabolic intermedi-

Table 2
Amount of different hydrophilic fractions of seawater removed by flocculants of different doses

	$FeCl_3$ (mg of Fe^{3+}/L)					$TiCl_4$ (mg of Ti^{4+}/L)				
	0.0[a]	0.5	1.0	3.0	5.0	0.0[a]	1.3	2.5	3.8	5.0
BP	0.14	0.08	0.07	0.05	0.04	0.09	0.06	0.04	0.01	0.00
HS	0.34	0.27	0.27	0.26	0.25	0.44	0.26	0.24	0.21	0.16
BB	0.21	0.19	0.16	0.16	0.13	0.18	0.13	0.11	0.11	0.10
LN	0.28	0.11	0.10	0.09	0.08	0.15	0.01	0.01	0.01	0.01

[a] Seawater with no flocculant.

ates and bacterial membranes moieties. Therefore, effective LN removal may reflect the reduction of microbial activity. Some researchers indicated that organic fouling is primarily caused by LN [2].

Both flocculation tests indicated high LN removal efficiencies, particularly with $TiCl_4$. Only trace of LN remained after $TiCl_4$ flocculation with removal efficiency reaching up to 93.0% (Table 2).

3.3. Sludge recovery

During coagulation processes, sludge disposal and treatment is the question pressing for serious environment considerations. In order to recover valuable TiO_2 nanoparticle from flocculated sludge, Ti-salt sludge was calcinated at 600°C to remove organic matters.

XRD pattern of recovered TiO_2 particles is shown in Fig. 2. Recovered TiO_2 was found to have only anatase phase after calcination at 600°C. Many researchers hydrothermally crystallised titanium dioxide gel and obtained anatase phase at temperature lower than 600°C [22]. However, the incineration temperature of 600°C was suggested in terms of energy consumption and better photocatalytic activity of TiO_2 produced from Ti-flocculated sludge [11].

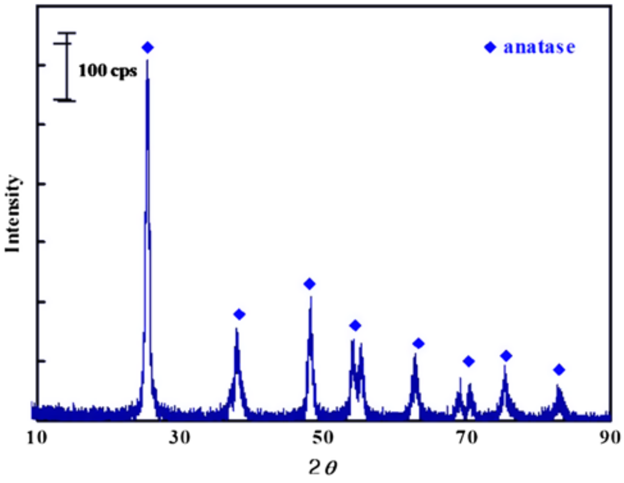


Fig. 2. XRD pattern of the TiO_2 recovered from $TiCl_4$ flocculation.

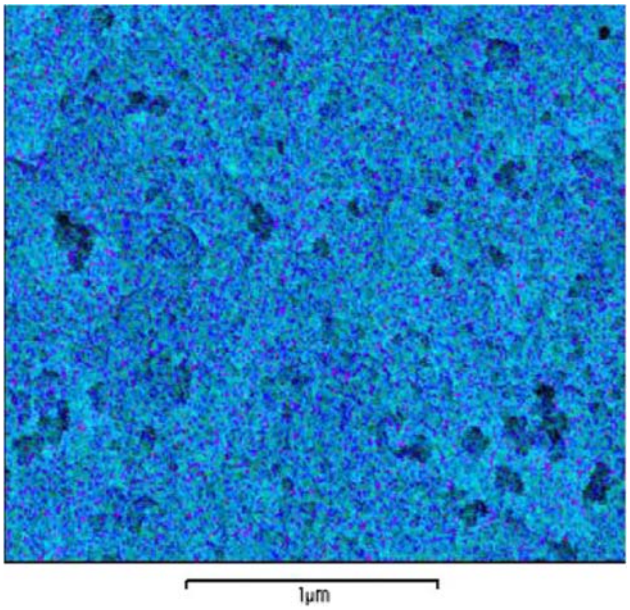


Fig. 3. SEM image of the TiO_2 recovered from $TiCl_4$ flocculation.

It was observed from SEM image of TiO_2 recovered from $TiCl_4$ flocculation that TiO_2 nanoparticles were doped with Si. Their atomic compositions of Ti, Si and O were 23.8%, 0.2% and 76.0%, respectively. In Fig. 3, violet small dots and light-blue background represented Si and Ti, respectively. Okour et al. [6] suggested that Si could be diminished through flocculation process and it was coated with TiO_2.

4. Conclusion

The performance of Ti-salt flocculation of seawater was compared to that with Fe-salt flocculation in terms of detailed organic fractionation matter removal. The following are the finding of the experimental study.

(1) The removal of hydrophilic compounds of seawater by $TiCl_4$ flocculation was superior compared to $FeCl_3$ flocculation and this removal increased significantly as $TiCl_4$ doses increased.
(2) Complete removal of biopolymers of NOM was achieved during $TiCl_4$ flocculation.
(3) Higher humics removal of 63.6% was observed with $TiCl_4$ flocculation compared to only 26.5% with $FeCl_3$ flocculation.
(4) Both flocculant showed low percentage removal for building blocks of NOM.
(5) $TiCl_4$ flocculation indicated high LMW neutrals removal even at low doses. LMW neutral is one of the significant compounds causing organic fouling of membranes.
(6) From XRD and SEM/EDX analyses, the recovered TiO_2 nanoparticles from $TiCl_4$ flocculated sludge were found to be Si-doped anatase structure.

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Abbreviations

BB	–	building blocks
BP	–	bio polymers
CDOC	–	chromatographic dissolved organic carbon
DOC	–	dissolved organic carbon
HOC	–	hydrophobic organic carbon
HS	–	humic substances
LC–OCD	–	liquid chromatography–organic carbon detector
LN	–	low-molecular weight neutrals
NOM	–	natural organic matter

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