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# Coagulation of dissolved organic matter in surface water by novel titanium (III) chloride: mechanistic surface chemical and spectroscopic characterisation

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## Abstract

Problems caused by residual organics in treated water include the formation of disinfection by-products (DBP) following reaction with chlorine and being a substrate for microbial regrowth in the drinking water distribution system. Dissolved organic matter (DOM) can only be partially removed by conventional treatment process i.e. coagulation by Al- and Fe-based salts. In the present study, the performance of titanium trichloride ( $TiCl_3$ ) as a coagulant for surface water treatment was studied and compared with conventionally used aluminum sulfate (alum). Jar test experiments were performed at various coagulant doses and pH levels to determine the optimum conditions based on removal efficiencies of dissolved organic carbon (DOC). The zeta potential values were analysed for assessing the destabilisation mechanism of DOM flocs. The  $TiCl_3$  showed a significantly higher capacity for DOC removal at pH around 3 at which charge neutralization was found to be the dominant mechanism for the floc formation. This was further evident from the relatively larger floc sizes obtained with  $TiCl_3$  treatment. However, destabilization of Ti-flocs occurred at pH 4.5 through an adsorption-enmeshment mechanism due to a highly negative zeta potential. Additionally, fluorescence spectroscopic analyses showed that  $TiCl_3$  was more efficient than alum in removing humic

27 compounds. A two-stage treatment process by alum and  $\text{TiCl}_3$ , either as the same chemical or both showed  
28 better performance than a single dose treatment. The results indicate that  $\text{TiCl}_3$  could be an effective  
29 alternative coagulant for the treatment of waters, particularly those of low alkalinity and high DOC  
30 concentration and low pH wastewaters for removal of hydrophobic compounds and particulate matter.

31 **Keywords:** Coagulation; Titanium trichloride; Dissolved organic matter; Fluorescence spectroscopy; Floc  
32 stabilization.

33

## 1. Introduction

The removal of dissolved and particulate organic matter from surface waters for drinking water supply using physio-chemical processes such as coagulation, adsorption, ion exchange, membrane filtration and advance oxidation have been well documented in the literature. Among them, coagulation is a widely used method for the removal of dissolved organic matter (DOM) and suspended particles [1-3] despite that DOM can only be partially removed by this process. Enhanced coagulation refers to maximizing the removal of DOM from drinking water sources by increasing the coagulant dose and/or optimizing coagulation pH. This removal occurs primarily through two major mechanisms: (1) charge neutralization, and (2) sweep coagulation or adsorption/entrapment where organic matter adsorbs onto the surface of insoluble metal hydroxide precipitates [4]. Conventional coagulants such as Al and Fe based salts (e.g. alum, ferric chloride, polyferric sulphate and polyaluminum chloride) are widely used for drinking water treatment for their reliable performances, commercial availability and relatively inexpensive costs. However, the use of high doses of these coagulants for maximizing DOM removal from source waters with high concentrations can result in production of large amounts of sludge that requires further treatment and solids waste disposal [5, 6]. Practices such as incineration and disposal to landfills are costly with potential environmental impacts [7]. Thus, water treatment plant operators and managers can face significant challenges in treatment processes when Al or Fe based coagulants are used, especially when operational conditions are challenged by poor source water quality.

With high concentrations of residual organic matter present in treated waters, potential problems can occur such as reduced aesthetic quality (colour, taste and odour compounds), reaction with chlorine lowering or removing chlorine residual and bacterial regrowth in the distribution system. Residual DOM in treated drinking water can readily react with chemical (oxidizing) disinfectants such as chlorine resulting in the formation of potentially carcinogenic, cytotoxic or genotoxic disinfection by-products such as trihalomethanes (THM) and nitrogenous DBPs (N-DBPs) such as haloacetonitriles (HAN) and halonitromethanes (HNM) [8, 9]. This is a general concern for drinking water supply companies and

59 authorities globally. In recent years, it has been reported that DOM levels in water resources have increased,  
60 which may be due to climate change [4, 10] and in Australia, to extreme climate events [11, 12]. In 2010-  
61 2011 and 2011-2012 strong La Niña events occurred in Australia that resulted in the Murray-Darling Basin  
62 experiencing high rainfall which led to major and widespread floods [13]. These events resulted in significant  
63 declines in water quality where dissolved organic carbon (DOC) levels exceeded 15 mg/L [12].

64 Drinking water treatment using conventional metal-based coagulants (Al and Fe) is able to remove  
65 only a fraction of organic matter present dependent on its characters where aromatic, hydrophobic and high-  
66 molecular weight (HMW) compounds as of humic substances are amenable to removal but low-molecular  
67 weight (LMW), hydrophilic compounds tend to be recalcitrant to removal by coagulation [14]. Research and  
68 development on particular hydrolyzed metal species such as  $Al_{13}$  as reported by Lin et al. [15] exemplifies  
69 efforts to improve performances of metal coagulants, including for improved DOC removals.

70 Research has been conducted to find alternative metal salts that have higher charge neutralization and  
71 greater DOC removal capacity with the formation of larger size flocs that have higher settling rates than  
72 conventional salts [16-19]. Highly charged Ti (IV) and Zr (IV) based coagulants such as titanium  
73 tetrachloride ( $TiCl_4$ ) and zirconium tetrachloride have been shown to have capacity for higher DOC removals  
74 with the formation of larger sized flocs than Al and Fe based coagulants [6, 17, 18, 20]. Various hydrolysed  
75 species of Ti such as  $Ti(OH)^{3+}$ ,  $Ti(OH)_2^{2+}$ ,  $Ti(OH)_3^+$ ,  $Ti(OH)_4^0$ ,  $Ti(OH)_5^{1-}$ ,  $Ti(O_2)_2(OH)_2^{2-}$  and  $Ti(O)(O_2)$   
76  $(OH)_2^{2-}$  are formed at different pH levels and Ti doses, and these species play an important role during the  
77 particle stabilization [21, 22]. The first investigation of Ti salt for coagulation was reported by Upton and  
78 Buswell [23] who found that  $Ti(SO_4)_2$ , as a tetravalent cationic salt, showed a better coagulation efficiency for  
79 fluoride removal than trivalent Al or Fe salts. Zhao et al. [24] developed a novel polytitanium tetrachloride  
80 (PTC) as pre-hydrolysed coagulant which showed better performance than  $TiCl_4$ . Shon et al. [16] reported  
81 that  $TiCl_4$  had good performance for the removal of various apparent molecular weight compounds of DOM  
82 from wastewater. They also reported that the Ti-based sludge formed following coagulation treatment can be  
83 converted to value added materials (e.g.,  $TiO_2$ ) in a simple process [16, 25, 26]. Zhao et al. [18] reported that

84 coagulation behavior of titanium tetrachloride ( $\text{TiCl}_4$ ) was very similar to Al and Fe based salts. However,  
85  $\text{TiCl}_4$  is volatile and forms cloudy  $\text{TiO}_2$  and HCl in humid air conditions at room temperature and being  
86 hazardous [27], there is need for other Ti based salts that are more stable under ambient conditions, are safe,  
87 reliable and readily prepared. This study investigated the potential of titanium (III) chloride as a coagulant  
88 under a range of conditions including coagulation pH and at various dose rates in comparison to and in  
89 combination with alum (aluminium sulphate). This study investigated the coagulation mechanisms of  $\text{TiCl}_3$  by  
90 exploring the surface chemistry of flocs and spectroscopic characterization of residual DOM post  $\text{TiCl}_3$   
91 treatment.

## 92 **2. Materials and methods**

### 93 **2.1. Water quality analysis**

94 Water samples were collected from the River Murray at Tailem Bend, South Australia ( $34.9285^\circ$  S,  
95  $138.6007^\circ$  E), located about 96 km away from the city of Adelaide. These samples were transported to the  
96 laboratory on ice and stored in a cold room at  $\leq 4^\circ\text{C}$  prior to the jar testing and water quality analyses. A  
97 portable pH meter (TPS, Model WP-91) was used to measure the pH of raw and treated waters (from jar  
98 tests). The turbidity was measured by a 2100N HACH turbidimeter. For the analyses of dissolved organic  
99 carbon (DOC), water samples were filtered through  $0.45\ \mu\text{m}$  pre-rinsed sterile cellulose membrane filters.  
100 DOC was measured by a TOC analyzer (Model 820, Sievers Instruments, USA).

101 Fluorescence excitation-emission matrix (F-EEM) spectra were acquired (Model LS55, PerkinElmer)  
102 to characterize DOM in terms of humic-like (HA), fulvic-like (FA), Protein1 (P1), Protein2 (P2) and soluble  
103 microbial by-product (SMP)-like components. A series of emission spectra (280–600 nm) were obtained with  
104  $0.5\ \text{nm}$  increments over excitation wavelength (200–500 nm) with  $5\ \text{nm}$  increments. The method of Chen et  
105 al. [28] was used to measure five different EEM regions for each sample. Samples for F-EEM analysis were  
106 pre-filtered through  $0.45\ \mu\text{m}$  pre-rinsed sterile cellulose membrane filters.

107 The zeta potential (ZP) value of flocs formed at various pH values and coagulant doses was  
108 determined using a Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK), with a detection range of  
109 0.3 nm to 10 µm (diameter) size particles at room temperature 25 °C.

## 110 **2.2. Coagulants**

111 Alum [ $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ] was obtained from Incitec Pivot Ltd - Port Adelaide, South Australia.  $\text{TiCl}_3$   
112 was sourced from Merck Schuchardt OHG, Germany. A stock solution of alum (1.6 g Al/L) was prepared by  
113 diluting 40.5 g of concentrated aluminum sulphate (approximately 7.6% w/w  $\text{Al}_2\text{O}_3$ ) in 1 L high purity Milli-  
114 Q<sup>®</sup> water. The same concentration (1.6 g Ti/L) of  $\text{TiCl}_3$  stock solution was prepared by dissolving  
115 approximately 13 mL of  $\text{TiCl}_3$  (30%) in 1 L of high purity Milli-Q<sup>®</sup> water. The freshly prepared alum and  
116  $\text{TiCl}_3$  solutions were stored overnight at room temperature to dissolve the metal salts and subsequently stored  
117 at 4°C prior to their use. The concentrations of Al and Ti in stock solutions were verified using inductively  
118 coupled plasma mass spectrometry (ICP-MS; Model: 7500c, Agilent Technologies, USA).

## 119 **2.3. Coagulation study**

120 To optimize the coagulation pH and coagulant dose, preliminary experiments were conducted using a  
121 standard jar test apparatus (Model FMS6V, SEM Pty, Brisbane, Australia) equipped with six paddle gang  
122 stirrers and Gator jars filled with 1 L water. The coagulation pH was controlled at different levels between 3  
123 and 9. The optimum coagulant dose was determined from the jar test using doses ranging from 2 to 40 mg/L  
124 (as the respective metal concentration) at a pre-determined optimum pH for each coagulant. For the target pH  
125 adjustment, the required amount of 0.5 M NaOH or 0.5 M HCl was determined by prior pH titration and then  
126 added to the test water before addition of coagulant.

127 Experiments were conducted using flash mixing @ 200 rpm for 1 min and 14 min of slow mixing @  
128 20 rpm then followed by a settling time of 15 min. The settled water (unfiltered turbidity of the supernatant)  
129 was measured immediately after 30 min of the coagulation experiment. After that, the filtered turbidity was  
130 measured following filtering the supernatant through a 11 µm pore size filter (Whatman No 1). All jar test

131 experiments were performed at room temperature (25°C). Coagulation efficiency was determined using the  
132 following Equation 1:

$$133 \quad \text{Removal (\%)} = \frac{(C_i - C_e) \times 100}{C_i} \quad (1)$$

134 Where,  $C_i$  and  $C_e$  are the initial and final concentrations in mg/L, respectively.

135 In a second coagulation experiment protocol, two coagulants (alum and  $\text{TiCl}_3$ ) were used to assess  
136 their effects individually and in combination. Initially, raw waters were treated by alum or  $\text{TiCl}_3$  at an  
137 optimum dose and optimum pH level determined from the preliminary experiments. The supernatants of  
138 treated waters were further treated with two different additional doses (one-half of the optimum dose and  
139 optimum dose) of alum and  $\text{TiCl}_3$ . The experimental conditions of the second jar test remained the same as  
140 for the preliminary jar experiment. The efficiency of each jar test protocol was assessed with respect to the  
141 relationship of residual DOC concentration, DOM characteristics (F-EEM), turbidity removal and floc zeta  
142 potential values.

#### 143 **2.4. Optimum coagulation dose**

144 In this study, optimum coagulant doses (for maximizing DOC removal at an operationally acceptable  
145 coagulant dose) were calculated based on DOC removal, where an additional 10 mg/L of coagulant resulted  
146 in less than 0.10 mg/L DOC reduction. TableCurve™ software was used to identify the relation between  
147 DOC residuals and coagulant doses, i.e. an exponential decay function, Equation (2).

$$148 \quad \text{DOC}_R = \text{DOC}_{\text{NC}} + \text{DOC}_C \times e^{-Cx} \quad (2)$$

149 Where,  $\text{DOC}_R$  is the DOC residual (mg/L) at a selected coagulant dose ( $x$ , mg/L),  $\text{DOC}_{\text{NC}}$  is non-  
150 coagulable DOC,  $\text{DOC}_C$  is the coagulable DOC ( $\text{DOC}_{\text{initial}} - \text{DOC}_{\text{NC}}$ ), and  $C$  is the DOC removal rate co-  
151 efficient determined from data of all jars of the jar test.

#### 152 **2.5. Floc size measurement**

153 Settled flocs were immediately collected after 30 min of coagulation experiment (jar tests). The  
154 suspension of flocs was stored in the pre-rinsed plastic bottles at room temperature prior to analysis. Average  
155 floc size was determined using a laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK). The



156 average sizes of alum and  $\text{TiCl}_3$  flocs were characterized according to three different volumetric diameters  
157 ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$  referring to 10%, 50% and 90% floc sizes, respectively). The average sizes of flocs of both  
158 the coagulants were compared at pH levels between 3 to 9 and doses between 2 to 40 mg/L, as metal  
159 concentrations. In most recent studies, the ' $d_{50}$ ' value was reported as the representative size of flocs to  
160 understand the coagulation mechanism of different metal salts [22].

## 161 **2.6. Floc characterization**

162 The morphology of Al and Ti flocs was observed under a scanning electron microscope (SEM). For  
163 this purpose, a drop of floc sample was taken onto a polished carbon/graphite mount. The mount was then  
164 deposited with a 40 nm pulsed carbon coating by using a Quorum QT150ES coating system. Samples were  
165 then examined by using a FEI Quanta 450 FEG Environmental Scanning Electron Microscope equipped with  
166 an energy dispersive X-ray analysis (EDAX) Apollo EDX detector. Images were taken in high vacuum mode  
167 and with a 30kV accelerating voltage using an Everhart-Thornley Detector (ETD) and a solid state Back  
168 Scattered Electron detector (BSED). Processed images having equal mixture (50:50) of signals from both the  
169 detectors were presented. EDAX spectra were acquired from selected areas on the samples for 100 sec. at a  
170 point.

171 For X-ray Diffraction (XRD), freeze dried floc samples were taken on a zero-background silica  
172 sample holder for collecting the XRD patterns which were acquired by using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ )  
173 on a PANalytical, Empyrean X-ray diffractometer operating at 40 kV and 40 mA between 2 and  $90^\circ 2\theta$  at a  
174 step size of  $0.026^\circ$ .

175 The thermal behaviour of Al and Ti flocs (sludge) was determined by thermogravimetric (TGA) and  
176 differential thermogravimetric (DTGA) analyses using a high-resolution TGA system (Model: Mettler-Toledo  
177 DSC-1, Mettler-Toledo International Inc., USA). The flocs were heated from  $25^\circ\text{C}$  to  $1,000^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$   
178  $^\circ\text{C}/\text{min}$  under a continuous  $\text{N}_2$  flow ( $50 \text{ mL}/\text{min}$ ).

179 For Fourier transform infrared (FTIR) spectroscopy analysis, floc suspensions of Al and Ti were  
180 centrifuged at 10,000 rpm for 15 min. Following washing in Milli-Q water, the pellets were freeze dried. The

181 samples were then mixed with dehydrated KBr and pressed into discs by using a hydraulic press. Infrared (IR)  
182 spectra were obtained using an Agilent Cary 600 Series FTIR Spectrometer. Spectra over the 4,000–400  $\text{cm}^{-1}$   
183 range were obtained by the co-addition of 64 scans with a resolution of 4  $\text{cm}^{-1}$ .

### 184 3. Results and Discussion

185 The water quality of the raw waters was analyzed immediately after collection, and the mean  $\pm$  S.D.  
186 values were as follows: pH  $7.2 \pm 0.1$ ; turbidity  $36 \pm 1$  NTU; DOC  $11.3 \pm 0.2$  mg/L and ZP  $-22.4 \pm 0.2$  mV.  
187 The F-EEM data showed that DOM present in raw waters had higher average abundances of HA-like (23%)  
188 and FA-like (44%) compounds compared with protein-like compounds (3% for P1; 18% for P2; 11% for  
189 SMP).

#### 190 3.1. Effect of coagulation pH on the coagulation performance

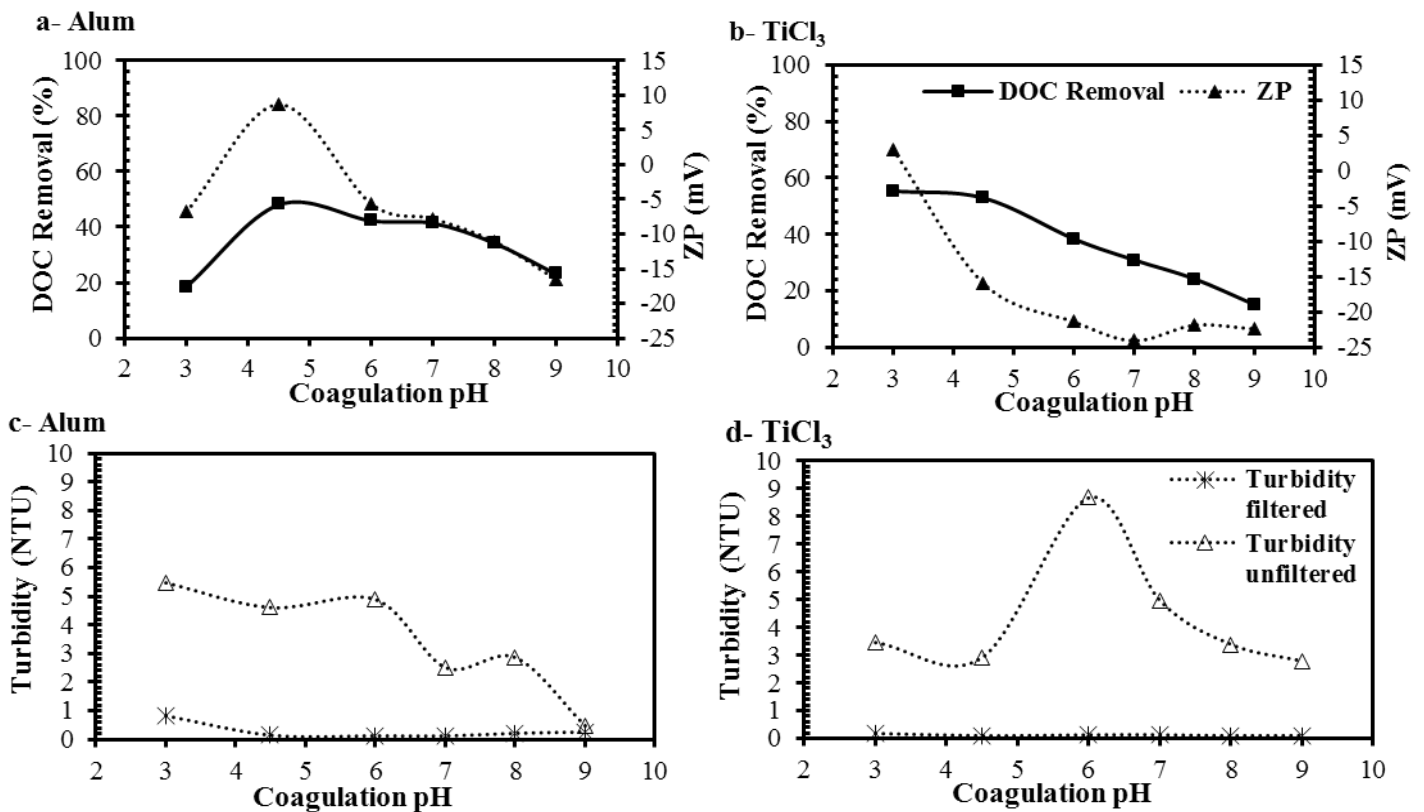
191 In initial jar test experiments, the coagulation performances of alum and  $\text{TiCl}_3$  were optimized using  
192 target coagulation pH levels ranging from 3 to 9. The efficiency of each coagulant was assessed in terms of  
193 DOC and turbidity removals at a pre-selected coagulant dose of 10 mg/L (Fig. 1). The performances of both  
194 alum and  $\text{TiCl}_3$  greatly depended on the coagulation pH as shown in Fig. 1. For alum, the DOC removal  
195 (48%) achieved at pH 4.5 was slightly higher than the removal achieved at pH 6 (~43% removal), whereas the  
196 lowest DOC removal (18%) was found at pH 3 (Fig. 1a, c).

197 In contrast,  $\text{TiCl}_3$  yielded a maximum DOC removal of about 56% at pH 3 (Fig. b, d). DOC removal  
198 (53%) achieved at pH 4.5 was slightly lower than the removal achieved at pH 3. However, for waters treated  
199 by  $\text{TiCl}_3$  at pH level more than 4.5, the percentage removal of DOC sharply decreased as the pH level  
200 increased (Fig. 1b, d). Among all the pH levels tested, the lowest DOC removal was found at pH around 9.

201 Zhao et al. [29] studied the effect of different hydrolyzed Al species on the coagulation efficiency  
202 where they found that at low pH conditions such as 4 or below, the monomeric  $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_{2-3}]^+$  and  
203 dimeric  $[\text{Al}_2\text{O}_2(\text{OH})(\text{H}_2\text{O})_{0-5}]^+$  Al species were produced as the major products. The increase in pH ( $> 4$ )  
204 resulted in the greater rate of hydrolysis and polymerization processes [29] which yielded low residual DOC  
205 compared to the  $\text{pH} \leq 4$  where higher residual DOC was observed.

206 For  $\text{TiCl}_3$ , the unfiltered turbidities at pH 3 and 4.5 were about 3 NTU whereas the turbidity at pH 6  
 207 was about 9 NTU (Fig. 1d). While for alum, the unfiltered turbidities at pH less than 6 was about 5 NTU.  
 208 Filtered (11  $\mu\text{m}$  filters) turbidities of alum treated waters were 0.8 NTU and 0.1 NTU at pH 3 and 6,  
 209 respectively (Fig. 1c), and of  $\text{TiCl}_3$  treated waters were 0.2 NTU and 0.1 NTU at corresponding pH levels.

210 Chow et al. [30] reported that the residual alum concentration in water following enhanced  
 211 coagulation at  $\text{pH} < 6.0$  is higher than that at  $\text{pH} > 6.0$ , and can exceed the Australian Drinking Water  
 212 Guideline (ADWG) limit of 0.2 mg/L. There were no apparent differences between pH 4.5 and 6.0 for DOC  
 213 removal, and therefore pH 6.0 was selected as the optimum coagulation pH for alum in this study. By  
 214 comparison, the optimum coagulation pH for  $\text{TiCl}_3$  was found to be 3 for maximum DOC removals.



215  
 216 **Fig. 1.** Effect of coagulation pH on the coagulation performances of alum and  $\text{TiCl}_3$ . (a) DOC removal  
 217 and zeta potential (ZP) changes with alum treatment, (b) DOC removal and ZP changes with  $\text{TiCl}_3$  treatment,  
 218 (c) residual turbidity levels on alum treated waters, and (d) on  $\text{TiCl}_3$  treated waters.

219 The ZP values of Al- and Ti-flocs were determined to assess removal mechanisms of DOM and  
 220 turbidity particles during destabilization. The highest ZP value of Al-flocs was about 10 mV. The

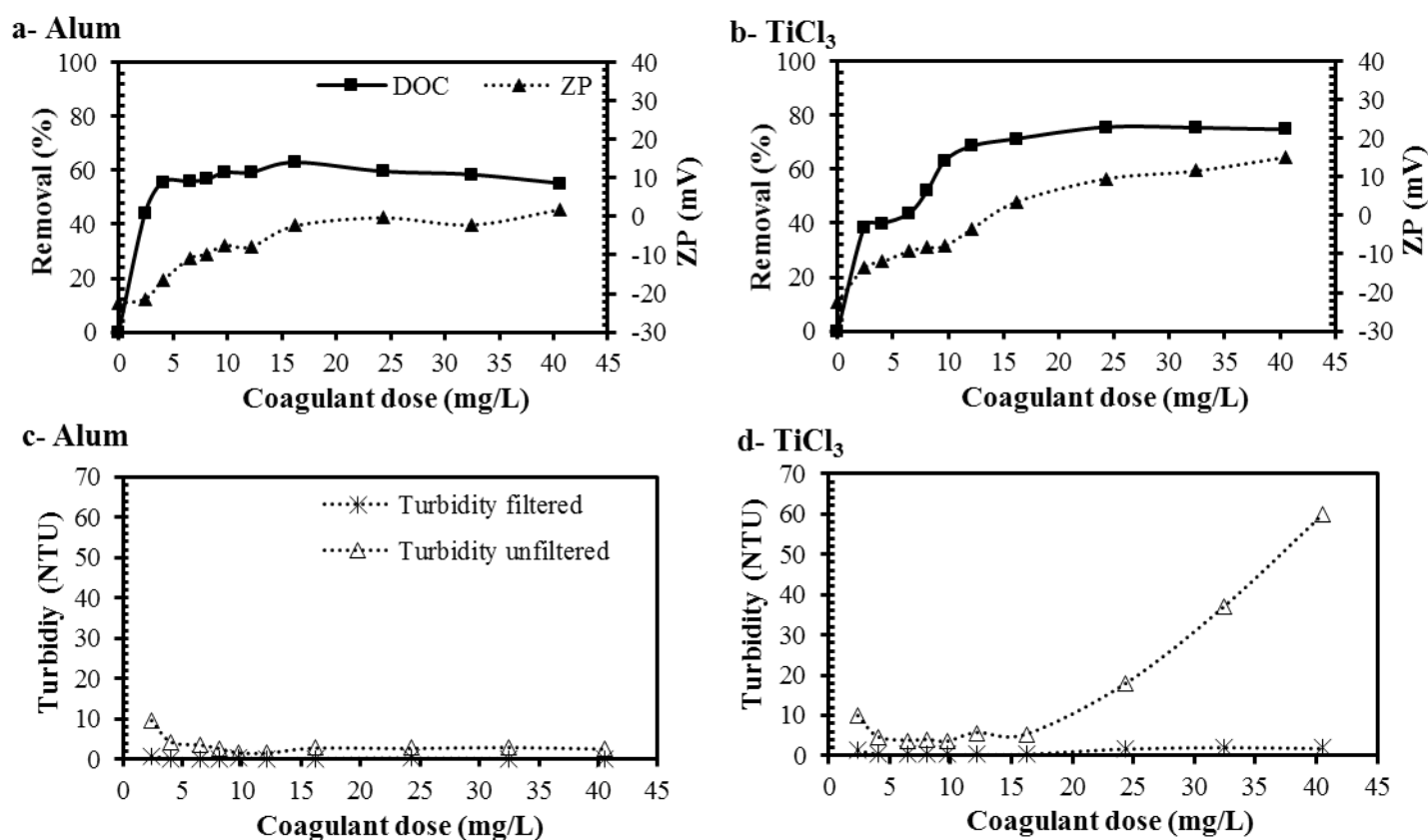
ZP of Ti-flocs was more negative than the Al-floc (except at pH 3). At the specific coagulant dose used (10 mg/L), the isoelectric point (IEP) of Al- and Ti-flocs were found at pH around 5.5 and 3.0, respectively (Fig. 1a, b). Furthermore, the ZP of Al-flocs was negative (-6.8 mV) at pH 3, while the ZP of Ti-flocs was positive (2.93 mV) at the same pH.

Zhao et al. [22] reported that natural organic matter (NOM) removal at pH < 6.0 was mainly due to the interaction of soluble Al species, such as  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}_2(\text{OH})_2^{4+}$  and  $\text{Al}_3(\text{OH})_4^{5+}$  with NOM particles. These hydrolysed species of metal salts would play an important role in neutralizing the negatively charged NOM to further stabilize these particles to form insoluble precipitates or flocs. Generally, for alum, NOM removal occurs due to the presence of insoluble/precipitated metal hydroxides ( $\text{Al}(\text{OH})_3$ ) at coagulation pH > 6.0 where the dominant hydroxide species are favorable for destabilizing organic matter by adsorption and/or enmeshment mechanisms [31, 32]. The DOC removal capacity was significantly reduced at pH  $\geq$  8.0 (Fig 1). This was probably due to the predominance of negatively charged hydrolysed alum species ( $\text{Al}(\text{OH})^{4-}$ ) which is not favorable for destabilizing NOM particles. Zhao et al. [22] also reported that  $\text{TiCl}_4$  instantly hydrolyzed to form Ti hydroxide at pH 6.0 which further reacted with humic acid to form the negatively charged Ti  $(\text{OH})_x^{(4-x)+}$ -HA complex. However, the hydrolysed species of Ti salt such as  $\text{Ti}(\text{OH})_5^{1-}$  and  $\text{Ti}(\text{O}_2)_2(\text{OH})_2^{2-}$  or  $\text{Ti}(\text{OH})_4$  can form at pH  $\geq$  9 because of high concentration of  $\text{OH}^-$  ions in the aqueous solution. In the alkaline pH range, these species would play an important role in the coagulation-flocculation process and generally where adsorption is considered to be a dominant mechanism [6]. In the current study, the higher negative ZP of Ti-flocs obtained at pH  $\geq$  6.0 indicated that the DOC removal efficiency was greatly reduced due to weak charge neutralization. The ZP of Ti-flocs were more negative at pH 4.5 than the ZP of Al-flocs, but the DOC removal by  $\text{TiCl}_3$  was quite close to or slightly greater than alum. The particular hydrolysed Ti species formed at this pH (4.5) appears highly amenable for the removal of DOC through adsorption and/or enmeshment. The results showed that the adsorption strength of the hydrolyzed Ti species was about equal to the charge neutralization strength of hydrolyzed Al species formed at pH 4.5.

### 3.2. Coagulant dose and organic removal

246 The coagulation performances of alum and  $\text{TiCl}_3$  as a function of various coagulant doses (2-40 mg/L  
 247 as the respective metal concentration) at their optimum pH levels (pH 6.0 for alum and pH 3.0 for  $\text{TiCl}_3$ ) are  
 248 shown in Figure 2. At low dose range (2-8 mg/L), alum achieved slightly higher DOC removal than  $\text{TiCl}_3$ . At  
 249 coagulant doses above 8 mg/L,  $\text{TiCl}_3$  showed a higher DOC removal than alum.

250 Using Equation 1, the optimum coagulant doses were determined, and found to be 6.5 mg/L and 16  
 251 mg/L for alum and  $\text{TiCl}_3$ , respectively. At the optimum dose, the percentage removal of DOC by alum (56%)  
 252 was much lower than by  $\text{TiCl}_3$  (71%), see Figures 2a & 2b. Further, the maximum DOC removal by alum was  
 253 found to be ~59% at high dose (> 2 times the optimum dose; > 13 mg/L as Al). By comparison,  $\text{TiCl}_3$   
 254 removal of DOC was found to be ~ 75% at a high dose (> 32 mg/L as Ti). This data indicates that at high  
 255 dose,  $\text{TiCl}_3$  can be more effective for DOC removal than alum. For coagulation by alum, non-coagulable  
 256 DOC was found to be 4.7 mg/L while for coagulation by  $\text{TiCl}_3$ , this was 2.8 mg/L.



257 **Fig. 2.** Effect of different doses of alum (at pH 6) and  $\text{TiCl}_3$  (at pH 3) on DOM removal efficiencies and zeta  
 258 potential (ZP) values of their respective flocs. (a) DOC removal and ZP changes with alum treatment, (b)  
 259

260 DOC removal and ZP changes with  $\text{TiCl}_3$  treatment, (c) residual turbidity levels on alum treated waters, and  
261 (d) on  $\text{TiCl}_3$  treated waters.

262 For both alum and  $\text{TiCl}_3$ , the residual turbidity decreased from 34 to  $\leq 3$  NTU in the coagulant dose  
263 ranged between 2-12 mg/L. Above 12 mg/L dose (as Ti), the unfiltered turbidity of  $\text{TiCl}_3$  treated waters  
264 significantly increased to 60 NTU, whereas for alum the unfiltered turbidity (after sedimentation) values were  
265 found to be  $< 3$  NTU at most of the doses tested (except at dose 2 mg/L). However, the filtered (residual)  
266 turbidities of alum and  $\text{TiCl}_3$  treated waters were below 0.5 NTU (except at the lowest dose of 2 mg/L) to a  
267 coagulant dose of 16 mg/L. At doses greater than 16 mg/L, the filtered turbidity of  $\text{TiCl}_3$  treated waters were  
268 up to  $\sim 2$  NTU while for alum treated waters these values remained below 0.2 NTU.

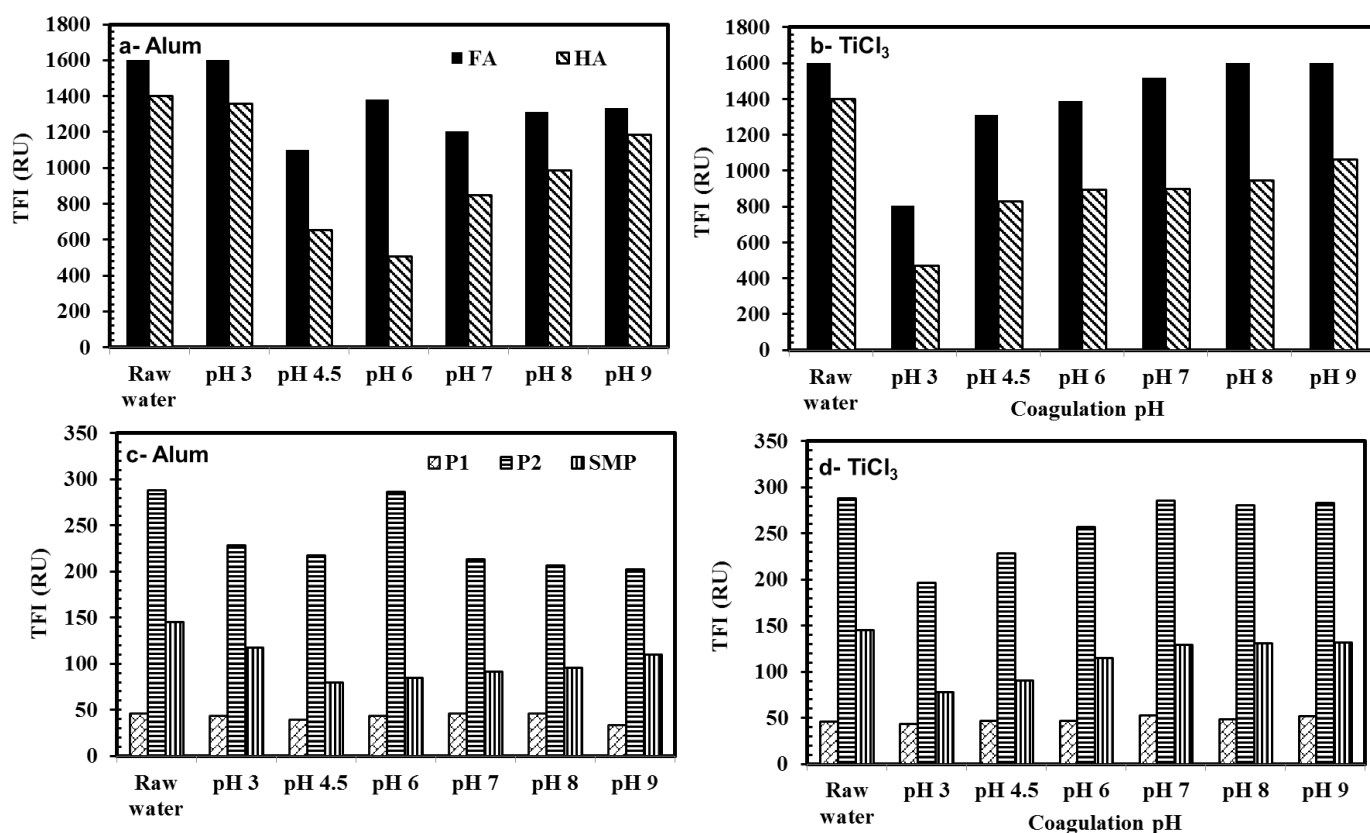
269 The relationship of ZP values with different alum and  $\text{TiCl}_3$  coagulant doses are shown in Fig. 2a & b.  
270 With higher coagulant dose, the ZP of Al- and Ti-flocs increased. At a dose of 16 mg/L, the ZP values of both  
271 the coagulants were approximately near to their IEPs where the charges of Al- and Ti-flocs were almost zero.  
272 In addition, at an alum dose above 16 mg/L, no further change was found in the ZP of Al-flocs, which  
273 indicate that excessive doses of alum had no significant role in charge neutralization. However, the higher  
274 doses of  $\text{TiCl}_3$  showed slight increases in ZP values of Ti-flocs, indicating greater DOC removal by sweep  
275 coagulation (at high doses with more positive ZPs).

### 276 **3.3. DOM characterisation in treated water by F-EEM**

277 The total fluorescence intensities (TFI, measured as the sum of all intensities of the various organic  
278 constituents within their excitation and emission regions) of the P1-, P2-, SMP-, FA- and HA-like compounds  
279 at different pH levels are shown in Fig. 3. Based on these TFI values, the percentage removals of P1-, P2-,  
280 SMP-, FA- and HA-like compounds by alum treatment at pH 6 were calculated as 6%, 1%, 42%, 14% and  
281 64%, respectively. For  $\text{TiCl}_3$  treated water, the corresponding percentage removal values at pH 3 were 6%,  
282 32%, 47%, 50% and 66%, respectively. In addition, the mean fluorescence intensity (MFI) values of the  
283 excitation and emission regions of P1-, P2-, SMP-, FA- and HA-like compounds for the alum treated water  
284 were about 0.04, 0.25, 0.09, 0.44 and 0.10 units, respectively. For  $\text{TiCl}_3$  treated water, the corresponding mean

285 MFI values were about 0.05, 0.18, 0.08, 0.26 and 0.09 units, respectively. These data indicate that  $\text{TiCl}_3$   
 286 removed more organic compounds at pH 3, (which was also chosen as the optimum pH for DOC removal by  
 287  $\text{TiCl}_3$ ) than alum at pH 6.

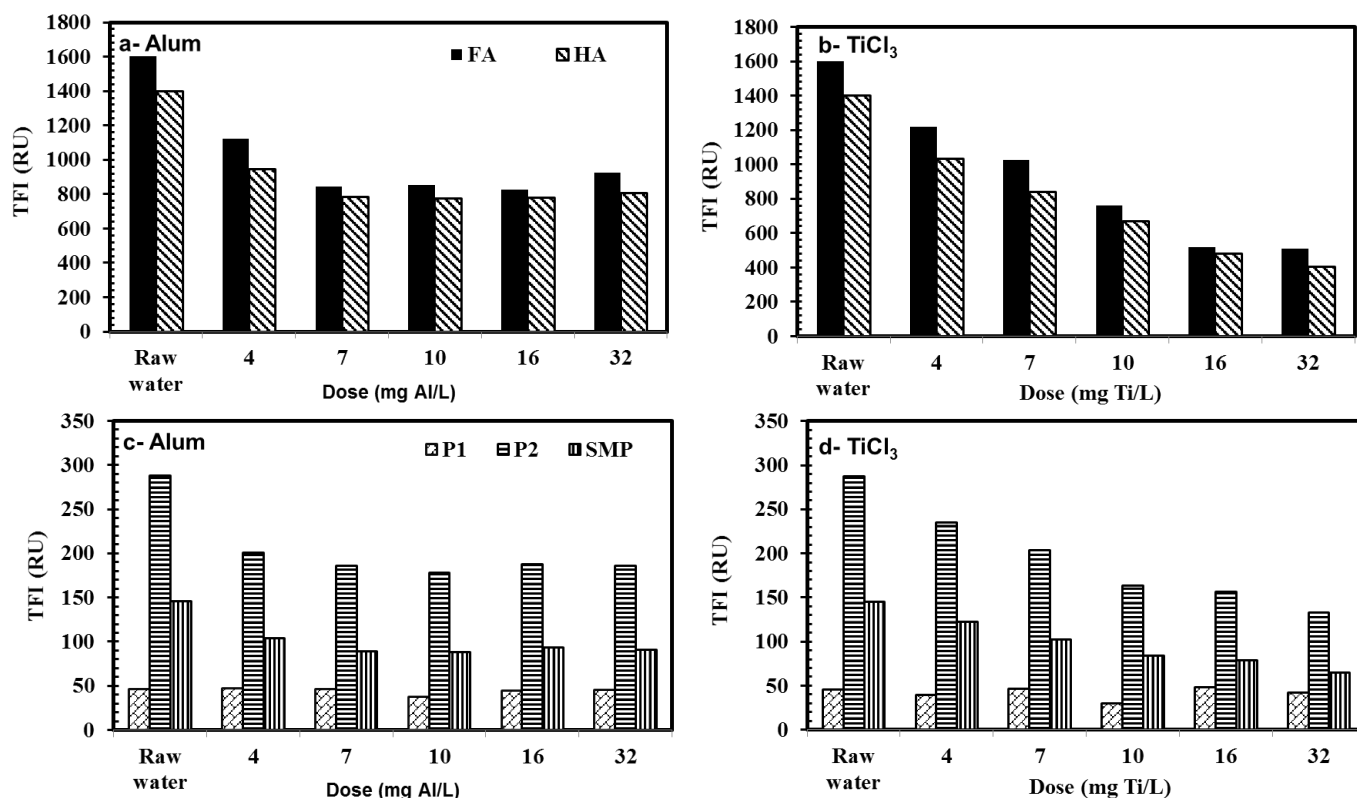
288 In case of  $\text{TiCl}_3$ , the percentage removals of both the humic fractions (FA and HA) decreased as the  
 289 coagulation pH increased (Fig. 3c). At pH 9, the removal of FA-like compounds was not evident in contrast to  
 290 the HA-like compounds with removal of 24%. The percentage removal of protein-like compounds showed the  
 291 same trend with removals decreasing as the coagulant pH increased (Fig. 3d). At pH 9, the removal of  
 292 protein-like compounds was either not detected (N.D.) or at low levels (N.D. for P1-like; 2% for P2-like; 9%  
 293 for SMP-like). For alum treated waters, the lowest percentage removals of the humic fractions (FA-like and  
 294 HA-like) were for water treated at pH 3 (N.D. and 3% for FA-like and HA-like compounds, respectively).  
 295 The percentage removal of protein-like compounds showed the same trend with the lowest values being for  
 296 alum treated water at pH 3.



297

298 **Fig. 3.** The TFI values of HA- and FA-like compounds in raw water and treated water by (a) alum, (b)  $\text{TiCl}_3$ ,  
 299 and of SMP-, P1- and P2-like compounds in raw water and treated by (c) alum, and (d)  $\text{TiCl}_3$  at the  
 300 coagulation pH levels tested.

301 The effect of coagulation treatment on different fractions (P1, P2, SMP, FA and HA) of DOM at  
 302 different coagulant doses are shown in Fig. 4. Removals of FA-like and HA-like compounds by alum  
 303 occurred to about 7 mg/L after which no further removal was evident (Fig. 4a). At optimum alum dose, the  
 304 percentage removals of P1-, P2-, SMP-, FA- and HA-like compounds were 9%, 37%, 40%, 47% and 45%,  
 305 respectively. At high dose, removals were not enhanced with the corresponding percentage removals being  
 306 4%, 35%, 36%, 48% and 44%, respectively.



307 **Fig. 4.** Total FI values of HA- and FA-like compounds in raw water and treated water by (a) alum, and (b)  
 308  $\text{TiCl}_3$ , and SMP-, P1- and P2-like compounds in raw water, and treated by (c) alum, and (d)  $\text{TiCl}_3$  at optimum  
 309 pH levels (pH 6 for alum and pH 3 for  $\text{TiCl}_3$ )  
 310

311 In the case of  $\text{TiCl}_3$ , higher removals of both HA and FA occurred to the maximum coagulant dose of  
 312 32 mg/L (Fig. 4b). At most of the doses tested, the residual TFI of  $\text{TiCl}_3$  treated waters (except at the low dose



of 4 mg/L) were lower, showing higher percentage removals than alum treated waters. The MFI showed the same trend, with lower values for water treated by  $\text{TiCl}_3$  compared with alum. Based on the TFI, the percentage removals of P1-, P2-, SMP-, FA- and HA-like compounds at optimum (for DOC removal)  $\text{TiCl}_3$  dose were 17%, 36%, 36%, 44% and 46%, respectively. At high dose, the corresponding percentage removals were 8%, 54%, 55%, 68% and 71%, respectively. These data show that  $\text{TiCl}_3$  had greater efficiency for removal of humic- and protein-like compounds at higher coagulant dose than alum. These results correlate with DOC removals at high coagulant doses where the ZP of Ti-flocs were much greater (more positive) than of Al-flocs (Fig. 2).

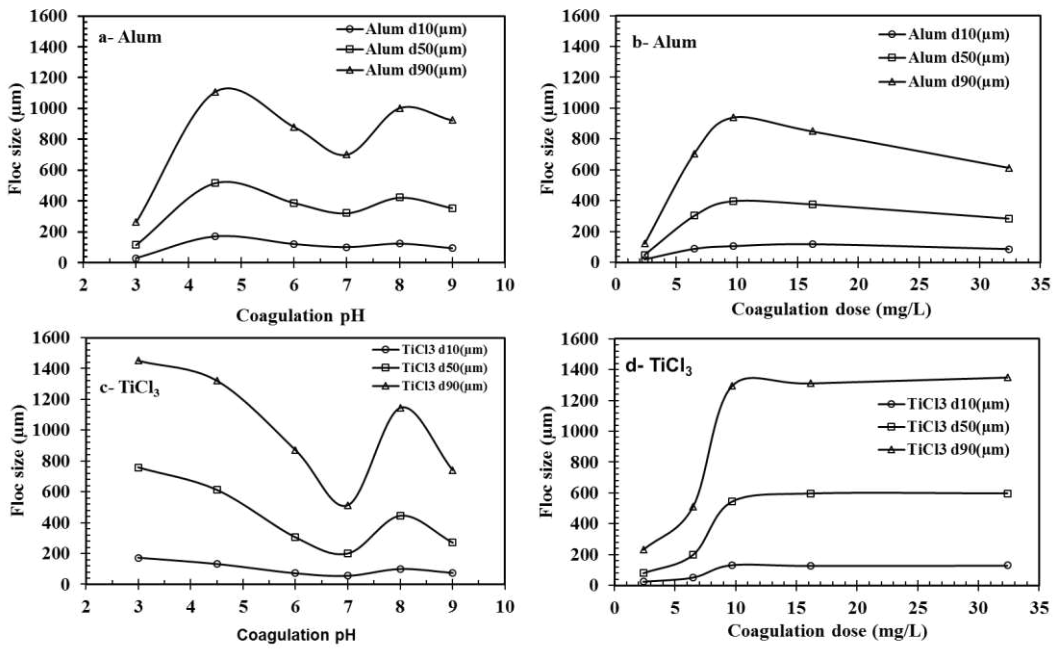
### 3.4. Floc characteristics

The sizes of flocs formed at various pH levels and coagulant doses for each coagulant are shown in Fig. 5. The average floc size (in  $\mu\text{m}$ ) is shown by three distributions ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ ). Among these, the  $d_{50}$  (50% of mass-based size distribution) is the most useful indicator of floc size, that has been employed in previous studies [6, 21]. For alum, the highest average floc sizes of  $d_{10}$ ,  $d_{90}$  and  $d_{50}$  occurred at pH 4.5, whereas the smallest average floc sizes of  $d_{10}$ ,  $d_{90}$  and  $d_{50}$  were at pH 3 (Fig. 5a). These results strongly correlate with earlier findings of low DOC removal (Fig. 1a) and higher residual turbidity (Fig. 1c), indicating the lowest coagulation efficiency of alum at pH 3. At pH 6, the average floc sizes of  $d_{90}$ ,  $d_{50}$  and  $d_{10}$  were 881  $\mu\text{m}$ , 387  $\mu\text{m}$  and 120  $\mu\text{m}$ , respectively (Fig. 5a). A steady decline in the floc size was observed as the coagulation pH increased from 4.5 to 7 and beyond pH 7, the larger size flocs were again formed (Fig. 5a).

For  $\text{TiCl}_3$ , the largest range of floc sizes was found at pH 3 (Fig. 5b). The size of the Ti-flocs tended to decrease as the coagulation pH increased from 3 to 7, increased as pH changed from 7 to 8, and then decreased again at pH 9 (Fig. 5b). The floc sizes of  $d_{90}$ ,  $d_{50}$  and  $d_{10}$  for  $\text{TiCl}_3$  were 1451  $\mu\text{m}$ , 758  $\mu\text{m}$  and 171  $\mu\text{m}$ , respectively, at pH 3, which were significantly larger than the floc sizes from alum at pH 6. This indicates that flocs from  $\text{TiCl}_3$  could form the largest size at its optimum pH condition. This is likely to have occurred due to its higher charge neutralization capacity than alum. Zhao et al. [22] reported that during  $\text{TiCl}_4$  coagulation, the charge effects were found to be more important at pH 6 than pH 10, and coagulation

338 efficiency was greatly influenced by the sweep coagulation mechanism at pH 10. In our study, the ZP of Ti-  
 339 flocs was higher (more positive) at pH 3, (probably because of the greater positive charge of hydrolysed Ti  
 340 species) than at pH 9, where the concentration of OH<sup>-</sup> ions was high, as reported by Zhao et al. [22].

341 For alum, the largest value of floc size d<sub>50</sub> was about 398 μm at a dose of 10 mg/L. Beyond this dose,  
 342 the value of d<sub>50</sub> remained constant or decreased slightly (Fig. 5c). For TiCl<sub>3</sub>, the floc size values for d<sub>90</sub>, d<sub>50</sub>  
 343 and d<sub>10</sub> reached equilibrium conditions at doses ≥ 10 mg/L (Fig. 5d). The floc size values of d<sub>90</sub>, d<sub>50</sub> and d<sub>10</sub>  
 344 for TiCl<sub>3</sub> at the optimum dose were 1311, 596 and 128 μm, respectively, and these values were markedly  
 345 higher than the corresponding floc sizes of alum (939, 397 and 105 μm). At high dose, the floc size values  
 346 showed the same trend with values higher for the water treated by TiCl<sub>3</sub> (1349 μm for d<sub>90</sub>, 597 μm for d<sub>50</sub> and  
 347 129 μm for d<sub>10</sub>) compared to that treated by alum (850, 377 and 118 μm, respectively).



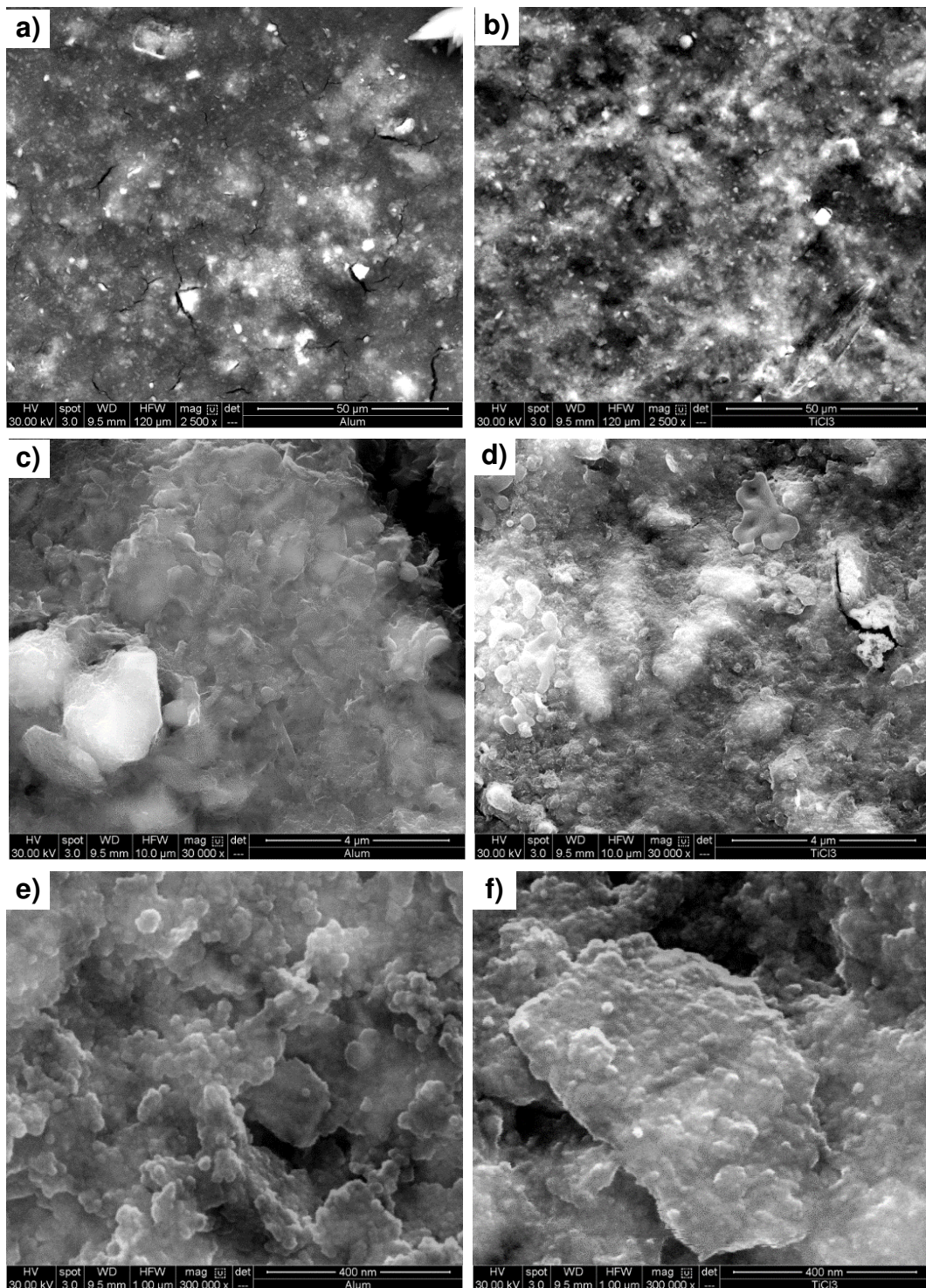
348  
 349 **Fig. 5.** Average floc sizes of d<sub>90</sub>, d<sub>50</sub> and d<sub>10</sub> of Al-floc (a) at tested pH levels, and (b) coagulation doses, and  
 350 of Ti-floc (c) at tested pH levels, and (d) coagulation doses

351 SEM images of flocs at three different magnification levels (1, 10 and 120 μm HFW (half field width))  
 352 are shown in Figure 6. As expected, the Ti floc showed a stronger secondary electron yield (a brighter light  
 353 scattering) than the aluminium (Al) floc due to greater z-contrast obtained from Ti. At a higher magnification,  
 354 the SEM images show the presence of clay mineral-like flakes which inevitably originated from the raw

355 surface water. Wu et al. [33] reported that both Al and Ti salts formed bulky flocs. In the present study, Al  
356 and Ti flocs had approximate diameters ranging from 9.5-44  $\mu\text{m}$  and 7-37  $\mu\text{m}$ , respectively. It was previously  
357 suggested that both Al and Ti would result in mesoporous (pore size: 30 – 80 nm) flocs which would have  
358 adsorptive and enmeshing abilities [33]. The micromorphology of the flocs observed at a higher  
359 magnification indicated the porous structure of the flocs, in the current study. The amorphous structure of Al  
360 and Ti flocs might be due to the residual organic matter [21]. Energy dispersive X-ray analysis (EDAX)  
361 spectra obtained at a 10  $\mu\text{m}$  HFW revealed an approximate elemental composition of the flocs (Figure 7a). In  
362 addition to confirming the presence of elements in flocs, the EDAX study indicated the presence of some  
363 alumina-silicate like compounds, and these results were found during the characterization of Al and Ti flocs  
364 by XRD analysis. In addition, constituents such as  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  salts of K, Ca, Na and Mg were present in the  
365 Al and Ti settled flocs. From the Al, Ti and O contents in the EDAX spectra, and with the appearance of  
366 small spherical bright structures observed in the SEM images, it could be assumed that some oxides or  
367 hydroxides of Al and Ti were formed in the flocs that were amorphous in nature. Zhao et al. [21] reported the  
368 XRD analyses of Ti (IV) sludge, incinerated at different temperatures between 200-1000  $^\circ\text{C}$  where the color  
369 of incinerated flocs turned from black (possibly due to residual organic matter) to white as the temperature  
370 increased. At the temperature range 600-800  $^\circ\text{C}$  and at 1000  $^\circ\text{C}$ , the anatase and rutile phase structures were  
371 observed, respectively.

372 Like the SEM results, XRD analysis showed the presence of alumina-silicate minerals in the flocs (Fig.  
373 7c). Matching the accrued patterns with those of the reference patterns in the International Centre for  
374 Diffraction Data (ICDD) library indicated the presence of montmorillonite, illite and kaolinite in the flocs.  
375 The primary deflection of these clay minerals appeared at d (basal spacing) values 17.25, 10.15 and 7.23  $\text{\AA}$ ,  
376 respectively (Fig. 7b). The key difference between the two flocs was observed in the appearance of the  
377 expanded montmorillonite deflection at  $d \approx 17.25 \text{\AA}$ . In general, the montmorillonite deflection should appear  
378 at d value around 13  $\text{\AA}$ . A greater d value in the floc samples indicated insertion of organic matter or the  
379 flocculating metals in the inter-layer space of montmorillonite [34, 35]. This indicated that the adsorption of

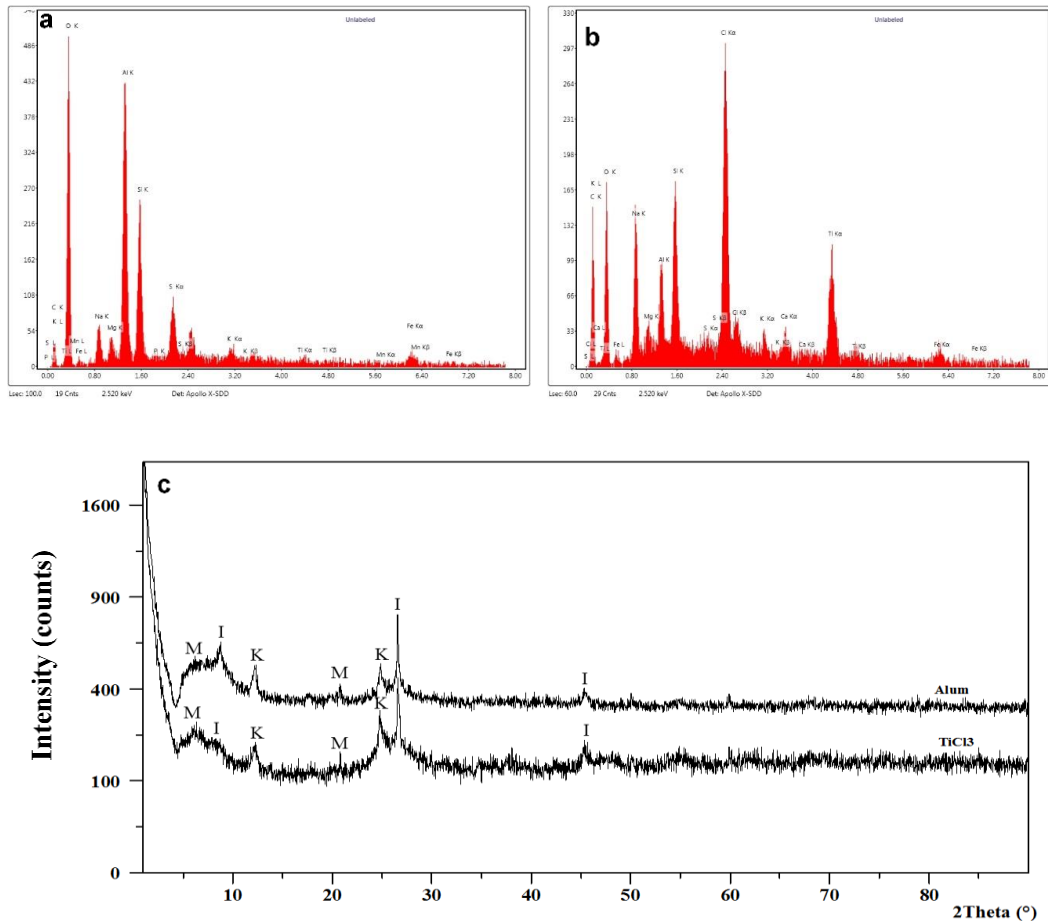
380 metal salts coagulants might occur at the inter-layer on particle surfaces. In the alum floc, this deflection peak  
381 created a hump which was similar to that of an Al-exchanged/pillared montmorillonite [35, 36].



382  
383 **Fig. 6.** Micromorphology of alum (graphs a, c and e) and  $\text{TiCl}_3$  (graphs b, d and f) flocs formed at  
384 optimum pH (3 for  $\text{TiCl}_3$  and 6 for alum) and at coagulant dose of 16 mg/L, observed under SEM at  
385 various magnification levels (graphs a&b, 2500 x; c&d, 30,00 x; e&f, 300,000 x)

386 The TGA and DTGA were conducted to examine the response of the flocs to gradually elevated  
387 temperature. These analyses are helpful to estimate the relative amount of organic matter present in the  
388 freeze-dried flocs. The weight loss steps of both floc types were nearly identical except the Al floc  
389 contributing to a greater amount of organic matter loss than the Ti floc (Fig. 8a, b). The TGA curves were  
390 examined by sectioning them into three distinct weight loss steps: (a) up to 100 °C due to the loss of water  
391 molecules, (b) from 150 to 550 °C potentially due to loss of tightly bound organic matter, and (c) from 550 to  
392 1000 °C due to the loss of other compounds. At these three steps, the percentage weight losses for Al floc  
393 were 13.7%, 8.5% and 7.3 %, respectively, and for Ti floc, the losses were 7%, 6.3% and 3.5%, respectively.  
394 Zhao et al. [21] reported that in the TG plot, the weight loss of Ti settled flocs at temperatures between 25-  
395 154 °C; 154-493 °C and 493-1000 °C were about 17%, 13% and 1%, respectively, due to loss of water  
396 content and organic matter. The amount of residual compounds was higher in the Ti floc than the Al floc due  
397 to a greater stability of Ti-compounds to an elevated temperature.

398 The FTIR spectra of the Al and Ti flocs were like the characteristic spectra of clay minerals, indicating  
399 flocculation of clay particles occurred by both the coagulants in treating the surface water (Figure 8c). The  
400 absorbance bands in the region between 3600 and 3700  $\text{cm}^{-1}$  corresponded to the structural hydroxyl groups  
401 of clay minerals and the water molecules in their interlayer space [37]. The band at around 3618  $\text{cm}^{-1}$  was  
402 assigned to the OH stretching region of structural hydroxyl groups for dioctahedral montmorillonite with Al-  
403 rich octahedral sheets [38]. The band at 1650  $\text{cm}^{-1}$  corresponded to the water molecules' bending vibration or  
404 OH deformation [39]. The band regions appearing between 1037 and 910  $\text{cm}^{-1}$  might be due to asymmetric  
405 stretching vibration of Si–O–Si groups of the tetrahedral sheet and bending vibration of Al–O–(OH)–Al of the  
406 octahedral sheet, respectively [40]. The band at 796  $\text{cm}^{-1}$  indicated traces of quartz present in the samples  
407 [41]. The absorption regions at 528  $\text{cm}^{-1}$  and 467  $\text{cm}^{-1}$  might be due to Al–O–Si and Si–O–Si bending  
408 vibrations, respectively [38]. Absorption peaks at 2360 and 2345  $\text{cm}^{-1}$  in Ti floc might be due to  
409 asymmetrical stretching and scissoring (degenerated) vibrations of O=C=O bonds, which were negligible in  
410 Al floc.



**Fig. 7.** EDAX spectra of alum (a) and TiCl<sub>3</sub> (b); c) XRD patterns of freeze dried alum and TiCl<sub>3</sub> flocs (M: montmorillonite; I: illite; K: kaolinite)

### 3.5. Effect of dual dose on the coagulation performance

For comparison of the efficiencies of multi-stage coagulation treatment for DOM removal, surface waters were initially treated with alum or TiCl<sub>3</sub> at the same dose (16 mg/L,) and at the optimum pH level of the respective coagulant (pH 6 for alum and pH 3 for TiCl<sub>3</sub>). Then, the supernatants of treated waters were further treated with two different additional doses (8 mg/L and 16 mg/L) of alum or TiCl<sub>3</sub>, at their optimum pH level (Table 1).

The %DOC removal was found to be higher in waters treated by two-stage alum doses (~67% for total dose of 24 mg Al/L; ~71% for total dose of 32 mg Al/L) compared to water treated by a single high dose of alum (58% for 32 mg Al/L). The ZP of settled flocs was also found to be higher in water treated by two-stage

424 alum doses (8.4 mV for total dose of 24 mg Al/L; 7.5 mV for total dose of 32 mg Al/L) compared with water  
425 treated by a single high dose of alum (-2.1 mV). These results indicate that alum in a two-stage treatment  
426 process can enhance DOC removal (in this study ~13%) than a single-stage treatment with a high dose.

427 Further, the percentage DOC removal was found to be higher in water treated by 16 mg Al/L of alum  
428 followed by a dose of  $\text{TiCl}_3$  (16 mg Al/L + 8 mg Ti/L: ~74%; 16 mg Al/L + 16 mg Ti/L: 76%) compared to  
429 water treated by two-stage of alum (~71% for total dose of 32 mg Al/L). The ZP of settled flocs was also  
430 found to be higher in waters treated by alum followed by  $\text{TiCl}_3$  (16 mg Al/L + 8 mg Ti/L: 9.5 mV; 16 mg  
431 Al/L + 16 mg Ti/L: 11.4 mV) compared to water treated by two-stage alum treatment (7.5 mV). The jar test  
432 protocol indicated that alum followed by  $\text{TiCl}_3$  treatment showed slightly better performance than the alum  
433 followed by alum treatment.

434 In the second jar test protocol, (Table 1) treatment by  $\text{TiCl}_3$  followed by alum or  $\text{TiCl}_3$  treatment  
435 followed again by  $\text{TiCl}_3$  showed no significant further removal of DOC. The single dose of  $\text{TiCl}_3$  yielded  
436 about 75% DOC removal which was very close to the DOC removal (about 74%) obtained in two stage  $\text{TiCl}_3$   
437 treatment (total dose equivalent to 32 mg/L). The zeta potential of the  $\text{TiCl}_3$  dual dose was higher than of the  
438 alum dual dose, as shown in Table 1.

439 At the highest coagulant dose, alum treatment followed by  $\text{TiCl}_3$  or  $\text{TiCl}_3$  followed by  $\text{TiCl}_3$  resulted  
440 in greater residual turbidity in comparison with treatment by alum followed by alum or  $\text{TiCl}_3$  followed by  
441 alum. These results are consistent with the finding we reported previously [42]. Hussain, et al. [42] reported  
442 that the combination of highly charged titanium and zirconium salts with alum showed extra advantages over  
443 a single coagulant treatment including, enhanced DOC removal. From these results it is concluded that the  
444 two-stage treatment of alum and  $\text{TiCl}_3$ , either the same coagulant or in combination showed better  
445 performance than a single dose treatment.

446 The optimum pH for  $\text{TiCl}_3$  coagulation presents both potential benefits and disadvantages. Assuming  
447 that  $\text{TiCl}_3$  is safe for application in the treatment of drinking water, it might have particular benefit for the  
448 treatment of low alkalinity source waters with high DOC, and for treatment of low pH industry process



449 wastewaters such as from the pulp and paper mill industry. Low alkalinity waters will have their pH levels  
 450 readily lowered through the addition and subsequent hydrolysis reaction of  $TiCl_3$ , and following coagulation,  
 451 likely to require limited chemical addition (e.g., caustic soda) for pH re-adjusted to neutral. Further  
 452 consideration would be that the water treatment infrastructure is corrosive resistant (i.e., to low pH waters).  
 453 However, it is unlikely to be practically suitable for the treatment of natural waters that have medium to high  
 454 levels of alkalinity for potable supply due to the need to lower the pH substantially by acid addition to reach  
 455 the optimum pH for coagulation and then further greater chemical addition (caustic soda or liming agents)  
 456 than needed for alum, to readjust the pH back to neutral prior to distribution.

457 **Table 1.** Effect of two-stage treatment of alum and  $TiCl_3$  on the coagulation efficiency

Total dose (mg/L)	Coagulation pH	Turbidity (NTU)	DOC (mg/L)	DOC Removal (%)	Zeta Potential (mV)	Mob ( $\mu m.cm/Vs$ )
Raw water	7.2	34.4	11.3	--	-22.4	-1.8
<b>Alum followed by alum or <math>TiCl_3</math> treatment</b>						
Al (16 mg/L) = A*	6	3.1	4.4	61.6	6.5	0.5
A* + Al 8 mg/L = 24 mg/L	6	0.8	3.8	66.7	8.4	0.7
A* + Al 16 mg/L = 32 mg/L	6	0.5	3.3	70.5	7.5	0.6
A* + Ti 8 mg/L = 24 mg/L	3	3.4	2.9	74.1	9.5	0.7
A* + Ti 16 mg/L = 32 mg/L	3	7.1	2.7	76.0	11.4	0.9
<b><math>TiCl_3</math> followed by alum or <math>TiCl_3</math> treatment</b>						
$TiCl_3$ (16 mg/L) = T*	3	3.2	3.9	65.6	7.0	0.6
T* + Al 8 mg/L = 24 mg/L	6	0.6	3.6	68.6	2.0	0.2
T* + Al 16 mg/L = 32 mg/L	6	0.5	3.2	71.9	6.8	0.5
T* + Ti 8 mg/L = 24 mg/L	3	10.0	3.1	72.5	10.9	0.9
T* + Ti 16 mg/L = 32 mg/L	3	14.1	2.9	74.4	19.1	1.5

458 Note: A\*= 16 mg Al/L of dose; T\*= 16 mg Ti/L of dose

#### 459 4. Conclusions

460 In this study, the coagulation performances of  $TiCl_3$  and alum in drinking water treatment were compared.  
 461 Results of jar tests revealed that the optimum pH for alum and  $TiCl_3$  were 3 and 6, respectively, and a dose of  
 462 16 mg/L for both coagulants yielded an optimum DOC removal.  $TiCl_3$  showed higher DOC removal than  
 463 alum at the respective optimum coagulation pH levels. The DOC and turbidity removals correlated with the



464 zeta potentials of Al- and Ti-flocs showing that the removal mechanisms were either charge neutralization or  
465 sweep coagulation, at different pH values and coagulant doses. The higher zeta potential of Ti-floc at pH 3  
466 indicated that charge neutralization was the dominant removal mechanism for DOC removal by  $\text{TiCl}_3$ .  
467 However, the higher negative zeta potential of Ti-flocs at  $\text{pH} > 4.5$  confirmed that the removal achieved at  
468 this pH occurred with a combination of adsorption, enmeshment or sweep coagulation. EEM data indicated  
469 that  $\text{TiCl}_3$  showed greater removal efficiency of humic compounds (both humic acids and fulvic acids) at  
470 optimum coagulant dose than alum. The average value of floc size ' $d_{50}$ ' of Ti-floc was much greater than that  
471 of alum. A two-stage treatment process showed an enhanced DOC removal compared with a single dose  
472 treatment. Overall,  $\text{TiCl}_3$  showed better results than alum in terms of DOM removal and floc size. The results  
473 from this study indicate that  $\text{TiCl}_3$  could have specific application in the treatment of low alkalinity waters  
474 with high concentrations of DOC, as well as for low pH wastewaters.

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