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 compounds. A two-stage treatment process by alum and $TiCl_3$, either as the same chemical or both showed better performance than a single dose treatment. The results indicate that $TiCl_3$ could be an effective alternative coagulant for the treatment of waters, particularly those of low alkalinity and high DOC concentration and low pH wastewaters for removal of hydrophobic compounds and particulate matter.

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

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

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

Research has been conducted to find alternative metal salts that have higher charge neutralization and greater DOC removal capacity with the formation of larger size flocs that have higher settling rates than conventional salts [16-19]. Highly charged Ti (IV) and Zr (IV) based coagulants such as titanium tetrachloride ($TiCl_4$) and zirconium tetrachloride have been shown to have capacity for higher DOC removals with the formation of larger sized flocs than Al and Fe based coagulants [6, 17, 18, 20]. Various hydrolysed 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 $Ti (O)(O_2) (OH)_2^{2-}$ are formed at different pH levels and Ti doses, and these species play an important role during the particle stabilization [21, 22]. The first investigation of Ti salt for coagulation was reported by Upton and Buswell [23] who found that $Ti(SO_4)_2$, as a tetravalent cationic salt, showed a better coagulation efficiency for fluoride removal than trivalent Al or Fe salts. Zhao et al. [24] developed a novel polytitanium tetrachloride (PTC) as pre-hydrolysed coagulant which showed better performance than $TiCl_4$. Shon et al. [16] reported that $TiCl_4$ had good performance for the removal of various apparent molecular weight compounds of DOM from wastewater. They also reported that the Ti-based sludge formed following coagulation treatment can be converted to value added materials (e.g., TiO_2) in a simple process [16, 25, 26]. Zhao et al. [18] reported that coagulation behavior of titanium tetrachloride ($TiCl_4$) was very similar to Al and Fe based salts. However, $TiCl_4$ is volatile and forms cloudy TiO_2 and HCl in humid air conditions at room temperature and being hazardous [27], there is need for other Ti based salts that are more stable under ambient conditions, are safe, reliable and readily prepared. This study investigated the potential of titanium (III) chloride as a coagulant under a range of conditions including coagulation pH and at various dose rates in comparison to and in combination with alum (aluminium sulphate). This study investigated the coagulation mechanisms of $TiCl_3$ by exploring the surface chemistry of flocs and spectroscopic characterization of residual DOM post $TiCl_3$ treatment.

2. Materials and methods

2.1. Water quality analysis

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

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

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

2.2. Coagulants

Alum [$Al_2(SO_4)_3.18H_2O$] was obtained from Incitec Pivot Ltd - Port Adelaide, South Australia. $TiCl_3$ was sourced from Merck Schuchardt OHG, Germany. A stock solution of alum (1.6 g Al/L) was prepared by diluting 40.5 g of concentrated aluminum sulphate (approximately 7.6% w/w Al_2O_3) in 1 L high purity Milli-Q® water. The same concentration (1.6 g Ti/L) of $TiCl_3$ stock solution was prepared by dissolving approximately 13 mL of $TiCl_3$ (30%) in 1 L of high purity Milli-Q® water. The freshly prepared alum and $TiCl_3$ solutions were stored overnight at room temperature to dissolve the metal salts and subsequently stored at 4ºC prior to their use. The concentrations of Al and Ti in stock solutions were verified using inductively coupled plasma mass spectrometry (ICP-MS; Model: 7500c, Agilent Technologies, USA).

2.3. Coagulation study

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

Experiments were conducted using flash mixing @ 200 rpm for 1 min and 14 min of slow mixing @ 20 rpm then followed by a settling time of 15 min. The settled water (unfiltered turbidity of the supernatant) was measured immediately after 30 min of the coagulation experiment. After that, the filtered turbidity was measured following filtering the supernatant through a 11 µm pore size filter (Whatman No 1). All jar test experiments were performed at room temperature (25°C). Coagulation efficiency was determined using the following Equation 1:

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

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

In a second coagulation experiment protocol, two coagulants (alum and $TiCl_3$) were used to assess their effects individually and in combination. Initially, raw waters were treated by alum or $TiCl_3$ at an optimum dose and optimum pH level determined from the preliminary experiments. The supernatants of treated waters were further treated with two different additional doses (one-half of the optimum dose and optimum dose) of alum and $TiCl_3$. The experimental conditions of the second jar test remained the same as for the preliminary jar experiment. The efficiency of each jar test protocol was assessed with respect to the relationship of residual DOC concentration, DOM characteristics (F-EEM), turbidity removal and floc zeta potential values.

2.4. Optimum coagulation dose

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

$$\mathrm{DOC}_R = \mathrm{DOC}_{\mathrm{NC}} + \mathrm{DOC}_{\mathrm{C}} \times e^{-Cx} \quad (2)$$

Where, DOC_R is the DOC residual (mg/L) at a selected coagulant dose (x, mg/L), DOC_{NC} is non-coagulable DOC, DOC_C is the coagulable DOC ($DOC_{initial}$ - DOC_{NC}), and C is the DOC removal rate co-efficient determined from data of all jars of the jar test.

2.5. Floc size measurement

Settled flocs were immediately collected after 30 min of coagulation experiment (jar tests). The suspension of flocs was stored in the pre-rinsed plastic bottles at room temperature prior to analysis. Average floc size was determined using a laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK). The average sizes of alum and $TiCl_3$ flocs were characterized according to three different volumetric diameters (d_{10}, d_{50} and d_{90} referring to 10%, 50% and 90% floc sizes, respectively). The average sizes of flocs of both the coagulants were compared at pH levels between 3 to 9 and doses between 2 to 40 mg/L, as metal concentrations. In most recent studies, the 'd_{50}' value was reported as the representative size of flocs to understand the coagulation mechanism of different metal salts [22].

2.6. Floc characterization

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

For X-ray Diffraction (XRD), freeze dried floc samples were taken on a zero-background silica sample holder for collecting the XRD patterns which were acquired by using CuK_{α} radiation (λ = 1.5418 Å) on a PANalytical, Empyrean X-ray diffractometer operating at 40 kV and 40 mA between 2 and 90° 2θ at a step size of 0.026°.

The thermal behaviour of Al and Ti flocs (sludge) was determined by thermogravimetric (TGA) and differential thermogravimetric (DTGA) analyses using a high-resolution TGA system (Model: Mettler-Toledo DSC-1, Mettler-Toledo International Inc., USA). The flocs were heated from 25 °C to 1,000 °C at a rate of 10 °C/min under a continuous N_2 flow (50 mL/min).

For Fourier transform infrared (FTIR) spectroscopy analysis, floc suspensions of Al and Ti were centrifuged at 10,000 rpm for 15 min. Following washing in Milli-Q water, the pellets were freeze dried. The samples were then mixed with dehydrated KBr and pressed into discs by using a hydraulic press. Infrared (IR) spectra were obtained using an Agilent Cary 600 Series FTIR Spectrometer. Spectra over the 4,000–400 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1}.

3. Results and Discussion

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

3.1. Effect of coagulation pH on the coagulation performance

In initial jar test experiments, the coagulation performances of alum and $TiCl_3$ were optimized using target coagulation pH levels ranging from 3 to 9. The efficiency of each coagulant was assessed in terms of DOC and turbidity removals at a pre-selected coagulant dose of 10 mg/L (Fig. 1). The performances of both alum and $TiCl_3$ greatly depended on the coagulation pH as shown in Fig. 1. For alum, the DOC removal (48%) achieved at pH 4.5 was slightly higher than the removal achieved at pH 6 (~43% removal), whereas the lowest DOC removal (18%) was found at pH 3 (Fig. 1a, c).

In contrast, $TiCl_3$ yielded a maximum DOC removal of about 56% at pH 3 (Fig. b, d). DOC removal (53%) achieved at pH 4.5 was slightly lower than the removal achieved at pH 3. However, for waters treated by $TiCl_3$ at pH level more than 4.5, the percentage removal of DOC sharply decreased as the pH level increased (Fig. 1b, d). Among all the pH levels tested, the lowest DOC removal was found at pH around 9.

Zhao et al. [29] studied the effect of different hydrolyzed Al species on the coagulation efficiency where they found that at low pH conditions such as 4 or below, the monomeric $[Al(OH)_2(H_2O)_{2-3}]^+$ and dimeric $Al_2O_2(OH)(H_2O)_{0-5}]^+$ Al species were produced as the major products. The increase in pH (> 4) resulted in the greater rate of hydrolysis and polymerization processes [29] which yielded low residual DOC compared to the pH ≤ 4 where higher residual DOC was observed.

For $TiCl_3$, the unfiltered turbidities at pH 3 and 4.5 were about 3 NTU whereas the turbidity at pH 6 was about 9 NTU (Fig. 1d). While for alum, the unfiltered turbidities at pH less than 6 was about 5 NTU. Filtered (11 µm filters) turbidities of alum treated waters were 0.8 NTU and 0.1 NTU at pH 3 and 6, respectively (Fig. 1c), and of $TiCl_3$ treated waters were 0.2 NTU and 0.1 NTU at corresponding pH levels.

Chow et al. [30] reported that the residual alum concentration in water following enhanced coagulation at pH < 6.0 is higher than that at pH > 6.0, and can exceed the Australian Drinking Water Guideline (ADWG) limit of 0.2 mg/L. There were no apparent differences between pH 4.5 and 6.0 for DOC removal, and therefore pH 6.0 was selected as the optimum coagulation pH for alum in this study. By comparison, the optimum coagulation pH for $TiCl_3$ was found to be 3 for maximum DOC removals.

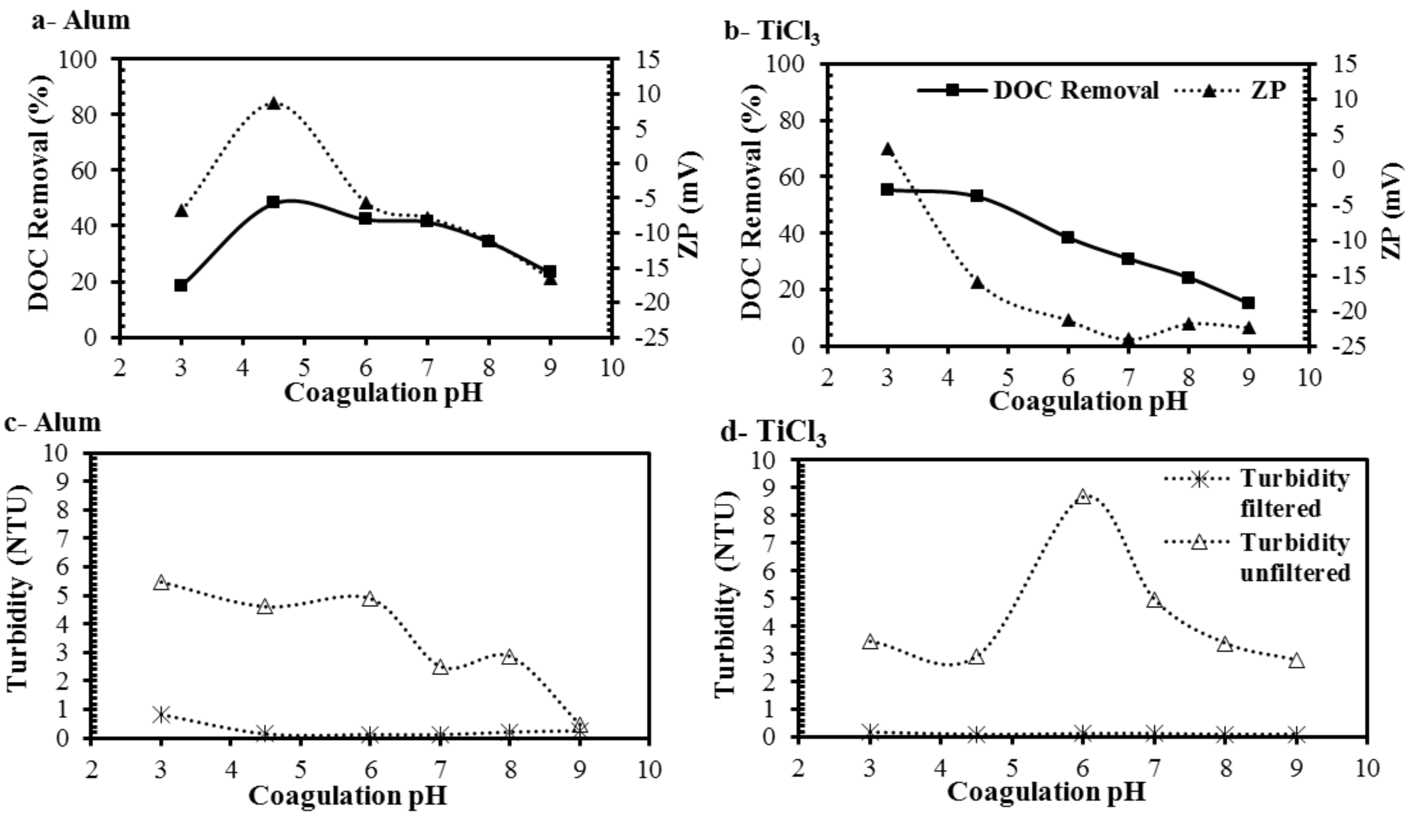

Fig. 1. Effect of coagulation pH on the coagulation performances of alum and $TiCl_3$. (a) DOC removal and zeta potential (ZP) changes with alum treatment, (b) DOC removal and ZP changes with $TiCl_3$ treatment, (c) residual turbidity levels on alum treated waters, and (d) on $TiCl_3$ treated waters.

The ZP values of Al- and Ti-flocs were determined to assess removal mechanisms of DOM and turbidity particles during destabilization. The highest ZP value of Al-flocs was about 10 mV at pH 4.5. 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 $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al_3(OH)_4^{5+}$ 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 ($Al(OH_3)$) 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 ≥ 8.0 (Fig 1). This was probably due to the predominance of negatively charged hydrolysed alum species ($Al(OH)^{4-}$) which is not favorable for destabilizing NOM particles. Zhao et al. [22] also reported that $TiCl_4$ instantly hydrolyzed to form Ti hydroxide at pH 6.0 which further reacted with humic acid to form the negatively charged Ti $(OH)_x^{(4-x)+}$-HA complex. However, the hydrolysed species of Ti salt such as $Ti(OH)_5^{1-}$ and Ti $(O_2)_2$ $(OH)_2^{2-}$ or $Ti(OH)_4$ can form at pH ≥ 9 because of high concentration of 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 ≥ 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 $TiCl_3$ 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

The coagulation performances of alum and $TiCl_3$ as a function of various coagulant doses (2-40 mg/L as the respective metal concentration) at their optimum pH levels (pH 6.0 for alum and pH 3.0 for $TiCl_3$) are shown in Figure 2. At low dose range (2-8 mg/L), alum achieved slightly higher DOC removal than $TiCl_3$. At coagulant doses above 8 mg/L, $TiCl_3$ showed a higher DOC removal than alum.

Using Equation 1, the optimum coagulant doses were determined, and found to be 6.5 mg/L and 16 mg/L for alum and $TiCl_3$, respectively. At the optimum dose, the percentage removal of DOC by alum (56%) was much lower than by $TiCl_3$ (71%), see Figures 2a & 2b. Further, the maximum DOC removal by alum was found to be ~59% at high dose (> 2 times the optimum dose; > 13 mg/L as Al). By comparison, $TiCl_3$ removal of DOC was found to be ~ 75% at a high dose (> 32 mg/L as Ti). This data indicates that at high dose, $TiCl_3$ can be more effective for DOC removal than alum. For coagulation by alum, non-coagulable DOC was found to be 4.7 mg/L while for coagulation by $TiCl_3$, this was 2.8 mg/L.

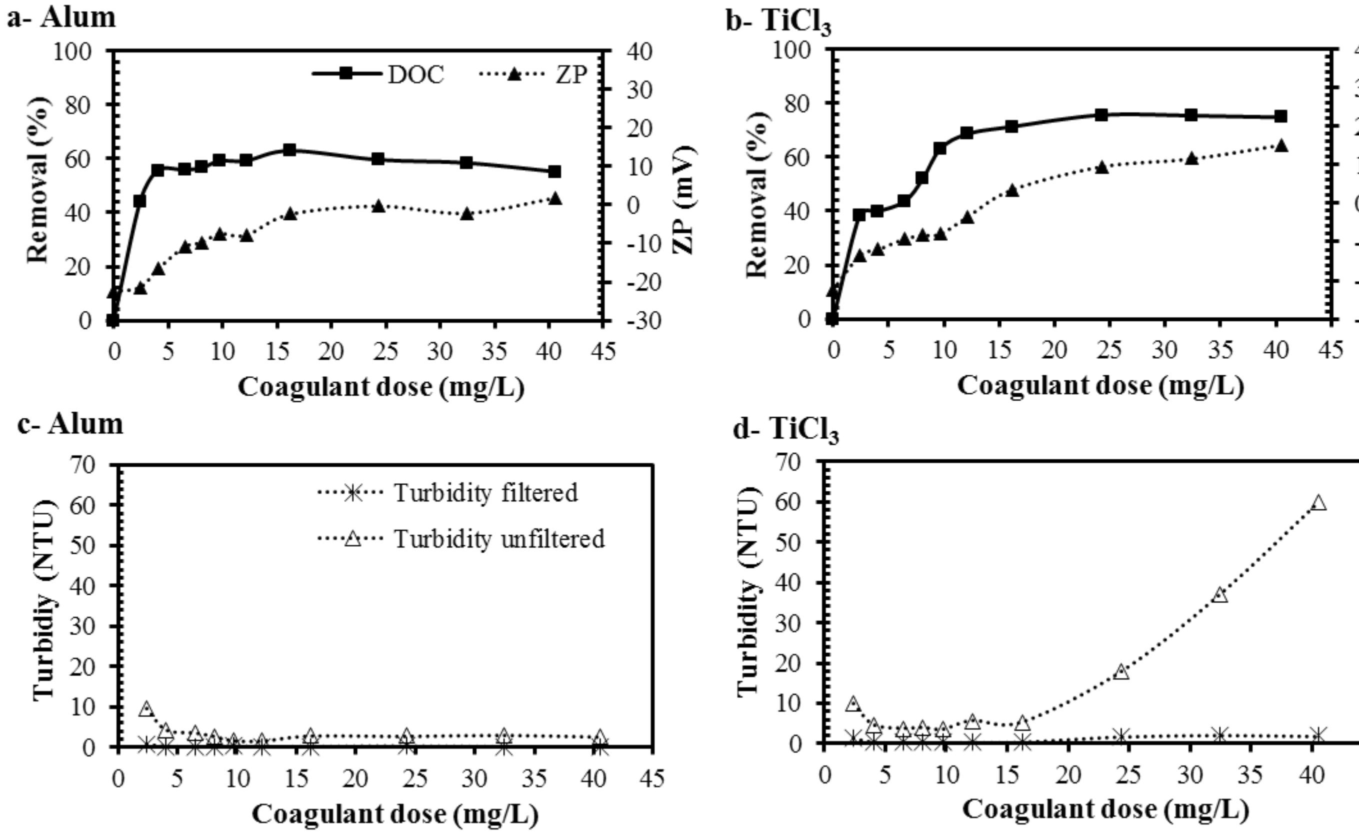

Fig. 2. Effect of different doses of alum (at pH 6) and $TiCl_3$ (at pH 3) on DOM removal efficiencies and zeta potential (ZP) values of their respective flocs. (a) DOC removal and ZP changes with alum treatment, (b)

DOC removal and ZP changes with $TiCl_3$ treatment, (c) residual turbidity levels on alum treated waters, and (d) on $TiCl_3$ treated waters.

For both alum and $TiCl_3$, the residual turbidity decreased from 34 to ≤ 3 NTU in the coagulant dose ranged between 2-12 mg/L. Above 12 mg/L dose (as Ti), the unfiltered turbidity of $TiCl_3$ treated waters significantly increased to 60 NTU, whereas for alum the unfiltered turbidity (after sedimentation) values were found to be < 3 NTU at most of the doses tested (except at dose 2 mg/L). However, the filtered (residual) turbidities of alum and $TiCl_3$ treated waters were below 0.5 NTU (except at the lowest dose of 2 mg/L) to a coagulant dose of 16 mg/L. At doses greater than 16 mg/L, the filtered turbidity of $TiCl_3$ treated waters were up to ~ 2 NTU while for alum treated waters these values remained below 0.2 NTU.

The relationship of ZP values with different alum and $TiCl_3$ coagulant doses are shown in Fig. 2a & b. With higher coagulant dose, the ZP of Al- and Ti-flocs increased. At a dose of 16 mg/L, the ZP values of both the coagulants were approximately near to their IEPs where the charges of Al- and Ti-flocs were almost zero. In addition, at an alum dose above 16 mg/L, no further change was found in the ZP of Al–flocs, which indicate that excessive doses of alum had no significant role in charge neutralization. However, the higher doses of $TiCl_3$ showed slight increases in ZP values of Ti-flocs, indicating greater DOC removal by sweep coagulation (at high doses with more positive ZPs).

3.3. DOM characterisation in treated water by F-EEM

The total fluorescence intensities (TFI, measured as the sum of all intensities of the various organic constituents within their excitation and emission regions) of the P1-, P2-, SMP-, FA- and HA-like compounds at different pH levels are shown in Fig. 3. Based on these TFI values, the percentage removals of P1-, P2-, SMP-, FA- and HA-like compounds by alum treatment at pH 6 were calculated as 6%, 1%, 42%, 14% and 64%, respectively. For $TiCl_3$ treated water, the corresponding percentage removal values at pH 3 were 6%, 32%, 47%, 50% and 66%, respectively. In addition, the mean fluorescence intensity (MFI) values of the excitation and emission regions of P1-, P2-, SMP-, FA- and HA-like compounds for the alum treated water were about 0.04, 0.25, 0.09, 0.44 and 0.10 units, respectively. For $TiCl_3$ treated water, the corresponding mean

MFI values were about 0.05, 0.18, 0.08, 0.26 and 0.09 units, respectively. These data indicate that $TiCl_3$ removed more organic compounds at pH 3, (which was also chosen as the optimum pH for DOC removal by $TiCl_3$) than alum at pH 6.

In case of $TiCl_3$, the percentage removals of both the humic fractions (FA and HA) decreased as the coagulation pH increased (Fig. 3c). At pH 9, the removal of FA-like compounds was not evident in contrast to the HA-like compounds with removal of 24%. The percentage removal of protein-like compounds showed the same trend with removals decreasing as the coagulant pH increased (Fig. 3d). At pH 9, the removal of protein-like compounds was either not detected (N.D.) or at low levels (N.D. for P1-like; 2% for P2-like; 9% for SMP-like). For alum treated waters, the lowest percentage removals of the humic fractions (FA-like and HA-like) were for water treated at pH 3 (N.D. and 3% for FA-like and HA-like compounds, respectively). The percentage removal of protein-like compounds showed the same trend with the lowest values being for alum treated water at pH 3.

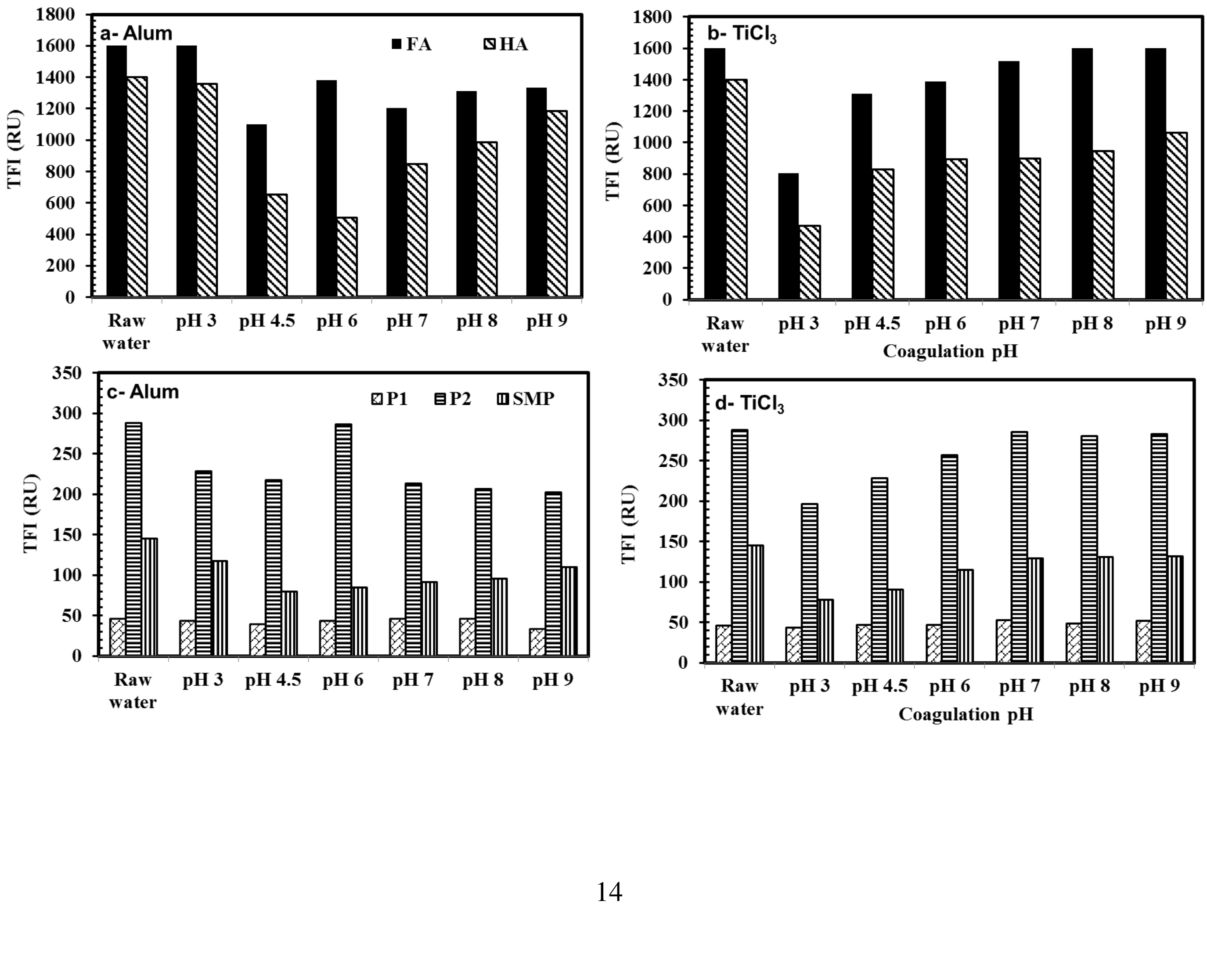

Fig. 3. The TFI values of HA- and FA-like compounds in raw water and treated water by (a) alum, (b) $TiCl_3$, and of SMP-, P1- and P2-like compounds in raw water and treated by (c) alum, and (d) $TiCl_3$ at the coagulation pH levels tested.

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

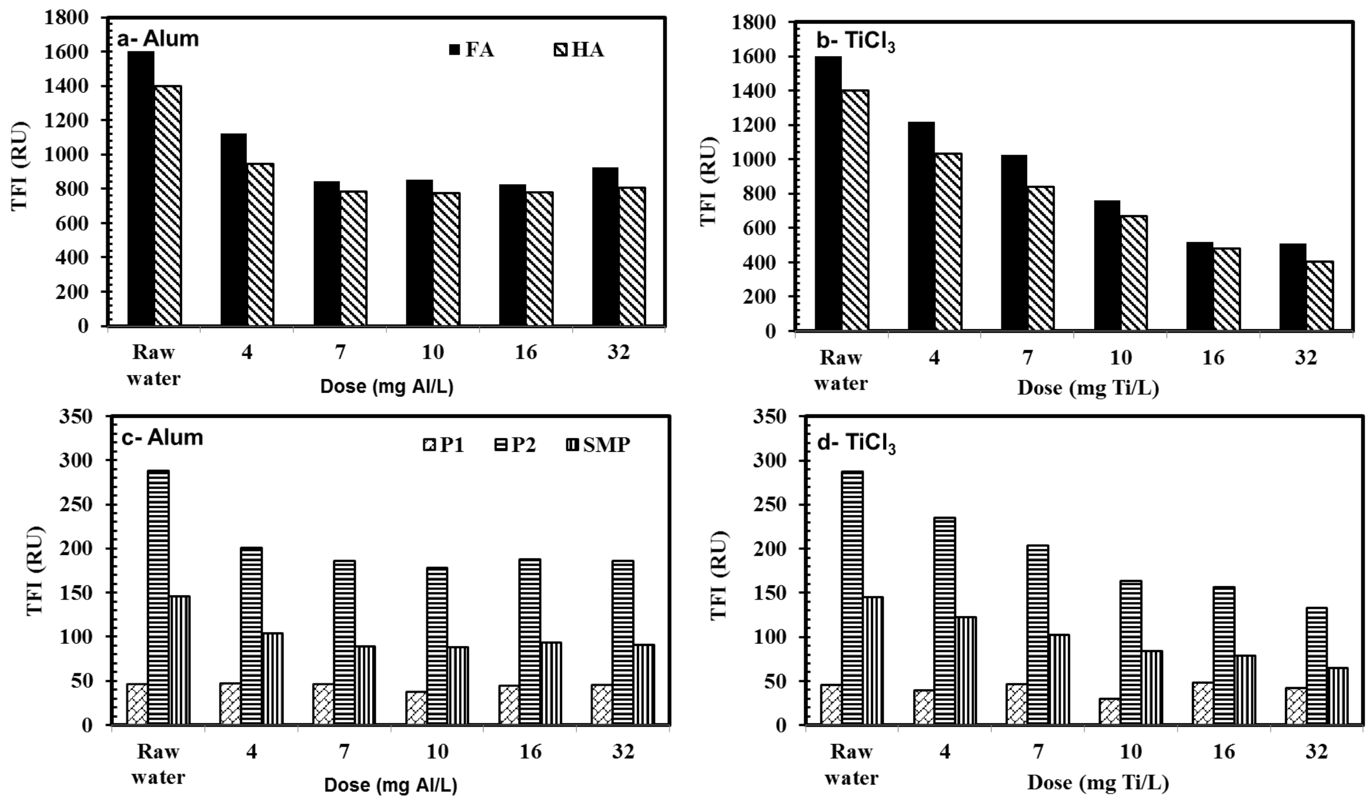

Fig. 4. Total FI values of HA- and FA-like compounds in raw water and treated water by (a) alum, and (b) $TiCl_3$, and SMP-, P1- and P2-like compounds in raw water, and treated by (c) alum, and (d) $TiCl_3$ at optimum pH levels (pH 6 for alum and pH 3 for $TiCl_3$)

In the case of $TiCl_3$, higher removals of both HA and FA occurred to the maximum coagulant dose of 32 mg/L (Fig. 4b). At most of the doses tested, the residual TFI of $TiCl_3$ 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 $TiCl_3$ compared with alum. Based on the TFI, the percentage removals of P1-, P2-, SMP-, FA- and HA-like compounds at optimum (for DOC removal) $TiCl_3$ 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 $TiCl_3$ 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 µm) 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 µm, 387 µm and 120 µm, 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 $TiCl_3$, 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 $TiCl_3$ were 1451 µm, 758 µm and 171 µm, respectively, at pH 3, which were significantly larger than the floc sizes from alum at pH 6. This indicates that flocs from $TiCl_3$ 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 $TiCl_4$ coagulation, the charge effects were found to be more important at pH 6 than pH 10, and coagulation efficiency was greatly influenced by the sweep coagulation mechanism at pH 10. In our study, the ZP of Ti-flocs was higher (more positive) at pH 3, (probably because of the greater positive charge of hydrolysed Ti species) than at pH 9, where the concentration of OH^- ions was high, as reported by Zhao et al. [22].

For alum, the largest value of floc size d_{50} was about 398 µm at a dose of 10 mg/L. Beyond this dose, the value of d_{50} remained constant or decreased slightly (Fig. 5c). For $TiCl_3$, the floc size values for d_{90}, d_{50} and d_{10} reached equilibrium conditions at doses ≥ 10 mg/L (Fig. 5d). The floc size values of d_{90}, d_{50} and d_{10} for $TiCl_3$ at the optimum dose were 1311, 596 and 128 µm, respectively, and these values were markedly higher than the corresponding floc sizes of alum (939, 397 and 105 µm). At high dose, the floc size values showed the same trend with values higher for the water treated by $TiCl_3$ (1349 µm for d_{90}, 597 µm for d_{50} and 129 µm for d_{10}) compared to that treated by alum (850, 377 and 118 µm, respectively).

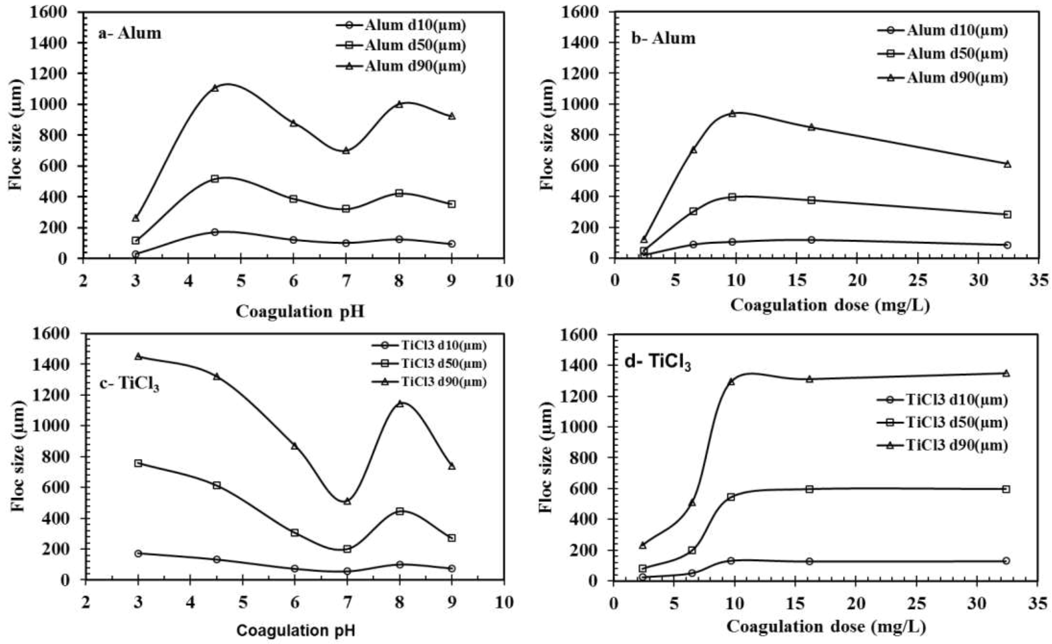

Fig. 5. Average floc sizes of d_{90}, d_{50} and d_{10} of Al-floc (a) at tested pH levels, and (b) coagulation doses, and of Ti-floc (c) at tested pH levels, and (d) coagulation doses

SEM images of flocs at three different magnification levels (1, 10 and 120 µm HFW (half field width)) are shown in Figure 6. As expected, the Ti floc showed a stronger secondary electron yield (a brighter light scattering) than the aluminium (Al) floc due to greater z-contrast obtained from Ti. At a higher magnification, the SEM images show the presence of clay mineral-like flakes which inevitably originated from the raw surface water. Wu et al. [33] reported that both Al and Ti salts formed bulky flocs. In the present study, Al and Ti flocs had approximate diameters ranging from 9.5-44 µm and 7-37 µm, respectively. It was previously suggested that both Al and Ti would result in mesoporous (pore size: 30 – 80 nm) flocs which would have adsorptive and enmeshing abilities [33]. The micromorphology of the flocs observed at a higher magnification indicated the porous structure of the flocs, in the current study. The amorphous structure of Al and Ti flocs might be due to the residual organic matter [21]. Energy dispersive X-ray analysis (EDAX) spectra obtained at a 10 µm HFW revealed an approximate elemental composition of the flocs (Figure 7a). In addition to confirming the presence of elements in flocs, the EDAX study indicated the presence of some alumina-silicate like compounds, and these results were found during the characterization of Al and Ti flocs by XRD analysis. In addition, constituents such as Cl^- or SO_4^{2-} salts of K, Ca, Na and Mg were present in the Al and Ti settled flocs. From the Al, Ti and O contents in the EDAX spectra, and with the appearance of small spherical bright structures observed in the SEM images, it could be assumed that some oxides or hydroxides of Al and Ti were formed in the flocs that were amorphous in nature. Zhao et al. [21] reported the XRD analyses of Ti (IV) sludge, incinerated at different temperatures between 200-1000 °C where the color of incinerated flocs turned from black (possibly due to residual organic matter) to white as the temperature increased. At the temperature range 600-800 °C and at 1000 °C, the anatase and rutile phase structures were observed, respectively.

Like the SEM results, XRD analysis showed the presence of alumina-silicate minerals in the flocs (Fig. 7c). Matching the accrued patterns with those of the reference patterns in the International Centre for Diffraction Data (ICDD) library indicated the presence of montmorillonite, illite and kaolinite in the flocs. The primary deflection of these clay minerals appeared at d (basal spacing) values 17.25, 10.15 and 7.23 Å, respectively (Fig. 7b). The key difference between the two flocs was observed in the appearance of the expanded montmorillonite deflection at $d \approx 17.25$ Å. In general, the montmorillonite deflection should appear at d value around 13 Å. A greater d value in the floc samples indicated insertion of organic matter or the flocculating metals in the inter-layer space of montmorillonite [34, 35]. This indicated that the adsorption of metal salts coagulants might occur at the inter-layer on particle surfaces. In the alum floc, this deflection peak created a hump which was similar to that of an Al-exchanged/pillared montmorillonite [35, 36].

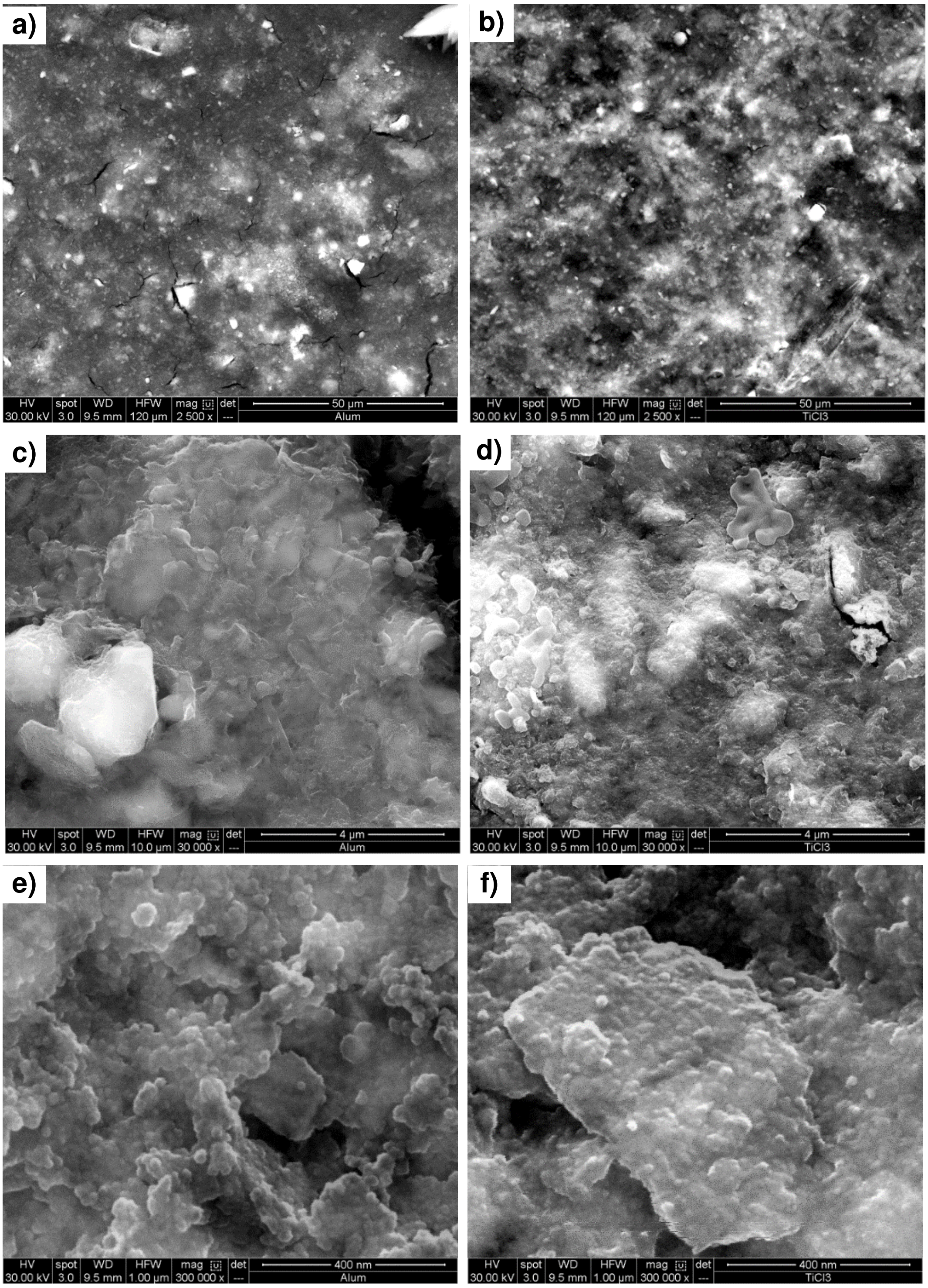

Fig. 6. Micromorphology of alum (graphs a, c and e) and $TiCl_3$ (graphs b, d and f) flocs formed at optimum pH (3 for $TiCl_3$ and 6 for alum) and at coagulant dose of 16 mg/L, observed under SEM at various magnification levels (graphs a&b, 2500 x; c&d, 30,00 x; e&f, 300,000 x)

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

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

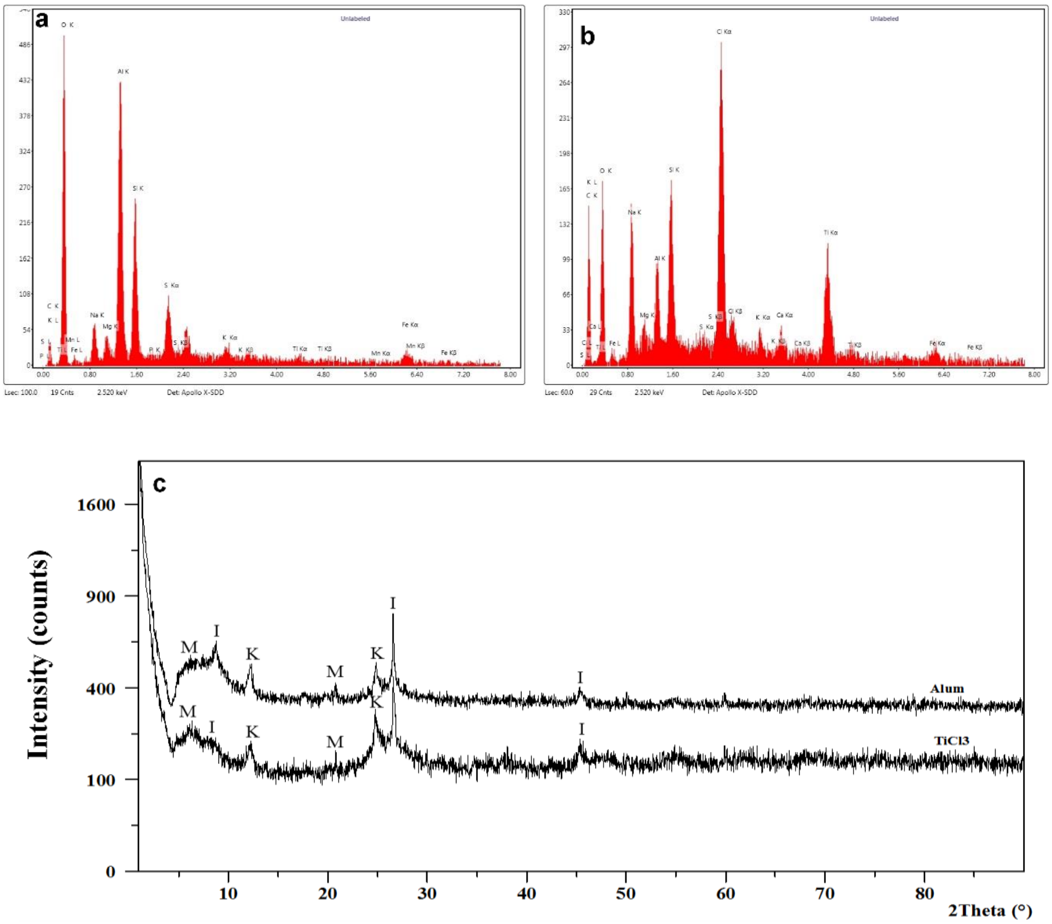

Fig. 7. EDAX spectra of alum (a) and $TiCl_3$ (b); c) XRD patterns of freeze dried alum and $TiCl_3$ flocs (M: montmorillonite; I: illite; K: kaolinite)

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 $TiCl_3$ 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 $TiCl_3$). Then, the supernatants of treated waters were further treated with two different additional doses (8 mg/L and 16 mg/L) of alum or $TiCl_3$, 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 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 treated by a single high dose of alum (-2.1 mV). These results indicate that alum in a two-stage treatment process can enhance DOC removal (in this study ~13%) than a single-stage treatment with a high dose.

Further, the percentage DOC removal was found to be higher in water treated by 16 mg Al/L of alum followed by a dose of $TiCl_3$ (16 mg Al/L + 8 mg Ti/L: ~74%; 16 mg Al/L + 16 mg Ti/L: 76%) compared to water treated by two-stage of alum (~71% for total dose of 32 mg Al/L). The ZP of settled flocs was also found to be higher in waters treated by alum followed by $TiCl_3$ (16 mg Al/L + 8 mg Ti/L: 9.5 mV; 16 mg Al/L + 16 mg Ti/L: 11.4 mV) compared to water treated by two-stage alum treatment (7.5 mV). The jar test protocol indicated that alum followed by $TiCl_3$ treatment showed slightly better performance than the alum followed by alum treatment.

In the second jar test protocol, (Table 1) treatment by $TiCl_3$ followed by alum or $TiCl_3$ treatment followed again by $TiCl_3$ showed no significant further removal of DOC. The single dose of $TiCl_3$ yielded about 75% DOC removal which was very close to the DOC removal (about 74%) obtained in two stage $TiCl_3$ treatment (total dose equivalent to 32 mg/L). The zeta potential of the $TiCl_3$ dual dose was higher than of the alum dual dose, as shown in Table 1.

At the highest coagulant dose, alum treatment followed by $TiCl_3$ or $TiCl_3$ followed by $TiCl_3$ resulted in greater residual turbidity in comparison with treatment by alum followed by alum or $TiCl_3$ followed by alum. These results are consistent with the finding we reported previously [42]. Hussain, et al. [42] reported that the combination of highly charged titanium and zirconium salts with alum showed extra advantages over a single coagulant treatment including, enhanced DOC removal. From these results it is concluded that the two-stage treatment of alum and $TiCl_3$, either the same coagulant or in combination showed better performance than a single dose treatment.

The optimum pH for $TiCl_3$ coagulation presents both potential benefits and disadvantages. Assuming that $TiCl_3$ is safe for application in the treatment of drinking water, it might have particular benefit for the treatment of low alkalinity source waters with high DOC, and for treatment of low pH industry process wastewaters such as from the pulp and paper mill industry. Low alkalinity waters will have their pH levels readily lowered through the addition and subsequent hydrolysis reaction of $TiCl_3$, and following coagulation, likely to require limited chemical addition (e.g., caustic soda) for pH re-adjusted to neutral. Further consideration would be that the water treatment infrastructure is corrosive resistant (i.e., to low pH waters). However, it is unlikely to be practically suitable for the treatment of natural waters that have medium to high levels of alkalinity for potable supply due to the need to lower the pH substantially by acid addition to reach the optimum pH for coagulation and then further greater chemical addition (caustic soda or liming agents) than needed for alum, to readjust the pH back to neutral prior to distribution.

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 (μm.cm/Vs)
Raw water	7.2	34.4	11.3	--	-22.4	-1.8
Alum followed by alum or $TiCl_3$ treatment						
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
$TiCl_3$ followed by alum or $TiCl_3$ treatment						
$TiCl_3$ (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

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

4. Conclusions

In this study, the coagulation performances of $TiCl_3$ and alum in drinking water treatment were compared. Results of jar tests revealed that the optimum pH for alum and $TiCl_3$ were 3 and 6, respectively, and a dose of 16 mg/L for both coagulants yielded an optimum DOC removal. $TiCl_3$ showed higher DOC removal than alum at the respective optimum coagulation pH levels. The DOC and turbidity removals correlated with the zeta potentials of Al- and Ti-flocs showing that the removal mechanisms were either charge neutralization or sweep coagulation, at different pH values and coagulant doses. The higher zeta potential of Ti-floc at pH 3 indicated that charge neutralization was the dominant removal mechanism for DOC removal by $TiCl_3$. However, the higher negative zeta potential of Ti-flocs at pH > 4.5 confirmed that the removal achieved at this pH occurred with a combination of adsorption, enmeshment or sweep coagulation. EEM data indicated that $TiCl_3$ showed greater removal efficiency of humic compounds (both humic acids and fulvic acids) at optimum coagulant dose than alum. The average value of floc size 'd_{50}' of Ti-floc was much greater than that of alum. A two-stage treatment process showed an enhanced DOC removal compared with a single dose treatment. Overall, $TiCl_3$ showed better results than alum in terms of DOM removal and floc size. The results from this study indicate that $TiCl_3$ could have specific application in the treatment of low alkalinity waters with high concentrations of DOC, as well as for low pH wastewaters.

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