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Comparison of coagulation behavior and floc characteristics of titanium tetrachloride ($TiCl_4$) and polyaluminum chloride (PACl) with surface water treatment

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ABSTRACT

Coagulation behavior of Titanium tetrachloride ($TiCl_4$) and polyaluminum chloride (PACl) was comparatively investigated in terms of the removal of turbidity and natural organic matter (NOM) with surface water. The growth, breakage and re-growth nature of flocs were also compared. The results show that the removals of chemical oxidation demand (COD_{Mn}) and dissolved organic carbon (DOC) were 51.5% and 78.4% at optimal dosage for $TiCl_4$ and 29.8% and 41.0% for PACl, respectively. The floc breakage and re-growth indicated that $TiCl_4$ and PACl coagulation occurred not only by charge neutralization but also by a form of sweep flocculation. Besides, flocs formed by PACl had better recoverability than the flocs formed by $TiCl_4$. Sludge produced from $TiCl_4$ flocculation was calcined at 600 °C to produce TiO_2, and the photocatalytic activity in removing reactive brilliant red (K-2BP) was evaluated in comparison with commercially available TiO_2 (P-25). The photocatalytic oxidation rates of K-2BP after 2 h photocatalytic reaction were 91.4% and 92.9% for as-prepared TiO_2 and P-25, respectively.

1. Introduction

Removal of organic matter in drinking water treatment is an essential requirement due to its potential to form carcinogenic disinfection-byproducts [1]. Coagulation, as the most widely applied unit process for the removal of particles and organic matter present in water [2], is becoming highly valued. Due to the effectiveness in treating a wide range of waters at a relatively low lost, aluminum salts become the most commonly used coagulant in water treatment.

Researches on polyaluminum chloride (PACl) have rapidly developed [3,4], whereas aluminum salts are suspected to be harmful to human and living things [5]. In addition, the main drawback of the flocculation process using aluminum salt coagulants is a large amount of sludge produced, which still need to be disposed of either into landfills or dumped into the ocean. To resolve the problem of sludge disposal, Shon et al. used $TiCl_4$ as a coagulant and the Ti-salt flocculated sludge was recovered to produce valuable by-product namely TiO_2 [6,7]. They also reported that the photocatalytic activity of recycled TiO_2 is better than that of commercially available TiO_2 (P-25). TiO_2 was the most widely used metal oxide for environmental applications as photocatalyst, cosmetics, paints, electronic paper, and solar cells [6,8,9]. Therefore, recycling of Ti-flocculated offers a novel solution to sludge disposal from water and wastewater treatment plants associated with production of TiO_2 with a wide range of environmental applications.

Size and structure of flocs after flocculation cause a critical effect on solid/liquid separation process [10] as the flocculation process is often prevalent with the regions of high shear force [11]. Therefore, flocs formed are strong enough to resist rupture under exposure to shear force and have a good recovery capacity. Floc growth is a process between the balance of floc formation and breakage [12–16]. Boller and Blaser [17] reported that small particles generally had lower removal efficiency by flocculation, since smaller particles generally settled down more slowly than larger particles of similar density. Li et al. [18] also found that broken flocs were difficult to regrow. Reduced floc size slows down the sedimentation rate and change particle transport mechanisms [19,20]. Some researchers found that re-growth of chalk aggregates could be reversible after high shear force was applied [21]. Chaignon et al. reported that the flocs formed by charge neutrality had complete recoverability [22]. Therefore, floc strength and recoverability are considered as an important parameter to provide valuable information in understanding the performance of a novel coagulant.

Although the particulate and organic matter removal is an essential requirement, little study on $TiCl_4$ flocculation has been

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conducted to the removal mechanisms of the pollutants and floc characteristics, such as the potential for flocs to regrow after being broken. In this study, coagulation behavior of PACl and $TiCl_4$ were comparatively investigated in terms of turbidity, dissolved organic carbon (DOC), UV_{254} absorbance, and chemical oxygen demand (COD_{Mn}) and zeta potential measurements. Furthermore, growth, breakage and re-growth properties of flocs formed by $TiCl_4$ and PACl were also simply explored. Sludge produced from $TiCl_4$ flocculation was calcined at 600 °C to produce TiO_2 and X-ray diffraction (XRD) was used to identify the particle structure. Photocatalytic activity of TiO_2 from sludge was evaluated using the photodecomposition of reactive brilliant red (K-2BP) in comparison with P-25.

2. Experimental

2.1. Water used in this study

The water source used in this study was withdrawn from Queshan Reservoir which is an important drinking water source in Jinan, China. The water was collected in winter season, January 2010 and the water temperature was at 4–8 °C. The detailed characteristics of this are shown in Table 1.

Table 1
Characteristics of the drinking water sources used in this study.

Turbidity (NTU)	UV_{254} (cm^{-1})	DOC (mg/L)	COD_{Mn} (mg/L)	pH
1.05 ± 0.03	0.05 ± 0.002	1.686 ± 0.05	2.50 ± 0.20	8.34–8.53

2.2. Preparation and characteristics of coagulants

$TiCl_4$ stock solution (20%, density = 1.148 g/ml) was obtained from Photo and Environment Technology Co. Ltd. (South Korea). PACl with a basicity value (B, OH/Al molar ratio) of 2.0 was synthesized. All the reagents used in the preparation of PACl were of analytical pure grade and deionized water was used for the preparation of all the solutions.

The procedures of PACl preparation are described as follows [23]: predetermined amount of $AlCl_3{\cdot}6H_2O$ and Na_2CO_3 powder was fully mixed and then slowly added into deionized water at constant speed for 30 min while stirring at 70–80 °C to obtain the desired basicity value of PACl. The mixture was stirred until no bubbles were formed and the solution became transparent. The product was allowed to keep more than 24 h before the properties of the coagulant were examined. Here the aluminum content was measured by ethylenediaminetetraacetic acid (EDTA) complexometric titration [24]. The properties of PACl used were indicated as follows: total Al (Al_T) content = 0.9875 mol/L, Al_a = 24.8%, Al_b = 32.1%, Al_c = 48.1%, pH = 2.85 ± 0.10.

2.3. Jar-test

Coagulation was conducted using a jar tester (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) at different coagulant dosages and different initial pH. A two-stage mixing process, including rapid (1.5-min stage at 200 rpm) and slow mixing (20-min stage at 40 rpm) was followed by a 20-min settling period, after which the supernatant samples were collected using a syringe from about 2 cm below the water surface for the measurements of turbidity, UV_{254} absorbance, zeta potential and DOC. The samples were prefiltered through a 0.45 μm fiber membrane before testing for UV_{254} (absorbance at 254 nm using a UV-754 UV/VIS spectrophotometer) and DOC (measured by a Shimadzu TOC-VCPH analyzer), while the turbidity was measured without microfiltration using a 2100P turbidimeter (Hach, USA) and zeta potential was analyzed with a Zetasizer 3000HSa (Malvern Instruments, UK). Coagulation experiments at different initial pH were conducted after optimal coagulant dosages were determined. HCl and NaOH solutions were added to adjust the initial pH.

2.4. Floc formation, breakage and re-growth

The dynamic floc sizes were measured using laser diffraction Mastersizer 2000 (Malvern, UK) as coagulation and flocculation processes proceeded. The suspension was monitored through optical unit of Mastersizer and back into the jar by a peristaltic pump (LEAD-1, Longer Precision Pump, China) on a return tube with a 5 mm internal diameter peristaltic pump tubing. The inflow and outflow tubes were positioned opposite one another at a depth just above the paddle in the holding ports. Size measurements of the formed floc were taken every 0.5 min for the duration of the jar test and the corresponding data were automatically recorded.

2.5. Floc strength and recovery factors

Floc strength factor (S_f) and recovery factor (R_f) are well-established parameters of describing floc strength and recoverability and can be calculated as follows [2,13,25]:

$$S_f = \frac{d_2}{d_1} \times 100 \qquad (1)$$

$$R_f = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \qquad (2)$$

where d_1 is the average floc size of the plateau before breakage, d_2 is the floc size after floc breakage period, and d_3 is the floc size after re-growth to the new plateau.

Here, the strength factor is an indicative of flocs strength, which refers to the ability to resist rupture by a velocity gradient, while the recovery factor indicates recoverability of the flocs. The larger values of strength factor indicate that the flocs are stronger than those with lower factors. Flocs with larger recovery factors show better recoverability after high shear, that is, better re-growth after breakage. In addition, the size data is expressed as an equivalent volumetric diameter, and d_{50} was selected as representative floc size in this paper [26], which refers to the 50% floc size.

2.6. TiO_2 preparation from Ti-salt flocculated sludge

Sludge produced from $TiCl_4$ flocculation was dewatered and then dried at 100 °C for 12 h. The dried sludge was grinded using a mortar and pestle, followed by calcination in a furnace at 600 °C for 12 h [6]. The color of the calcined flocs changed from black to white indicating TiO_2 formation and the majority of volatile organic matter was evaporated. TiO_2 produced from sludge was washed with deionized water for three times, centrifuged at 3000 rpm for 5 min, and finally dried in an oven at 100 °C for 12 h [27]. The catalyst produced was, hereafter, called "as-prepared TiO_2".

2.7. XRD image and photocataltic activity of TiO_2

XRD images of as-prepared TiO_2 and P-25 were analyzed to identify the particle structure. The photocatalytic activity of as-prepared TiO_2 and P-25 was comparatively investigated using photodecomposition of K-2BP. Experiments were conducted in an open fixed-bed photoreactor [28], fitted with a 250 W high-pressure mercury lamp (λ_{max} = 365 nm). The constant irradiation intensity of the lamp at the surface of dye solution was 15 W/m^2, which was measured with digital illuminometer (TN-2340, Taiwan). Aqueous solution of K-2BP (20 mg/L) with 0.1 g TiO_2 was stirred for 30 min under darkness before irradiation. Then the solution suspension

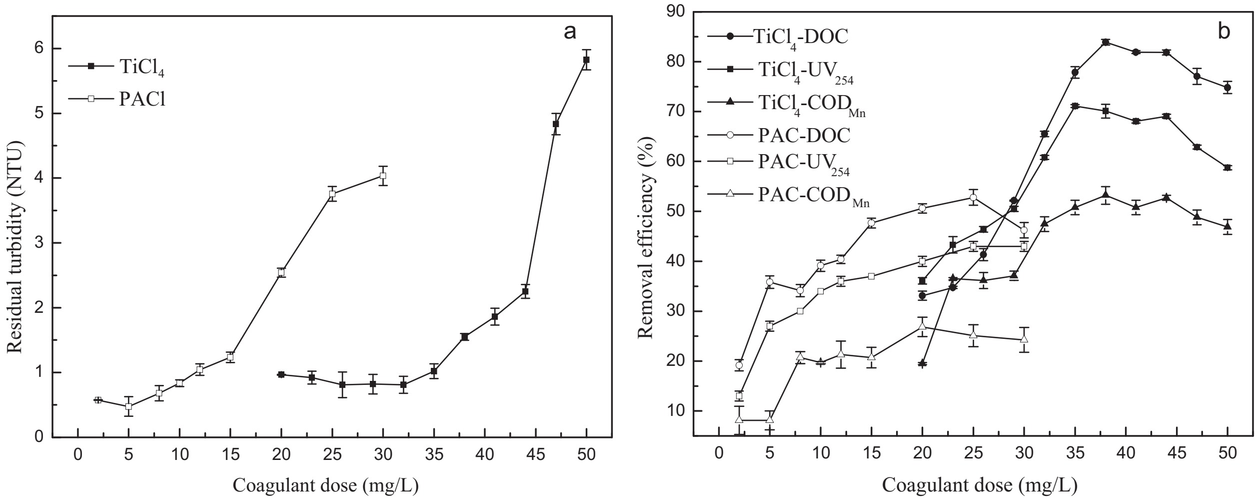

Fig. 1. Effect of coagulant dosage on residual turbidity (a) and UV_{254}, DOC, COD_{Mn} removal (b).

was illuminated with high-pressure mercury lamp and stirred by a peristaltic pump. The samples (5 ml) were extracted at regular intervals and subsequently filtered through a 0.45 μm fiber membrane. The filtrate was analyzed by recording the variation of the maximum absorption wavelength (550 nm). Photocatalytic oxidation rates with as-prepared TiO_2 and P-25 were comparatively evaluated by measuring the change in dye concentration as a function of irradiation time. The absorbance was converted to concentration through the standard curve method of K-2BP. Degradation efficiencies of K-2BP were calculated by

$$R = \frac{C}{C_0} \tag{3}$$

where C and C_0 are the concentration of K-2BP when the irradiation time was a elapsed time (t) and 0, respectively.

3. Results and discussion

3.1. Effect of coagulant dosage in removing organic matter

Fig. 1 shows the variation of residual turbidity, UV_{254}, COD_{Mn} and DOC removal efficiencies in terms of coagulant dosages (2–30 mg/L for PACl as Al and 20–50 mg/L for $TiCl_4$ as Ti). Fig. 1(a) shows that the coagulant dosage significantly affected the residual turbidity. For both PACl and $TiCl_4$, the residual turbidity of effluents decreased with the increasing coagulant dosages and consistently increased as the coagulant dosages further increased. The residual turbidity was higher than 1 NTU at the coagulant dosage of 12 mg/L as Al for PACl and 35 mg/L as Ti for $TiCl_4$.

Fig. 1(b) shows the removal efficiency of organic indicators using PACl and $TiCl_4$ in terms of UV_{254}, COD_{Mn} and DOC. The results showed that overall organic removal increased with the increasing in coagulant dosage. However, the UV_{254}, COD_{Mn} and DOC removal efficiencies presented the declining trend when the dosage of $TiCl_4$ coagulant was higher than 44 mg/L. Besides, the removals of UV_{254} and COD_{Mn} decreased as dosage of PACl was more than 25 mg/L.

The final pH values of the solutions for each experiment were also recorded. It should be noted that the effluent pH after $TiCl_4$ flocculation decreased to 5.51 at the optimal concentration, while the pH after PAC flocculation remained neutral. Similar finding was reported by Shon et al. [7], suggesting that the low effluent pH could be resolved by using coagulant aids such as $Ca(OH)_2$.

Based on the experimental results mentioned above, a combined optimal dosage for organic and turbidity removal was about 35 mg-Ti/L for $TiCl_4$ and 12 mg-Al/L for PACl, respectively. All the removals of organic matter with $TiCl_4$ were better than those with PACl. For example, UV_{254}, COD_{Mn} and DOC removal efficiencies by $TiCl_4$ were 71.1%, 50.8% and 77.9% at the optimal dosage, respectively, while UV_{254}, COD_{Mn} and DOC removal efficiencies of PACl were 36.0%, 21.3% and 40.3% at the optimal dosage, respectively. Gao and Yue [29] also found that coagulating species with higher cationic charge perform better than those with lower cationic charge. The optimal concentrations were chosen for further detailed investigation on the effect of solution pH and floc characteristics.

Zeta potential of colloids with various coagulant dosages is shown in Fig. 2. The zeta potential rapidly increased from negative to positive with the increasing coagulant dosage. The results were consistent with the classical view of particle coagulation [30]: (a) low dosages of coagulants are not effective, (b) higher coagulant dosages provide charge neutralization and flocculation is rapid enough to provide settleable flocs, (c) the increasing dosages reverse the charges on the particles and produce a stable suspension, and (d) further increase in dosages produces a substantial quantity of metal hydrolysis species that enmesh positively charged particles in settleable sweep flocs. The flocs formed with high dosages of coagulants consisted of positive charge (Fig. 2). This charge repulsion resulted in the restabilization of suspension and deterioration in water quality, followed by a sharp increase in residual turbidity (Fig. 1(a)). For PACl, high NOM removal efficiency was

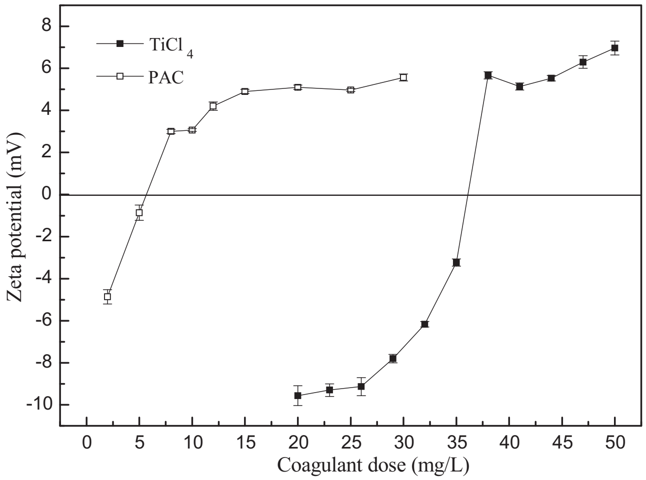

Fig. 2. Zeta potential at different coagulant dosages.

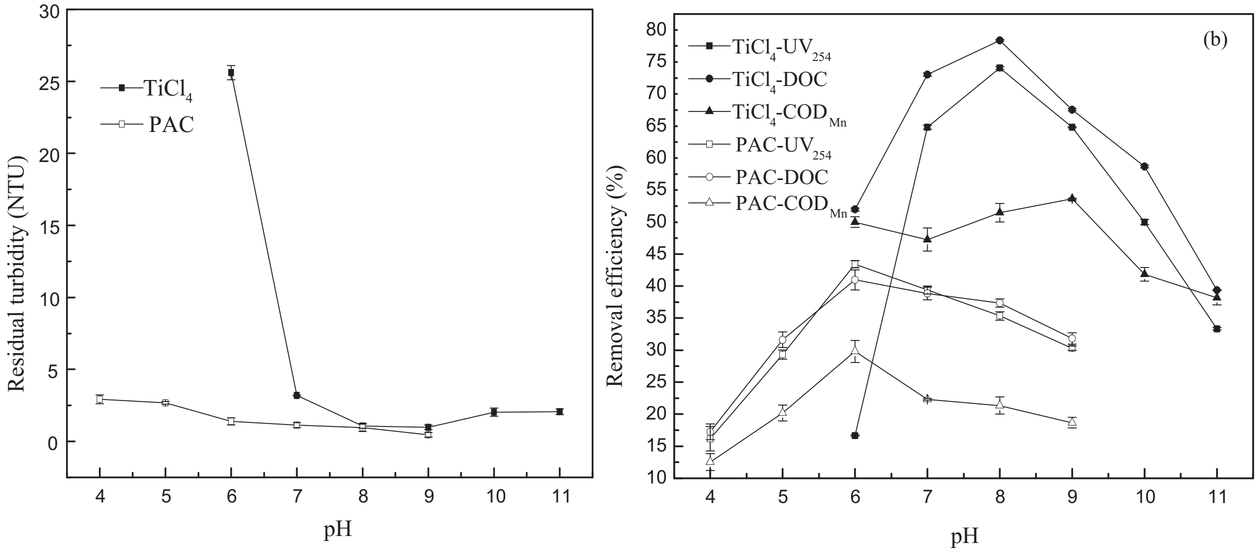

Fig. 3. Effect of initial pH with different coagulants at optimum dosage in terms of (a) residual turbidity and (b) UV_{254}, DOC, and COD_{Mn} removal.

achieved under optimum dosage when zeta potential was +4.2 mV, which indicated that adsorption of NOM and NOM-complexes on amorphous $Al(OH)_3$ (s) was also important mechanism involved in NOM removal besides charge neutralization. Similar results were found by Gregor et al. [31]. They reported that a combination of charge neutralization and entrapment/adsorption of NOM onto metal precipitates was the major floc formation route for PACl. For $TiCl_4$, the maximum NOM removal efficiencies were obtained when zeta potential was negative (−3.23 mV). This indicated that charge neutralization was not the only mechanism involved in turbidity and NOM removal, physical entrapment of colloids within coagulant precipitates and adsorption also played an important role.

3.2. *Effect of initial pH on coagulation performance*

Fig. 3 shows the effect of initial pH with different coagulants at optimal dosage in terms of residual turbidity, UV_{254}, DOC and COD_{Mn} removal. For PACl, residual turbidity of the effluent was on the decline trend in the test range of pH, and dropped below 1 NTU when the pH increased to 8 and above. Obviously, PACl had a significantly higher turbidity removal than $TiCl_4$ in acidic conditions. In acidic conditions, hydrolysis of $TiCl_4$ may be restrained, while PACl coagulant is seldom affected. However, at higher pH, $TiCl_4$ coagulant is gradually hydrolyzed, resulting in better turbidity removal. This also indicates that more hydroxide ions are required for $TiCl_4$ hydrolysis. The results also indicate that physical entrapment of colloids and adsorption play an important role in turbidity removal.

Fig. 3(b) shows the UV_{254}, COD_{Mn} and DOC removal efficiencies of $TiCl_4$ and PACl at different pH. The removal patterns of UV_{254}, COD_{Mn} and DOC using $TiCl_4$ and PACl at the tested range of pH were similar. For $TiCl_4$, maximum UV_{254}, COD_{Mn} and DOC removal were 74.1%, 51.5% and 78.4% at pH 8. Further increase of pH achieved poorer removal efficiencies. UV_{254}, COD_{Mn} and DOC removal decreased to about 33.3%, 38.2% and 39.4%, respectively, at pH 11. Comparatively, $TiCl_4$ was observed to have higher DOC removal than UV_{254} and COD_{Mn}. Fig. 4 shows that the optimal coagulation pH corresponded with the condition where the zeta potential of particles was very close to zero (+0.03 mV). This implies that the charge neutralization plays an important role during coagulation process. With regard to PACl, the results in Fig. 3(b) show that the removal of UV_{254}, COD_{Mn} and DOC increased with the initial increase of pH and achieved the highest removal at pH 6 and subsequently decreased with further increase of pH. The optimal removal of organic matter was achieved at pH 6. This is in a good agreement with previous study [32]. It is generally accepted that the complexation of natural NOM with soluble metal species into insoluble precipitates is the main removal route at pH < 6, while the removal of NOM is believed to be dominated by adsorption onto precipitated metal hydroxides at pH > 6 [31]. As to PACl, when the pH is lower than 6, the positive hydrolyzates such as $Al(OH)_2{}^+$, $Al_2(OH)_2{}^{4+}$ and $Al_3(OH)_4{}^{5+}$ could easily neutralize the negative charges and further destabilize the colloids. When the pH is between 6 and 8, $Al(OH)_3$ is formed in the solution [33] and the NOM is easily adsorbed and co-precipitated by the hydrolyzates. When the pH is higher than 8, it is difficult for the suspension to destabilize because of the transformation of the hydrolyzates into $Al(OH)_4{}^-$ [33]. In this study, the optimal NOM removal was achieved at pH 6 for PACl, which indicated that the removal mechanism involves both precipitation by forming insoluble complexes and adsorption of NOM onto hydroxide solids. As to $TiCl_4$, maximum NOM removal were reached at pH 8, suggesting that adsorption onto precipitated metal hydroxides play an important role.

3.3. *Dynamic variation of floc size during flocculation*

Flco growth during the 20-min period of flocculation at the optimal dosage and pH of $TiCl_4$ and PACl coagulant was investigated and the results are shown in Fig. 5. Compared to PACl, $TiCl_4$ coagulant exhibited faster floc growth rate and larger floc size. The floc through the $TiCl_4$ flocculation process showed a sharp increase in size during the first 4.5 min, achieving the largest floc size of 839.2 μm, followed by a slight decrease in floc size during the next 16.5 min. The sharp growth of floc size in the first 4.5 min is likely due to the aggregation of particles. The extended stirring resulted in the breakage of aggregated flocs. Due to the gradual reduction in floc size as the coagulation proceeded for $TiCl_4$, the floc size at the end of the slow stir phase was selected as the floc size in the steady stage. The order of floc size at the steady stage was $TiCl_4$ (560.4 μm) > PACl (452.8 μm). The results indicated that the optimal duration of slow mixing is about 4.5 min for $TiCl_4$ flocculation. Boller and Blaser [34] reported that larger particles generally settled down more quickly than smaller particles of similar density. So, as to $TiCl_4$, a short retention time coupled with larger floc size formation can lead to smaller and more compact flocculation and sedimentation units. In contrast, the flocs formed by PACl coagulant

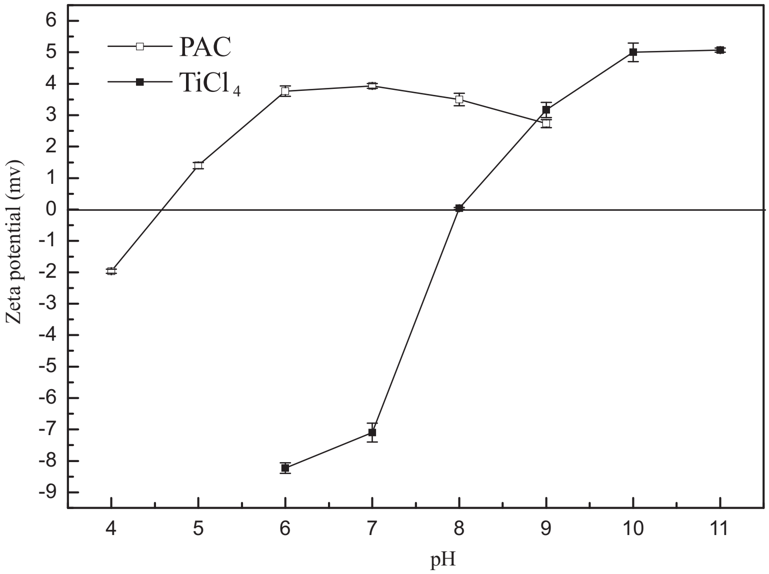

Fig. 4. Effect of initial pH on zeta potential.

were more stable and the breakage of flocs seldom appeared during the growth period. The floc growth rates during the coagulation process apparently varied in the order: $TiCl_4$ > PACl.

3.4. Floc breakage and recovery

The results of floc formation, breakage and re-formation are shown in Fig. 6. The floc size significantly increased after the slow stir phase, implying that the appropriate balance between floc growth and breakage was reached. When the shear rate at 200 rpm was introduced subsequently, the floc size showed apparent decrease immediately. Once the original slow stir speed was reintroduced, the floc began to regrow. However, the floc could not regrow to anywhere near their previous size for both $TiCl_4$ and PACl coagulant. The floc sizes after the re-growth period complied with the following order: $TiCl_4$ (325.4 μm) > PACl (258.0 μm). To investigate floc variations in detail, strength and recovery factors, calculated using Eqs. (1) and (2), were used to interpret the floc strength and recoverability (Table 2). It was found that the strength factors of $TiCl_4$ and PACl were 53.1and 37.8, respectively. In comparison to PACl, the flocs formed by $TiCl_4$ showed lower recoverability after breakage as reflected by lower recovery factor (Table 2). That can be explained as follows: It may be pointed out that, the breakage and re-growth of flocs were partly controlled by coagulation mechanisms of different coagulants. As mentioned earlier, the optimum pH of $TiCl_4$ coagulant was 8.0, and thus, adsorption of NOM onto hydroxide solid might be the dominant removal mechanism. It has been reported that the flocs formed by charge neutralization have total recoverability [22], while sweep and adsorption flocs have poor re-growth after breakage [19,35]. So, the flocs formed by $TiCl_4$ showed lower ability to resist shear and worse re-growth after breakage.

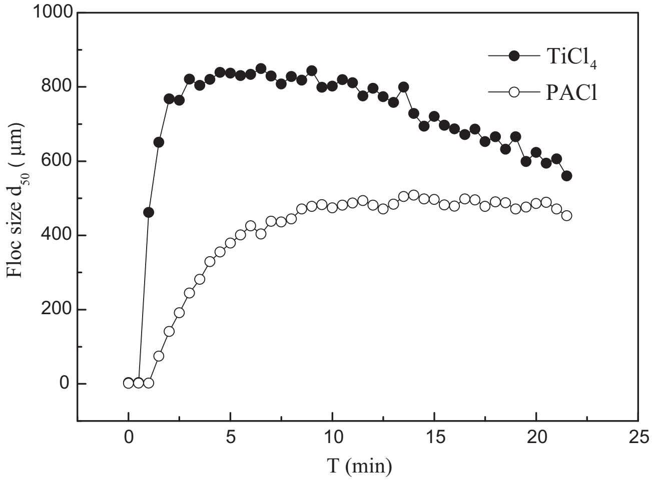

Fig. 5. Growth rate of aggregated flocs at optimum dosage and pH of PACl and $TiCl_4$ coagulant.

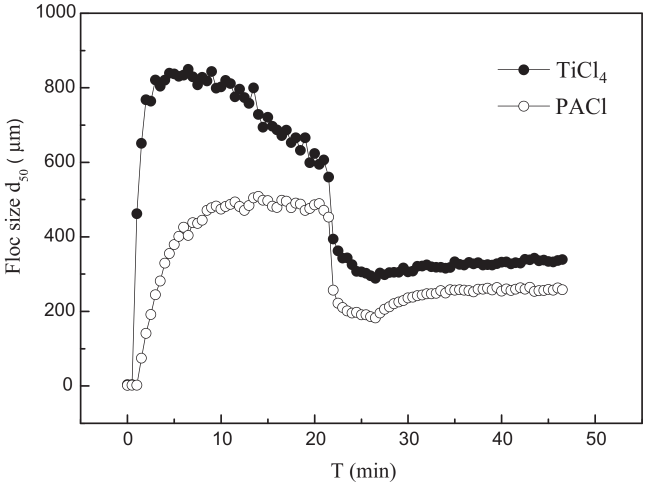

Fig. 6. Breakage and re-growth of different coagulant flocs (d_{50}) after exposure to shear for duration of 5 min.

Table 2
Strength and recovery factors of flocs (d_{50}) after 5 min of breakage followed by re-growth for 20 min.

Coagulants	Strength factor (S_f)	Recovery factor (R_f)
$TiCl_4$	53.1	10.6
PACl	37.8	25.1

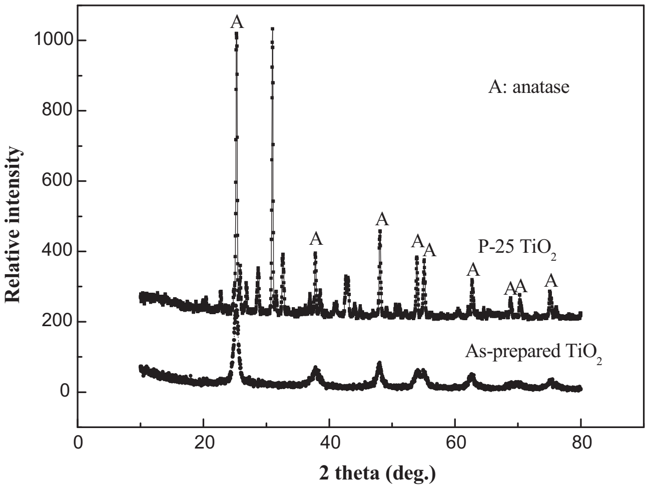

Fig. 7. XRD patterns of as-prepared TiO_2 and P-25.

3.5. Characterization of TiO_2 produced from Ti-salt flocculated sludge

During coagulation, sludge disposal is one of the most costly and environmentally problematic challenges of modern water treatment. In this study, a new process which could significantly lower the cost of waste disposal, protect the environment and public health and yield economically useful by-product was investigated. This work uses $TiCl_4$ coagulation to recover valuable byproduct (TiO_2) produced from the Ti-salt flocculated sludge. The sludge was calcined at 600 °C to produce functional photoreactive TiO_2 nanomaterials.

3.5.1. XRD pattern

XRD images were made to identify the crystal structure of as-prepared TiO_2 sample and P-25 (Fig. 7). As-prepared TiO_2 was found to have only anatase phase after calcination of 600 °C. Similar findings were obtained by Shon et al. [6] when they calcinated the sludge from synthetic wastewater flocculated by $TiCl_4$. On the other hand, the P-25 showed the mixture of anatase and rutile TiO_2.

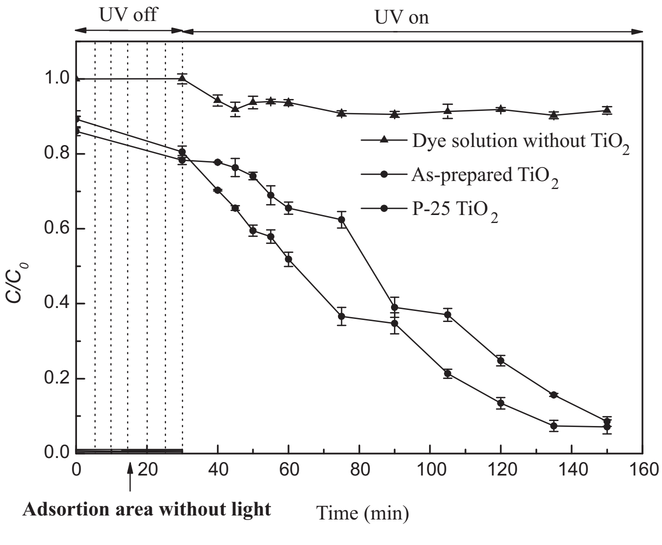

Fig. 8. Adsorption and photodegradation of K-2BP using different TiO_2 under UV irradiation (initial concentration of K-2BP was 20 mg/L).

3.5.2. Photocatalytic activity

Photocatalytic activity of TiO_2 produced from Ti-salt flocculated sludge with reservoir water was studied in terms of degradation of K-2BP dye (Fig. 8). To avoid any error due to adsorption, the suspension was initially stirred for 30 min in the dark to establish adsorption–desorption equilibrium between K-2BP and TiO_2 surface. Without any light source, initial adsorption on the surface of both as-prepared TiO_2 and P-25 was observed in the first 30 min, which decreased to 0.89 and 0.86 in terms of C/C_0, respectively. Removal of K-2BP under UV irradiation in the absence of TiO_2 was also evaluated and any degradation of K-2BP was not observed. The removal of K-2BP with P-25 was slightly higher than that with as-prepared TiO_2 under UV irradiation. However, after 2 h photocatalytic reaction, as-prepared TiO_2 indicated the same removal of K-2BP compared with that of P-25. The photocatalytic oxidation rates of K-2BP after 2 h photocatalytic reaction were 91.4% and 92.9% for as-prepared TiO_2 and P-25, respectively. It is generally accepted that the anatase phase is the most active TiO_2 compared with rutile and brookite [36,37].

4. Conclusions

The coagulation performance of $TiCl_4$ compared to PACl was investigated with Queshan reservoir water in terms of the basic water quality parameters, the coagulation mechanisms, and the growth, breakage and re-growth of aggregated flocs. $TiCl_4$ coagulation was very effective in removing turbidity and organic matter compared with the PACl. The average size of flocs formed by $TiCl_4$ was larger than those by PACl during growth period. However, flocs formed by PACl presented a better reformation capacity based on the higher recovery factors than flocs formed by $TiCl_4$. The flocs not only were formed by charge neutralization mechanism and but also might be held together by a chemical bonding rather than the physical bond. The sludge produced from test water using $TiCl_4$ coagulation was calcined at 600 °C to produce TiO_2 photocatalysts. As-prepared TiO_2 was found to be anatase phase and could remove the majority of the dye after 2 h photocatalytic reaction.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.11.014.

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