**Coagulation performance and floc characteristics of polytitanium tetrachloride (PTC) compared with titanium tetrachloride (TiCl4) and iron salts in humic acid-kaolin synthetic water treatment**

L. Chekli, a, J. Galloux, a Y.X. Zhao, b B.Y. Gao c and H.K. Shon a, \*

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

b Key Laboratory for Special Functional Aggregated Materials of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, People’s Republic of China.

c Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, 27 Shanda South Road, Jinan, 250100, People’s Republic of China.

\*Corresponding author: Email: [Hokyong.Shon-1@uts.edu.au](mailto:Hokyong.Shon-1@uts.edu.au); Phone: (+61) 02 9514 2629

**Abstract:**

Polymeric metal coagulants are increasingly used to improve the coagulation/flocculation process efficiency, yet the research on the development of titanium and particularly polytitanium salts remains very limited. In this study, the performance of recently developed polytitanium tetrachloride (PTC) coagulant was compared with both titanium tetrachloride (TiCl4) and a commonly used coagulant, ferric chloride (FeCl3) in terms of water quality parameters and floc properties. Compared with FeCl3 coagulant, titanium-based coagulants had broader region of good flocculation in terms of pH and coagulant dose. Further, they achieved higher removal of UV254 and turbidity but lower dissolved organic carbon (DOC) removal. Charge neutralisation, physical entrapment of colloids within coagulant precipitates and adsorption were found to be the main coagulation mechanisms for TiCl4 while sweep coagulation and adsorption were found to play a more important role for both FeCl3 and PTC. The aggregated flocs formed by PTC flocculation had the largest floc size of around 836 µm with the highest floc growth rate. A little distinction of the floc strength factor was found among the coagulants tested (i.e. 44.8%, 44.2% and 38.9% for FeCl3, TiCl4 and PTC respectively) while TiCl4 coagulant yielded the flocs with the highest floc recovery factor. This study indicates that Ti-based coagulants are effective and promising coagulants for water purification. Besides, the resulted flocculated sludge can be recycled and produce functional TiO2 photocatalyst which is a significant advantage over conventional coagulants.

**Keywords:** Coagulation, Polytitanium tetrachloride, Floc size, Floc structure, Strength factor, Recovery factor.

# Introduction

Natural organic matter (NOM) is generally composed of a variety of organic compounds with a wide range of molecular weights [[1](#_ENREF_1)]. It has been found to be responsible for odour, taste, colour and bacterial regrowth in potable water and has also the potential to form carcinogenic disinfection-by-products (DBPs) [[2](#_ENREF_2)]. Humic acid (HA) consists of polycyclic aromatic macromolecules with a variety of oxygen-containing functional groups, and accounts for about 50–90% of the total freshwater organic matter [[3](#_ENREF_3)]. Because HA forms the major component of NOM present in natural freshwater, it has therefore has been recognised as an important generator of DBPs [[4](#_ENREF_4), [5](#_ENREF_5)]. The effective removal of HA present in water has thus become increasingly crucial in modern water treating processes. Coagulation and flocculation are the most commonly used processes to remove HA and colloidal particles in drinking water, seawater and wastewater [[6](#_ENREF_6)].

Aluminium (Al) and iron (Fe) salts are widely employed as effective coagulants as they showed good performance for the removal of a broad range of impurities including organic substances such as HA [[7](#_ENREF_7)]. However, the main drawback of conventional coagulants relies on the large quantity of sludge produced after treatment. In fact, the treatment of sludge after coagulation/flocculation is considered to be one of the most costly and environmentally problematic challenges of all water treatment processes [[8](#_ENREF_8), [9](#_ENREF_9)]. To circumvent the issue of sludge disposal, a novel titanium-based coagulant has been proposed by Shon et al. [[10](#_ENREF_10)]. Titanium tetrachloride (TiCl4) was investigated as an alternative coagulant and showed comparable or higher performance than conventional Al and Fe salts [[11](#_ENREF_11)]. Besides, TiCl4 coagulant has been shown to produce larger flocs with higher growth rate resulting in better settleability. The main advantage of TiCl4 is that the flocculated sludge can be recycled to produce a valuable by-product via calcination: namely titanium dioxide (TiO2) [[12-15](#_ENREF_12)]. TiO2 is the most widely used metal oxide with wide applications in paints, cosmetics, solar cells, photocatalysts or electronic paper [[16](#_ENREF_16), [17](#_ENREF_17)]. Another advantage of Ti-based coagulants compared to conventional Al and Fe coagulants relies on the reported low toxicity of titanium and relative compounds. In fact, they are rarely included in any water quality guidelines [[14](#_ENREF_14), [18](#_ENREF_18), [19](#_ENREF_19)]. Titanium is one of the most abundant elements on the earth and is found in almost all living things, rocks, water bodies, and soils. According to Emsley [[20](#_ENREF_20)], titanium is non-toxic, even in large doses and does not play any adverse or toxicity role inside the human body. An estimated quantity of 0.8 milligrams of titanium is ingested by humans each day, but most passes through without being absorbed. Because it is biocompatible (it is non-toxic and is not rejected by the body), titanium is used in a gamut of medical applications including surgical implements and implants, such as hip balls and sockets (joint replacement) that can stay in place for up to 20 years. Titanium has the inherent ability to osseointegrate, enabling use in dental implants that can remain in place for over 30 years.

Finally, the World Health Organization’s (WHO) environmental health guidelines call for a Ti concentration in drinking water supplies of 0.5-15 μg/L [[18](#_ENREF_18)] and results from our previous study [[10](#_ENREF_10)] showed that only 10 μg/L of Ti salts remained in the supernatant after the TiCl4 flocculation of wastewater.

However, one of the main drawbacks of titanium salts is related to the charge neutralisation (adsorption-destabilisation) of optimum coagulant efficiency occurring at low pH of 3.0-5.0 after coagulation due to the large quantity of H+ released during the titanium hydrolysis process [[10](#_ENREF_10), [11](#_ENREF_11)]. Based on earlier studies on inorganic polymeric coagulants [[21-23](#_ENREF_21)], this issue could be resolved by developing polytitanium salts that might minimise the release of H+ through prehydrolyzed titanium coagulants. Also, similar to other inorganic polymer coagulants, polytitanium salts may perform better than titanium salts in terms of organic matter removal and pH dependence. Besides, the advantage of using prehydrolyzed coagulants is that the hydrolysis ions occurs during the preparation stage of the coagulants, not after their addition to the real water, which consequently results in a better control of the coagulation process [[24](#_ENREF_24)]. Furthermore, they are useful for reducing the need for pH adjustment through prehydrolysis, less sensitive to low temperature, and showed great performance in removing numerous pollutants [[22](#_ENREF_22), [25](#_ENREF_25)]. Additionally, they are usually cheaper than organic polymeric coagulants [[26](#_ENREF_26)]. The first study to synthesis and characterise polytitanium salts as coagulants has been recently explored by Zhao et al. [[27](#_ENREF_27)]. Polytitanium tetrachloride (PTC) solutions with different basicity values B (i.e. OH/Ti molar ratio) were prepared using a slow alkaline titration method. Compared to TiCl4, higher or comparable turbidity and organic matter removal efficiency was achieved by PTC with improved floc characteristics in terms of size, growth rate, and structure. Besides, the sludge produced after PTC flocculation can also be recycled to prepare functional TiO2 photocatalyst which showed similar performance as commercially available P-25 TiO2 for the photodecomposition of acetaldehyde.

Floc characteristics are key parameters influencing coagulation performance in the solid/liquid separation process [[28](#_ENREF_28)]. Smaller particles settle more slowly than larger particles of similar density [[29](#_ENREF_29)]. Thus, small particles generally have lower removal efficiency by coagulation-flocculation than larger particles. The ability of flocs to resist breakage and recoverability after they have been broken has a significant impact on water treatment plants (WTP), since the unit processes in WTP have prevalent regions of high shear [[30](#_ENREF_30)]. Floc strength and recoverability are therefore considered as important parameters in understanding coagulation behaviour.

In this study, coagulation performance of PTC and TiCl4 coagulants was assessed in terms of turbidity, dissolved organic carbon (DOC), and UV254 absorbance, zeta potential and floc size and then compared with a commonly used coagulant, namely FeCl3. Furthermore, a detailed investigation was also conducted to better understand the growth, breakage and re-growth of flocs formed by all three coagulants.

# Materials and Methods

## Coagulants and test water

TiCl4 solution (>> 99% purity) was obtained from Sigma Aldrich (Australia). Stock solution of TiCl4 was prepared by slowly adding a predetermined volume (i.e. 46.4 mL) of concentrated TiCl4 solution to cubes of frozen deionized water drop by drop under continuous stirring to obtain a final 20% w/w TiCl4 solution (density ρ = 1.26 g/mL). Stock solution of FeCl3 was prepared at a concentration of 10 g/L by dissolving 2 g of powder in 200 mL of deionized water. The preparation of PTC coagulant can be found elsewhere [[27](#_ENREF_27)]. In brief, a predetermined amount (i.e. 63.3 mL) of sodium hydroxide (NaOH) solution (200 g/L) was added to 200 mL of the TiCl4 (20%) solution using a slow alkaline titration method under intensive agitation. In their study, Zhao et al. [[27](#_ENREF_27)] found that PTC coagulant with a B value (i.e. OH/Ti ratio) of 1.5 achieved the best performance and this value was therefore chosen for this study. It should be noted that coagulant dose is calculated as mmolTi/L and mmolFe/L for titanium coagulants and FeCl3, respectively.

A concentrated stock solution of HA (1.0 g/L) was prepared by dissolving 1.0 g of HA (technical grade, Sigma-Aldrich, Australia) directly in deionized water. The synthetic water used for the coagulation experiments was prepared by diluting the HA stock solution with tap water to obtain a final HA concentration of 10 mg/L. The raw water turbidity was increased by adding kaolin to obtain a final turbidity ranging from 15 NTU to 25 NTU. The measured UV254 absorbance, DOC, zeta potential and pH of the prepared synthetic water was: 0.257 cm-1 ± 0.04 cm-1, 8.04 mg/L ± 0.74 mg/L, -39.1 mV ± 1.3 mV and 7.7 respectively.

## Jar-test

Standard jar tests were conducted using a programmable jar-tester (PB-900TM, Phipps and Bird, USA). After the coagulant was added to 500 mL of the synthetic water, rapid mixing (i.e. 200 rpm) was applied for 1.5 min followed by slow mixing at 40 rpm for a duration of 20 min which was finally followed by 20 min of quiescent settling. Water samples were collected from 2 cm below water surface for measurements. The water samples were pre-filtered using 0.45 μm membrane syringe filter before testing UV254 (absorbance at 254 nm using a UV-754 UV/VIS spectrophotometer) and DOC (measured by a Shimadzu TOC-VCPH analyser). Turbidity and floc zeta potential were directly measured without filtration using a 2100P turbidimeter (Hach, USA) and Zetasizer (Malvern Instruments, UK), respectively.

Coagulation/flocculation experiments under different pH and coagulant dose conditions were conducted during preliminary tests in order to determine the region of good flocculation for each coagulant. For these preliminary experiments, the target coagulation pH value was achieved by adding appropriate quantities of HCl and NaOH solutions (0.1 M).

## Floc characterization

A laser diffraction instrument (Mastersizer 2000, Malvern, UK) was used to measure dynamic floc size as the coagulation and flocculation process proceeded. The schematic diagram of the on-line monitoring system for dynamic floc size is detailed in Figure 1. The median equivalent diameter, d50, was selected as the representative floc size, although the same trends were observed for d10 and d90 floc sizes.

**Figure 1**

To investigate the floc properties (i.e. strength and recoverability), the procedures of coagulation tests were as follows: Following the floc growth phase (i.e. 15 min at 40 rpm), the aggregated flocs were exposed to a shear force of 200 rpm for 1 min, followed by a slow mixing of 40 rpm for 20 min to allow floc regrowth. Floc strength factor (SF) and recovery factor (RF), which are used to evaluate the stability and propensity for formation of the flocs were determined as follows [[6](#_ENREF_6), [31](#_ENREF_31)]:

(1)

(2)

where d1 is the average aggregate size of the plateau before applying the shear force, d2 is the average aggregate size after aggregate breakage, and d3 is the average aggregate size after regrowth to a new plateau.

Greater SF values are indicative of flocs that are better able to resist shear. These flocs are thus considered to be stronger than those in a suspension with a lower SF. Similarly, an increase in the RF value indicates the presence of flocs that have better regrowth after exposure to high shear.

The floc growth rate was also determined by calculating the slope of the rapid growth region [[32](#_ENREF_32)]:

(3)

Previous studies have determined the fractal dimension (FD) of formed flocs by using Mastersizer 2000 [[6](#_ENREF_6), [33](#_ENREF_33), [34](#_ENREF_34)]. The total scattered light intensity I, the scattering vector Q and the FD followed a power law as follow [[35](#_ENREF_35)]:

(4)

The scattering vector Q is defined as follow [[34](#_ENREF_34)]:

(5)

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

Densely packed flocs will have higher DF value while low DF values result from high branched and loosely bound structure.

# Results and discussion

## Determination of flocculation region

Samples of flocculation experiments were classified into three categories to determine the region of good flocculation: (a) No visible flocculation (i.e. either clear liquid samples with no observed hydrolysis or turbid samples with obvious hydrolysis but no visible flocs); (b) unsatisfactory flocculation with turbidity removal efficiency < 90%; (c) good flocculation with turbidity removal efficiency > 90% and (d) optimum flocculation conditions with highest turbidity removal efficiency. The data of category c defined the region of good flocculation for each coagulant as shown in Figure 2.

**Figure 2**

Figure 2 shows that the flocculation region of titanium-based coagulants (i.e. PTC and TiCl4) occurred in a broader pH environment and dosages than FeCl3 coagulant. For each coagulant tested, pH 7 seemed to be the optimum pH where the highest turbidity removal was achieved. At this pH, PTC flocculated readily at each dosage tested whereas at pH 5, good flocculation was observed at dosages lower than 0.2 mmolTi/L. These findings are not in good agreement with a previous study on PTC [[27](#_ENREF_27)] where it was found that pH 9 was the optimum pH before coagulation in the dosage range 8-10 mgTi/L. TiCl4 showed very good performance for turbidity removal in the pH range 7-9which is in accordance with several previous studies by Zhao et al. [[11](#_ENREF_11), [12](#_ENREF_12)] where it was found that TiCl4 coagulant displayed high and stable turbidity removal under alkaline conditions. In fact, at high pH, TiCl4 coagulant is gradually hydrolysed, resulting in better turbidity removal. This also indicates that more hydroxide ions are required for TiCl4 hydrolysis. However, the results obtained in this study also differed from another study on Ti-based coagulants where it was found that the flocculation region of titanium hydroxide was in the pH range 4-6 [[19](#_ENREF_19)]. It has to be noted that titanium sulfate was used in this study; therefore that presence of SO42- as counter ions (instead of Cl-) may have an effect on the resulted region of good flocculation, especially on the pH range.

## Coagulation performance: floc zeta potential, removal of turbidity, UV254 and DOC

Coagulation performance of the tested coagulants was investigated in terms of zeta potential, and removal of turbidity, UV254 and DOC, with the results being gathered in both Figure 3 and Table 1.

Figure 3 shows the changes in floc zeta potential which is generally used to evaluate the destabilisation ability of coagulants. Changes in floc zeta potential are also often regarded as an effective tool to investigate coagulation mechanism, which is usually explained in terms of charge neutralisation and sweep flocculation [[36](#_ENREF_36)]. Under the optimum coagulant dose conditions, the floc zeta potential values after coagulation for FeCl3, TiCl4 and PTC were -1.2 mV, -0.4 mV and -2.1 mV, respectively, suggesting that charge neutralisation plays a major role during the flocculation process of all three coagulants. Various studies from Zhao et al. [[12](#_ENREF_12), [37](#_ENREF_37)] already demonstrated that the main coagulation mechanism for TiCl4 was through charge neutralisation. In the case of FeCl3, Cheng [[22](#_ENREF_22)] reported that the possible coagulation mechanisms arising between FeCl3 and HA were charge neutralisation and adsorption. It was also stated that the fraction removed by charge neutralisation was less than that removed by adsorption in the pH range of 7.5-9. In this study, the initial pH of the synthetic water was about 7.7 which suggested that the adsorption might also play a more important role in the flocculation of the HA present in the synthetic water by FeCl3. This might be one of the reasons why FeCl3 achieved better DOC removal (i.e. 50.2% compared to 41.7% and 36.1% for Ti-salts) even though charge neutralisation was comparatively weak. For PTC, the only study reported by Zhao et al. [[27](#_ENREF_27)] suggested that charge neutralisation may be the predominant coagulation mechanism as zeta potential values close to zero were found after flocculation.

However, the zeta potential values of -2.1 mV and -1.2 mV obtained with PTC and FeCl3 respectively suggest that complete charge neutralisation was not achieved resulting in the negative surface charges on floc surface. This indicates that during the coagulation process of both PTC and FeCl3, sweep coagulation and adsorption also play an important role to facilitate the floc aggregation besides charge neutralisation.

**Figure 3**

The coagulants performance displayed in Table 1shows that both Ti-based coagulants achieved better performance in terms of turbidity and UV254 removal while FeCl3 showed higher performance for DOC removal as discussed earlier. It can be noted that PTC achieved comparable turbidity and UV removal with TiCl4 with a much lower optimum dose suggesting that the use of PTC instead of TiCl4 will result in a cost-effective treatment.

In the first study on PTC [[27](#_ENREF_27)], higher DOC removal was achieved (i.e. 61.5% for PTC prepared with a B value of 1.5). However, the synthetic water used in this study had different physico-chemical characteristics and especially a lower initial DOC value (5.14-5.58 mg/L against 8.04 mg/L in the present study). Besides, the B value of 1.5 was chosen in the present study for comparison but also because it was previously found to be the optimum value to achieve the best coagulation performance. It is therefore possible that another B value would have result in better coagulation performance to treat the present synthetic water.

**Table 1**

## Dynamic variation of floc size during flocculation

Floc formation, breakage and regrowth process with FeCl3, TiCl4 and PTC under optimum coagulant dose conditions were on-line monitored by using Mastersizer 2000 and the results are displayed in Figure 4.

As show in Figure 4, the floc size gradually increased after the introduction of the slow mixing speed (i.e. 40 rpm) for all coagulants tested, reaching the stable plateau during slow stirring phase, which suggests that appropriate balance between floc growth and breakage was reached. When the shear force was then introduced (i.e. rapid mixing at 200 rpm for 1 minute), the floc size immediately decreased, resulting in the flocs being up to 60% smaller than the original value. When the slow mixing speed was reintroduced, the flocs began to regrowth, but none of the flocs formed by all three coagulants recovered to the initial floc size.

**Figure 4**

Each tested coagulant exhibited different floc sizes and floc growth rates (Table 2). Compared to FeCl3, TiCl4 and PTC had faster floc growth rate with larger floc size, indicating that TiCl4 and PTC need shorter period to form larger aggregates. Boller and Blaser [[29](#_ENREF_29)] explained that a short retention time coupled with larger floc size formation will likely lead to smaller and more compact flocculation and sedimentation units as larger particles generally settled down more rapidly than smaller particles of the same density. The floc growth rate during the coagulation process varied in the following order: PTC > TiCl4 > FeCl3 and the order of floc size d1 was PTC (836.9 µm) > TiCl4 (764.3 µm) > FeCl3 (722.2 µm). These results clearly indicate the advantage of using titanium-based coagulants over Fe-salts since the resultant flocs are with much larger size regardless of floc growth, breakage and regrowth process. Besides, as it is known that fine flocs are more prone to suspend in the supernatant, larger flocs will then achieve better removal efficiency by settling. This may explain the lower turbidity removal efficiency of FeCl3 compared to Ti-based coagulants.

**Table 2**

## Floc breakage and recovery

Floc strength factor (SF) and floc recovery factor (RF) were calculated using equations (1) and (2) to investigate the floc strength and recoverability. Results are gathered in Table 2 and show that the SF of FeCl3, TiCl4 and PTC were 44.8, 44.2 and 38.9 while the RF were 20.4, 42.0 and 20.5 respectively. Breakage and reformation of flocs are generally partly controlled by the characteristics of different coagulants. The FeCl3 coagulants showed the highest SF but with no significant difference from that of TiCl4 and PTC. The flocs formed by TiCl4 showed the highest RF while FeCl3 and PTC showed the lower but similar RF values. Previous studies have already reported that the flocs formed by sweep flocculation (i.e. FeCl3 and PTC in this study) had weaker recoverability after breakage than those by charge neutralisation (i.e. TiCl4 in this study) [[38](#_ENREF_38), [39](#_ENREF_39)]. However, even though TiCl4 showed the highest RF value, the flocs did not regrow to their initial size before breakage, suggesting that charge neutralisation is not the only coagulation mechanisms responsible for TiCl4 coagulation. Gregor et al. [[40](#_ENREF_40)] stated that the main removal route of HA via coagulation varies depending on the pH conditions as follow: precipitation by forming insoluble complexes at pH < 6, and adsorption of HA onto hydroxide solid at pH > 6. As the optimum coagulation pH for TiCl4 was 7.0, adsorption of HA onto hydroxide solid might be the dominant removal mechanism. Zhao et al. [[11](#_ENREF_11)] explained that that floc growth process for TiCl4 coagulant could be interpreted as follow: During the first minutes, the floc size sharply increased due to charge neutralisation between negatively charged HA present in water and Ti4+. As the coagulation process continued, the flocs aggregated to form even larger flocs (i.e. d50 > 800 µm) possibly resulted from the physical enmeshment of the colloids within the coagulant precipitates combined with chemical sorption. Then, the flocs size slowly decreased (i.e. d50 ~ 700 µm) possibly due to the disturbance on the aggregated flocs on extended mixing.

Figure 5 presents the particle size distribution (PSD) of the three coagulants before breakage, after breakage and after regrowth. Analysis of PSD showed that, for all tested coagulants, the size of the flocs after breakage is under half the original value. After regrowth, there is an obvious shift to larger sizes indicating the floc reformation after the breakage period. Compared to TiCl4, fewer changes were observed between the PSD before breakage and after floc regrowth for FeCl3 and PTC which implies the poor floc regrowth after breakage and which is confirmed by the lower RF obtained for these two coagulants.

**Figure 5**

## Floc structural analysis

The floc fractal dimension (FD) of all three coagulants was calculated based on equations (4) and (5) to compare the floc compaction degree. Floc FD is another important parameter which influences floc density and thus affects solid/liquid separation process [[41](#_ENREF_41)]. Results are presented in Table 2 and showed that the floc FD values followed the order of FeCl3 > TiCl4 > PTC. This is in accordance with a previous study [[21](#_ENREF_21)] which demonstrated that the larger the floc size, the smaller the fractal dimension. Besides, it can be seen that the FD followed the same trend as the SF which indicates that flocs having high SF will also present a high degree of compactness. This was also demonstrated in a previous study by Wang et al. [[42](#_ENREF_42)] where they found a tight relationship between floc structure and floc strength.

**Conclusions**

The performance of recently developed PTC coagulant was investigated for synthetic wastewater treatment compared with TiCl4 and conventional FeCl3 in terms of water quality parameters, coagulation mechanisms and flocs characteristics. The following conclusions are drawn from the present study:

1. PTC and TiCl4 presented a broader flocculation region in terms of pH and coagulant dose for turbidity removal and can thus potentially be applied over a wider range of pH than FeCl3. Besides, PTC and TiCl4 achieved higher turbidity and UV254 removal.
2. During the initial floc growth period, PTC showed the fastest growth rate (i.e. 278.9 µm/min) with the largest floc size of 836 µm, which suggests significant advantages in terms of compact mixing and sedimentation tanks.
3. The strength factor and fractal dimension of all three coagulants were quite similar and followed the same order: FeCl3 > TiCl4 > PTC; suggesting a close relationship between floc strength and structure. However, PTC and FeCl3 showed similar but lower values of recovery factors, proposing that PTC flocs require more careful handling during the separation process.
4. Charge neutralisation combined with physical entrapment of colloids within floc precipitates and adsorption were the main mechanisms involved in TiCl4 coagulation. Sweep coagulation and adsorption were found to be the primary mechanisms for both PTC and FeCl3.

**Acknowledgements**

This work was supported by the Australia Research Council Discovery Projects (ARC DP 103103129), a grant from the Chinese National Natural Science Foundation (NO.51278283) and China Postdoctoral Science Foundation (2014M560557).

**References**

1. Kabsch-Korbutowicz, M., Application of ultrafiltration integrated with coagulation for improved NOM removal, Desalination 174 (2005) 13-22.

2. Hu, C., H. Liu, J. Qu, et al., Coagulation behavior of aluminum salts in eutrophic water: significance of Al13 species and pH control, Environ. Sci. Technol. 40 (2006) 325-331.

3. Aiken, G.R., D.M. McKnight, R.L. Wershaw, et al., Humic substances in soil, sediment, and water: geochemistry, isolation and characterization, John Wiley & Sons, New York, 1985.

4. Kazpard, V., B. Lartiges, C. Frochot, et al., Fate of coagulant species and conformational effects during the aggregation of a model of coagulation of humic acid: the performance of preformed and non-preformed Al species, Water Res 40 (2006) 1965-1974.

5. Shi, B., Q. Wei, D. Wang, et al., Coagulation of humic acid: the performance of preformed and non-preformed Al species, Colloids Surf., A 296 (2007) 141-148.

6. Jarvis, P., B. Jefferson, and S.A. Parsons, Breakage, regrowth, and fractal nature of natural organic matter flocs, Environ. Sci. Technol. 39 (2005) 2307-2314.

7. Duan, J. and J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100 (2003) 475-502.

8. Kane, M., Conventry Area Sewage Sludge Disoposal Scheme: Development of Strategy and Early Operating Experiences, Water and Environment Journal 1 (1987) 305-314.

9. Nassar, A.M., M. Smith, and S. Afifi, Palestinian experience with sewage sludge utilizing reed beds, Water and Environment Journal 23 (2009) 75-82.

10. Shon, H., S. Vigneswaran, I.S. Kim, et al., Preparation of Titanium Dioxide (TiO2) from Sludge Produced by Titanium Tetrachloride (TiCl4) Flocculation of Wastewater, Environ. Sci. Technol. 41 (2007) 1372-1377.

11. Zhao, Y.X., B.Y. Gao, H.K. Shon, et al., Coagulation characteristics of titanium (Ti) salt coagulant compared with aluminum (Al) and iron (Fe) salts, J. Hazard. Mater. 185 (2011) 1536-1542.

12. Zhao, Y., B. Gao, B. Cao, et al., Comparison of coagulation behavior and floc characteristics of titanium tetrachloride (TiCl4) and polyaluminum chloride (PACl) with surface water treatment, Chem. Eng. J. 166 (2011) 544-550.

13. Shon, H., S. Vigneswaran, J. Kandasamy, et al., Preparation and characterization of titanium dioxide (TiO2) from sludge produced by TiCl4 flocculation with FeCl3, Al2 (SO4) 3 and Ca (OH) 2 coagulant aids in wastewater, Sep. Sci. Technol. 44 (2009) 1525-1543.

14. Lee, B., S. Kim, H. Shon, et al., Aquatic toxicity evaluation of TiO2 nanoparticle produced from sludge of TiCl4 flocculation of wastewater and seawater, J. Nanopart. Res. 11 (2009) 2087-2096.

15. Okour, Y., H. Shon, I. El Saliby, et al., Preparation and characterisation of titanium dioxide (TiO2) and thiourea-doped titanate nanotubes prepared from wastewater flocculated sludge, Bioresour. Technol. 101 (2010) 1453-1458.

16. Hoffmann, M.R., S.T. Martin, W. Choi, et al., Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69-96.

17. Obee, T.N. and R.T. Brown, TiO2 photocatalysis for indoor air applications: effects of humidity and trace contaminant levels on the oxidation rates of formaldehyde, toluene, and 1, 3-butadiene, Environ. Sci. Technol. 29 (1995) 1223-1231.

18. World Health Organization. Environmental Health Criteria 24: Titanium. 1982 [accessed 2014]; Available from: <http://www.inchem.org/documents/ehc/ehc/ehc24.htm>.

19. Wu, Y.-F., W. Liu, N.-Y. Gao, et al., A study of titanium sulfate flocculation for water treatment, Water Res. 45 (2011) 3704-3711.

20. Emsley, J., Nature's building blocks: an AZ guide to the elements, Oxford University Press, 2011.

21. Cao, B., B. Gao, X. Liu, et al., The impact of pH on floc structure characteristic of polyferric chloride in a low DOC and high alkalinity surface water treatment, Water Res. 45 (2011) 6181-6188.

22. Cheng, W.P., Comparison of hydrolysis/coagulation behavior of polymeric and monomeric iron coagulants in humic acid solution, Chemosphere 47 (2002) 963-969.

23. Zhan, X., B. Gao, Q. Yue, et al., Coagulation behavior of polyferric chloride for removing NOM from surface water with low concentration of organic matter and its effect on chlorine decay model, Sep. Purif. Technol. 75 (2010) 61-68.

24. Jiang, J.-Q. and N.J. Graham, Pre-polymerised inorganic coagulants and phosphorus removal by coagulation- a review, Water Sa 24 (1998) 237-244.

25. Edzwald, J.K. and J.E. Tobiason, Enhanced coagulation: US requirements and a broader view, Water Sci. Technol. 40 (1999) 63-70.

26. Sinha, S., Y. Yoon, G. Amy, et al., Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes, Chemosphere 57 (2004) 1115-1122.

27. Zhao, Y., S. Phuntsho, B. Gao, et al., Preparation and Characterization of Novel Polytitanium Tetrachloride Coagulant for Water Purification, Environ. Sci. Technol. 47 (2013) 12966-12975.

28. Yu, W., G. Li, Y. Xu, et al., Breakage and re-growth of flocs formed by alum and PACl, Powder Technology 189 (2009) 439-443.

29. Boller, M. and S. Blaser, Particles under stress, Water Sci. Technol. 37 (1998) 9-29.

30. McCurdy, K., K. Carlson, and D. Gregory, Floc morphology and cyclic shearing recovery: comparison of alum and polyaluminum chloride coagulants, Water Res. 38 (2004) 486-494.

31. Yukselen, M.A. and J. Gregory, Breakage and re-formation of alum flocs, Environ. Eng. Sci. 19 (2002) 229-236.

32. Xiao, F., P. Yi, X.-R. Pan, et al., Comparative study of the effects of experimental variables on growth rates of aluminum and iron hydroxide flocs during coagulation and their structural characteristics, Desalination 250 (2010) 902-907.

33. Wei, J., B. Gao, Q. Yue, et al., Comparison of coagulation behavior and floc structure characteristic of different polyferric-cationic polymer dual-coagulants in humic acid solution, Water Res. 43 (2009) 724-732.

34. Lin, J.-L., C. Huang, C.-J.M. Chin, et al., Coagulation dynamics of fractal flocs induced by enmeshment and electrostatic patch mechanisms, Water Res. 42 (2008) 4457-4466.

35. Rieker, T.P., M. Hindermann-Bischoff, and F. Ehrburger-Dolle, Small-angle X-ray scattering study of the morphology of carbon black mass fractal aggregates in polymeric composites, Langmuir 16 (2000) 5588-5592.

36. Gregory, J. and J. Duan, Hydrolyzing metal salts as coagulants, Pure Appl. Chem. 73 (2001) 2017-2026.

37. Zhao, Y., B. Gao, H. Shon, et al., Floc characteristics of titanium tetrachloride (TiCl4) compared with aluminum and iron salts in humic acid–kaolin synthetic water treatment, Sep. Purif. Technol. 81 (2011) 332-338.

38. Aguilar, M., J. Saez, M. Llorens, et al., Microscopic observation of particle reduction in slaughterhouse wastewater by coagulation–flocculation using ferric sulphate as coagulant and different coagulant aids, Water Res. 37 (2003) 2233-2241.

39. Jarvis, P., B. Jefferson, and S. Parsons, The duplicity of floc strength, Water Science & Technology 50 (2004) 63-70.

40. Gregor, J., C. Nokes, and E. Fenton, Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation, Water Res. 31 (1997) 2949-2958.

41. Gregory, J., The role of floc density in solid-liquid separation, Filtration & separation 35 (1998) 367-366.

42. Wang, Y., B.-Y. Gao, X.-M. Xu, et al., Characterization of floc size, strength and structure in various aluminum coagulants treatment, J. Colloid Interface Sci. 332 (2009) 354-359.

**List of Tables**

Table 1: Residual turbidity, UV254 removal and DOC removal of each coagulant under optimum coagulant dose (initial turbidity = 19 NTU; UV254 = 0.257 cm−1; DOC= 8.04 mg/L; pH= 7.7).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Coagulants | Optimal dosage (mmol/L) | Residual turbidity (NTU) (% removal) | UV254 removal (%) | DOC removal (%) |
| FeCl3 | 0.15 | 1.0 (94.8 %) | 88.5 | 50.2 |
| TiCl4 | 0.40 | 0.53 (97.2 %) | 93.5 | 41.7 |
| PTC | 0.15 | 0.50 (97.4 %) | 89.6 | 36.1 |

Table 2: Summary of floc size before breakage (d1), after breakage (d2) and after regrowth (d3), floc growth rate, strength and recovery factors and fractal dimension (FD) of the formed flocs for each coagulant tested.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Coagulants | d1 (µm) | d2 (µm) | d3 (µm) | Floc growth rate (µm/min) | SF (%) | RF (%) | FD |
| FeCl3 | 722.2 | 323.2 | 404.6 | 162.90 | 44.8 | 20.4 | 2.51 |
| TiCl4 | 764.3 | 338.3 | 517.1 | 248.50 | 44.2 | 42.0 | 2.48 |
| PTC | 836.9 | 325.7 | 430.6 | 278.90 | 38.9 | 20.5 | 2.40 |

**List of Figure captions**

**Figure 1:** Schematic diagram of the on-line monitoring system for the dynamic floc sizes.

**Figure 2:** Flocculation zone of (a) FeCl3, (b) TiCl4 and (c) PTC (initial turbidity = 19 NTU; UV254 = 0.257 cm−1; DOC= 8.04 mg/L; pH= 7.7).

**Figure 3:** Zeta potential of tested coagulants after flocculation (under optimum coagulant dose conditions, see Table 1).

**Figure 4:** Growth, breakage and regrowth profile of HA flocs formed by FeCl3, TiCl4 and PTC under optimum dose conditions (The optimum coagulant dose conditions, see Table 1; Initial solution pH condition).

**Figure 5:** Floc size distribution before breakage, after breakage and after regrowth of (a) FeCl3, (b) TiCl4 and (c) PTC under optimum coagulant dose conditions (The optimum coagulant dose condition, see Table 1; Initial solution pH condition).

C:\Users\995130\paper2\collegues\Laura Chekli\2014\TiCl4 with Jordan\SPT\revised\Figure 1.TIF

Figure 1

C:\Users\995130\paper2\collegues\Laura Chekli\2014\TiCl4 with Jordan\SPT\revised\Figure 2.TIF

Figure 2

C:\Users\995130\paper2\collegues\Laura Chekli\2014\TiCl4 with Jordan\SPT\revised\Figure 3.TIF

Figure 3

C:\Users\995130\paper2\collegues\Laura Chekli\2014\TiCl4 with Jordan\SPT\revised\Figure 4.TIF

Figure 4

C:\Users\995130\paper2\collegues\Laura Chekli\2014\TiCl4 with Jordan\SPT\revised\Figure 5.TIF

Figure 5