

An effective method of wastewater treatment using titanium salt and a coagulant aid of chitosan

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Keywords

chitosan; flocculation; pH, sludge; Ti salt; wastewater.

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doi:10.1111/wej.12414

Abstract

Titanium (Ti) salt has been used in wastewater flocculation and significantly decreases the pH of wastewater which is not industrially preferable. Thus, this study aims to use a natural polymer, chitosan, with Ti salt to observe a significant impact on pH of Ti salt flocculation and significantly reduce the produced sludge volume. The impact of chitosan addition on Ti salt flocculation pH, Ti salt optimum dose, Ti sludge, turbidity and organic removal was investigated. The results showed that using an optimum dose of 25 mg/L of Ti salt, Ti salt flocculation pH sharply decreased to 3.20 with turbidity and organic removal reaching 80 and 70%, respectively. The addition of chitosan to the Ti salt is found to be very effective due to the ability of chitosan foils to bridge the neutralised wastewater particles. The use of low doses of Ti salt with chitosan had an impact on flocculation pH and resulted in 40% of Ti sludge reduction.

Introduction

The growing demand for environmentally friendly coagulants has sparked an attention of applying new coagulants and/or natural polymers in water and wastewater treatment plants that can replace the conventional metal coagulants and synthetic polymers (Divakaran and Pillai, 2002; Rojas-Reyna *et al.*, 2010).

Ti salt, as an inorganic coagulant, is an attractive alternative to inorganic metal coagulants. Ti salt used in the flocculation of wastewater showed a high flocculation performance in terms of turbidity and organic removal. The sludge of Ti salt flocculation was processed to produce titania photocatalysts. However, despite the demerits of Ti salt coagulant, it showed the best flocculation performance at low pH of flocculated wastewater. The pH of Ti salt of titanium tetrachloride (TiCl_4) and titanium sulfate ($\text{Ti}(\text{SO}_4)_2$) flocculation with wastewater at the optimum dose was in the range of 3–4 (Shon *et al.*, 2007; 2009; Okour *et al.*, 2009), while the pH of flocculated wastewater using metal salt coagulant of ferric chloride (FeCl_3) and aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$) at optimum doses was between 5.50 and 6.50. The low pH of Ti salt could be due to the high acidic nature of Ti-hydroxides accompanied with forming of H^+ ions in the water solution when compared with Fe- and Al-hydroxides (Adin *et al.*, 1998).

In industrial applications, the use of wastewater with low pH causes a nuisance by increasing the corrosive tendency of the treated wastewater and the cost of post-treatment. The problem could be simply solved by post-treatment after Ti salt flocculation by the addition of sodium hydroxide (NaOH), or by using a coagulant aid simultaneously with Ti salt flocculation to neutralise the pH of the flocculated wastewater. A coagulant aid such as FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$ and calcium hydroxide ($\text{Ca}(\text{OH})_2$) could be simultaneously added during Ti salt flocculation to neutralise the low pH of the flocculated wastewater. The coagulant aids showed comparable organic removal to Ti salt flocculation. While, FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ coagulant aids increased the pH range by a small amount, the $\text{Ca}(\text{OH})_2$ coagulant aid significantly adjusted the pH due to the increase of OH^- ions from $\text{Ca}(\text{OH})_2$ at an optimum dose of 20 mg/L for TiCl_4 and 40 mg/L for $\text{Ca}(\text{OH})_2$. Although the addition of $\text{Ca}(\text{OH})_2$ helped in neutralising the pH of wastewater, the $\text{Ca}(\text{OH})_2$ dose added was relatively high as a flocculant aid and did not help in reducing the TiCl_4 dose (Shon *et al.*, 2009).

To resolve this problem, the authors recommend using an organic polymer as a coagulant aid instead of a metal salt with Ti salt flocculation. Chitosan as a natural polymer could be an appropriate coagulant aid candidate to be used with Ti salt flocculation due to its biodegradability, low cost and safety for human health (Veneroni *et al.*, 1996; Roussy

et al., 2005; Sanghi *et al.*, 2006). Most of the natural or synthetic polymers used in wastewater flocculation as coagulants or coagulant aids have a slight impact on the pH of flocculated wastewater, while using metal salt coagulants as flocculant aids could assist in the decrease of pH of wastewater as the metal salts are acidic in nature. Besides, the addition of a natural polymer before or after a metal salt coagulant helped in decreasing the amount of the metal salt coagulant (Pan *et al.*, 1999; Bratby, 2006).

Chitosan is extracted by means of de-acetylation from chitin by alkaline treatment (Gibbs *et al.*, 2003). Chitin, extracted from crustacean shells, is one of the most abundant natural polymers after cellulose. Chitosan is used as a coagulant or coagulant aid for a wide variety of applications, including river water (Divakaran and Pillai, 2002), dyes (Szygula *et al.*, 2009), drinking water (Abebe *et al.*, 2016) and industrial wastewater (Rao, 2015).

However, chitosan, when used as a primary coagulant in low turbid water or wastewater, failed to flocculate the suspended particles and colloids and exhibited low turbidity removal. Although chitosan flocculation significantly improved in terms of turbidity removal and floc properties when modified by starch (You *et al.*, 2009) or used in high turbid water or wastewater (Divakaran and Pillai, 2002; Rao, 2015), however, it had a narrow flocculation range of optimum doses; a small increase in the dose can restabilise the flocculated water or wastewater system. Therefore, some researchers pointed out that chitosan cannot be recommended as a primary coagulant from an industrial point of view (Szygula *et al.*, 2009; Rojas-Reyna *et al.*, 2010).

On the other hand, chitosan showed the best flocculation performance as a coagulant aid rather than as a primary coagulant. Chitosan was used as a coagulant aid coupled with metal coagulants (inorganic–organic dual coagulants) in wastewater treatment by (Pan *et al.*, 1999; Hesami *et al.*, 2014). The addition of chitosan mainly improves the floc characteristics in terms of floc size, density, settleability and shear strength as flocculation destabilisation was already established by the metal coagulant.

Thus, the main objectives of this research are to adjust the low pH performance of TiCl_4 flocculation where the highest turbidity and organic matter removal are obtained using a chitosan polymer as a coagulant aid; then, to investigate the impact of chitosan addition on pH variation of TiCl_4 flocculation, amount of TiCl_4 optimum dose, wastewater characteristics in terms of turbidity and organic removal, settled flocs and produced Ti sludge volume; and finally to suggest an appropriate mechanism for the Ti salt and chitosan flocculation system.

Materials and methods

Preparation of TiCl_4 solution

Ninety-eight per cent concentrated TiCl_4 was supplied by Sigma–Aldrich, Australia. A syringe attached with a needle was used to draw 20 mL of TiCl_4 from the bottle. Then, a few drops of TiCl_4 were slowly added to cubes of frozen distilled water under continuous stirring. Upon contact with humid air, TiCl_4 formed yellowish opaque clouds of titanium dioxide (TiO_2) and hydrogen chloride (HCl) was evolved. As a result of mixing with distilled water, the yellowish opaque clouds turned to a transparent solution. The volume ratio of TiCl_4 to H_2O (v/v) was 1 : 4 to obtain 20% of TiCl_4 solution, which then was diluted to 10% of TiCl_4 for experimental use.

Preparation of chitosan solution

Chitosan, coarse ground flakes and powder with a degree of de-acetylation above 75, was supplied by Sigma–Aldrich, Australia. Six 100 mL of HCl solutions of pH 0.1, 0.5, 1, 2, 3 and 4 were prepared. Then, 100 mg of chitosan powder was accurately weighed and mixed slowly with each prepared HCl solution for 1 hour. The concentration of the prepared solutions was 1.0 g/L. The dissolution of chitosan was very slow for solutions of pH below 1 and above 2, whereas the dissolution was faster for solutions of pH 1 and 2. The solutions were prepared fresh before each set of experiments for consistency, but it was observed that the prepared solutions could be stored in closed bottles in a refrigerator for at least three months without affecting the flocculation performance of wastewater. This may be attributed to the very slow rate of association between chitosan chains.

Coagulation and flocculation process

Characteristics of synthetic wastewater (SWW)

The compounds and the characteristics of SWW used in this study which represented biologically treated sewage effluent in a wastewater treatment plant are shown in Table 1. The pH of SWW was adjusted by adding a diluted acid or base to reach a final pH of 6.8–7.2 which resembled a neutral pH range. The initial turbidity of SWW was around 4.30 to 4.5 NTU which resembled low turbid wastewater. Dissolved organic carbon (DOC) and ultraviolet (UV) absorbance at 254 nm of SWW were ranged from 9 to 10 mg/L and 2.90 to 3.10 cm^{-1} , respectively.

Table 1 Constituents of SWW used in this study, all compounds were dissolved in tap water (Seo *et al.*, 1997)

Compounds	Concentration (mg/L)	Molecular weight (Daltons)	Fraction by organic matter
Beef extract	1.8	300, 100, 70	0.065
Peptone	2.7	34 300, 100, 80	0.138
Humic acid	4.2	1500, 300	0.082
Tannic acid	4.2	6300	0.237
Sodium lignin sulfonate	2.4	12 100	0.067
Sodium lauryl sulphate	0.94	34 300	0.042
Arabic gum powder	4.7	900, 300	0.213
Arabic acid (polysaccharide)	5.0	38 900	0.156
(NH ₄) ₂ SO ₄	7.1	0	0
K ₂ HPO ₄	7.0	0	0
NH ₄ HCO ₃	19.8	0	0
MgSO ₄ •7H ₂ O	0.71	0	0

Jar tester procedure

Firstly, TiCl₄ and chitosan were used separately as primary coagulants. A conventional jar tester (Phipps and Bird, USA) with six 1-L beakers was filled with SWW. Rapid mixing at 100 rpm was carried out for 1 min for TiCl₄ with doses of 1–35 mg/L and 2 min for chitosan with doses of 0.10–12 mg/L. Later on, the mixing speed was reduced to 10 rpm for 25 min for TiCl₄ and 45 min for chitosan. Then, the mixers were turned off to allow for the settling of aggregated flocs for 45 min.

Secondly, TiCl₄ was used as a primary coagulant with chitosan as a coagulant aid. TiCl₄ coagulant was added first in the jar tester and mixed for 1 min, followed by the direct addition of chitosan for another 1 min at the same rapid mixing. The same procedure of rapid mixing was repeated by adding chitosan first then followed by TiCl₄ coagulant and the addition of both TiCl₄ and chitosan simultaneously. Then, the mixer speed was reduced to 10 rpm for 45 min, followed by 45 min of settling time. Samples for measurements were drawn from 5 cm below SWW surface without disturbing the sediment.

Ti-chitosan sludge reduction

To determine the amount of the sludge produced from TiCl₄ flocculation alone and Ti-chitosan flocculation, several flocculation experiments were performed using SWW with a dose of 10–30 mg/L for TiCl₄ flocculation alone and doses of 1–20 mg/L for TiCl₄ and 1–10 mg/L for chitosan using dual TiCl₄-chitosan flocculation. Then, the settled sludge of TiCl₄ and Ti-chitosan flocculation was transferred to an Imhoff cone. The sludge produced was determined by direct reading of the volume of the sludge in mL per 500 mL of SWW solution. Then, sludges were dried at 100°C to determine the amount of the dry sludge produced during each flocculation.

Analysis

A pH meter (90-FL, Australia) and a turbidimeter (HACH 2100P, USA) were used to measure the pH and turbidity of SWW supernatant. Twenty-five millilitres of each coagulant was taken for turbidity measurement after the 45-min settling period. DOC was measured using the UV-persulfate TOC analyser (Multi NC2000, Analytikjena, Germany). All samples were filtered through a 0.45-µm membrane prior to DOC measurement. UV absorbance at 254 nm was determined using a UV-vis spectrophotometer (N 595, Shimadzu, Kyoto, Japan) in a 1-cm quartz cell. Measurements of the pH, turbidity, DOC and UV-254 absorbance for each coagulant were taken three times and the mean value was recorded.

Results and discussion

Low pH performance of TiCl₄ flocculation

TiCl₄ was used as a primary coagulant in the flocculation of SWW. SWW, with an average pH of 7.0, was flocculated with different selected doses of TiCl₄ ranging from 1 to 35 mg/L. The effect of the applied TiCl₄ doses on pH variation, ratio of residual turbidity, DOC and UV-254 absorbance of flocculated SWW is shown in Fig. 1.

TiCl₄ doses greatly affected the pH of the flocculated SWW. The applied doses of 1–35 mg/L reduced the flocculation pH to 6.65 and 2.85, respectively. The highest turbidity, DOC and UV-25 absorbance removal of 80, 70 and 90%, respectively, were obtained at low flocculated SWW with a pH of 3.2–3.4 with optimum doses of 25–30 mg/L.

The low pH of SWW could be explained by how TiCl₄ was hydrolysed. The hydrolysis of TiCl₄ in SWW solution produced Ti-hydroxides and H⁺ ions. As H⁺ ions increased due to increasing TiCl₄ dose, a significant decrease in the pH of flocculated SWW occurred. The H⁺ ions increased

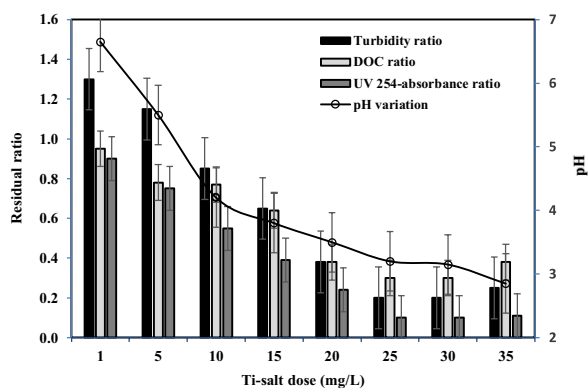


Fig. 1. Effect of TiCl_4 doses on the ratio of turbidity, organic matter and pH of flocculated SWW.

the positive charge of Ti-hydrolysed species adsorbed on the negatively charged suspended particles and colloids of SWW forming more Ti-precipitates. The maximum turbidity and organic matter performance occurred at optimum doses of 25–30 mg/L. When the doses were above 30 mg/L, a further decrease in turbidity and organic removal was observed indicating system re-stabilisation due to charge reversal. Thus, charge neutralisation mechanism played a dominant role in the flocculation of negative particle surfaces of SWW and positively charged titanium hydroxide species.

Chitosan as a primary coagulant

Chitosan solubility for better flocculation performance

Chitosan in an acidic solution behaves as a cationic polyelectrolyte due to the protonation of the amine group ($-\text{NH}_2$). The protonation of amine groups, depending on the solution pH, initiates chitosan dissociation and increases chitosan solubility. High solubility of chitosan species leads to increase in the degree of protonation of amine groups which improves the efficiency of the flocculation process by binding with negatively charged particles, colloids and organic (Rinaudo *et al.*, 1999).

As-prepared chitosan solutions, with a different pH range, were used in this study to find the highest chitosan solubility in an acidic solution. Chitosan solutions with different pH of 0.1–4 were prepared. It was observed that at pH below 1 and above 2, chitosan solubility was very poor and most of the chitosan particles remained suspended in the solution. At pH 1, the solubility improved with some chitosan particles remaining suspended as a thin gel in the solution. However, at pH 2, the solubility significantly improved and traces of chitosan species

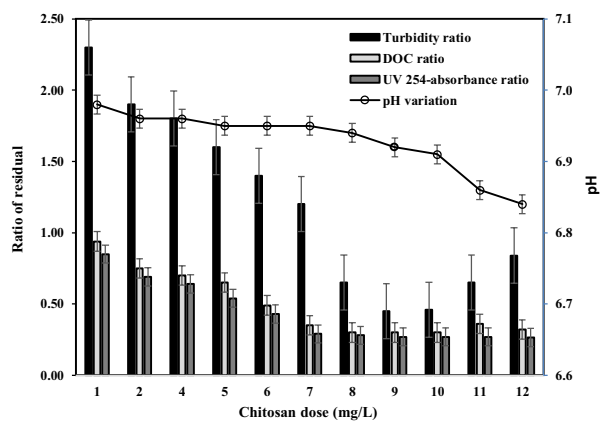


Fig. 2. Effect of chitosan doses on residual turbidity, organic matter and pH of flocculated SWW. Vertical error bars are shown.

remained suspended even though the stirring was continued for a long time. Therefore, prepared chitosan solutions of pH 2 were chosen for coagulation and flocculation with SWW.

Low flocculation performance of chitosan

Chitosan was used as a primary coagulant in the flocculation of SWW. The flocculation performance of chitosan in terms of ratio of residual turbidity, organic matter and pH variation of flocculated SWW using different chitosan doses of 1–12 mg/L is shown in Fig. 2.

The applied chitosan doses of 1–12 mg/L showed an insignificant drop of the flocculated SWW pH. The pH drop ranged from 6.98 to 6.84, respectively. This could be to the limited acidity impact of the addition of chitosan solution of pH 2 on the ionic strength of different compounds and salts in SWW (Szygula *et al.*, 2009) and due to the incapability of chitosan chains to form insoluble hydrolysis species to decrease the pH of flocculated SWW.

Chitosan flocculation showed a low turbidity removal occurred at a narrow range of optimum doses. At chitosan dose of 1 mg/L, the ratio of residual turbidity of SWW sharply increased up to 2.30, then it gradually decreased with increase in the chitosan doses and reached a minimum residual turbidity ratio of 0.45 (turbidity removal of 55%) at a narrow range of optimum doses of 9–10 mg/L. Then, any increase in the chitosan dose above the optimum range resulted in a sharp reduction in turbidity removal indicating destabilisation of the suspended particles and colloids due to charge reversal. Due to low turbidity removal, the settled flocs formed with chitosan flocculation were small, light and scattered throughout the supernatant solution. The flocs were hard to settle down by gravity for a long time.

On the other hand, the organic removal of chitosan flocculation was much higher than the turbidity removal with a wider range of optimum doses of 8–11 mg/L compared with turbidity optimum doses of 9–10 mg/L. The ratio of residual DOC and UV-254 absorbance was found to be 0.30 and 0.35 (70 and 75% of organic removal, respectively). When chitosan dose was higher than 11 mg/L, a sharp reduction in the organic removal occurred indicating the destabilisation of negatively charged organic matter due to charge reversal by an excessive adsorption of overdose of positively charged chitosan species. Thus, chitosan was found to be effective in precipitating more organic matter compared to suspended particles and colloids. However, low turbidity removal with poor floc properties and narrow range of optimum doses would prevent the use of chitosan as a primary coagulant.

The properties of chitosan in terms of molecular weight and charge density accompanied with the SWW characteristics could explain the contradictory performance of chitosan flocculation. In this study, we used chitosan with a low to moderate molecular weight and a high positive charge density to flocculate negatively charged particles of SWW. Some researchers indicated that a polymer with high positively charged density was most effective in organic removal, whereas a polymer with high molecular weight was the most effective in turbidity removal. Therefore, the ability of positively charged chitosan species to neutralise and then bind to the negatively charged organic compounds of humic substances in SWW was more favourable than to neutralise the charge of the suspended colloidal particles. Thus, charge neutralisation mechanism played a dominant role for chitosan flocculation (Bratby, 2006; Rojas-Reyna *et al.*, 2010).

Enhancing TiCl_4 flocculation performance by chitosan addition

Turbidity removal of SWW

Selected doses of TiCl_4 and chitosan in the range of 1–20 and 0.10–6.0 mg/L, respectively, were applied to determine the optimum doses for maximum turbidity removal (Fig. 3). The best turbidity removal results were obtained when chitosan was directly added after TiCl_4 while no flocs were formed or very low turbidity removal was obtained when chitosan was added before or simultaneously with TiCl_4 . This is related to the Ti–chitosan mechanism which is illustrated in the next section. The optimum doses for the complete destabilisation for turbidity removal of TiCl_4 flocculation were 25–30 mg/L while 9–10 mg/L of chitosan dose was needed. Figure 3 shows that the use of dual coagulation of TiCl_4 and chitosan has a different impact on the SWW components that considerably decreased

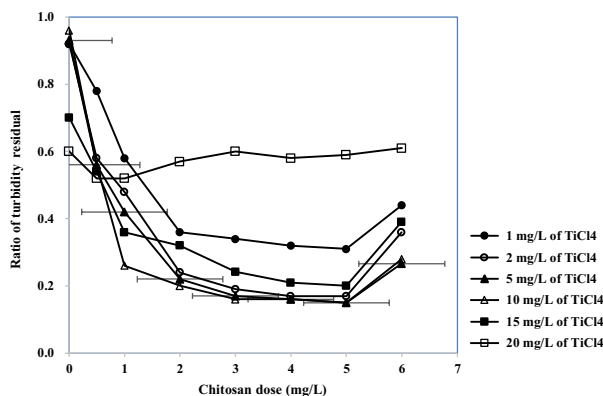


Fig. 3. Effect of the addition of chitosan doses on the residual turbidity of TiCl_4 flocculation. Horizontal error bars are shown.

the turbidity, that is, optimum doses for a complete destabilisation for both TiCl_4 and chitosan.

At low chitosan doses of 0.10–1.0 mg/L, regardless of the TiCl_4 doses applied, Ti–chitosan flocculation showed low turbidity removal by the formation of small flocs which were too difficult to settle down. However, when the chitosan dose was increased from 2 to 5 mg/L, the density of the aggregate flocs increased and better turbidity removal was obtained with TiCl_4 doses ranging from 2 to 10 mg/L. With 5 mg/L of chitosan dose, turbidity removal of Ti–chitosan flocculation once more decreased dramatically regardless of the TiCl_4 dose applied. At TiCl_4 doses ≥ 15 mg/L, Ti–chitosan flocculation showed again low turbidity removal rate, regardless of the chitosan dose added. Therefore, Ti–chitosan flocculation was found to be more efficient when TiCl_4 and chitosan doses were kept from 2 to 10 mg/L and 2 to 5 mg/L, respectively.

pH variation of SWW

Ti–chitosan flocculation system was applied to neutralise the pH of TiCl_4 flocculation of SWW and to improve the flocculation performance of TiCl_4 . The effect of applied doses of Ti–chitosan flocculation on the pH variation of flocculated SWW is demonstrated in Fig. 4.

Ti–chitosan flocculation showed a little impact on the pH of SWW for doses of TiCl_4 from 1 to 20 mg/L, regardless of chitosan doses. The pH of SWW dropped from 6.80 at 1 mg/L of TiCl_4 to 5.80 at 20 mg/L of TiCl_4 , while at TiCl_4 doses ≥ 25 mg/L, the pH of SWW significantly dropped below 2.6. Only TiCl_4 doses showed an effect on pH, while chitosan doses had an insignificant effect due to the limited acidity impact of chitosan solution of pH 2 on the ionic strength of different compounds in SWW.

The pH of SWW at turbidity optimum doses of 2–10 mg/L for TiCl_4 and 2–5 mg/L for chitosan was 6.4 to 6.8. The pH drop in SWW was less than 0.60 from the initial pH

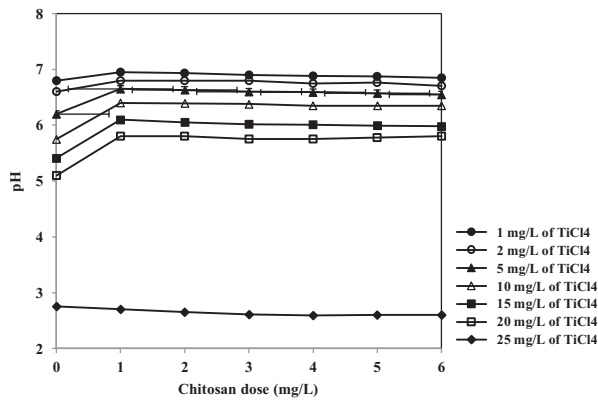


Fig. 4. Effect of the addition of chitosan doses on the pH variation of TiCl_4 flocculation. Horizontal error bars are shown.

of 7.0. The low pH drop in the SWW was related to the use of low doses of TiCl_4 . Low doses could reduce the surface charge of negatively suspended matter and colloids of some SWW particles on adsorption while other particles would remain stable. Therefore, the optimum conditions for a complete destabilisation were not attained yet because of insufficient Ti-hydroxide species and H^+ ions available. However, at TiCl_4 doses ≥ 25 mg/L, a complete destabilisation occurred due to the availability of charged adsorptive Ti-hydroxide species and H^+ ions. The adsorption of Ti-hydroxide species onto negatively charged suspended particles and colloids of SWW formed Ti-precipitates. So, the negative surface charge of SWW components was considerably reduced which led to a further reduction in the pH.

Organic removal of SWW

The effect of the applied chitosan doses on residual organic matter of TiCl_4 flocculation in terms of DOC and UV-254 absorbance is shown in Figs. 5 and 6. Ti-chitosan flocculation removed the majority of the DOC and UV-254 absorbance of 85 and 90%, respectively, at doses ranging from 2 to 15 mg/L for TiCl_4 and 2 to 6 mg/L for chitosan. While DOC and UV-254 absorbance removals decreased at doses below 2 mg/L and above 15 mg/L for TiCl_4 , regardless of chitosan doses, the flocculation range of TiCl_4 and chitosan widened at optimum doses of 2–15 mg/L for TiCl_4 and 2–6 mg/L for chitosan compared to turbidity removal. Ti-chitosan flocculation showed high removal of UV-254 absorbance compared to DOC. This could be explained due to the high tendency of positively charged chitosan species to bind and remove the aromatic compounds compared with the humic substances. The hydrophobic interactions of the amine groups with the aromatic compounds are mainly more favourable (Szygula *et al.*,

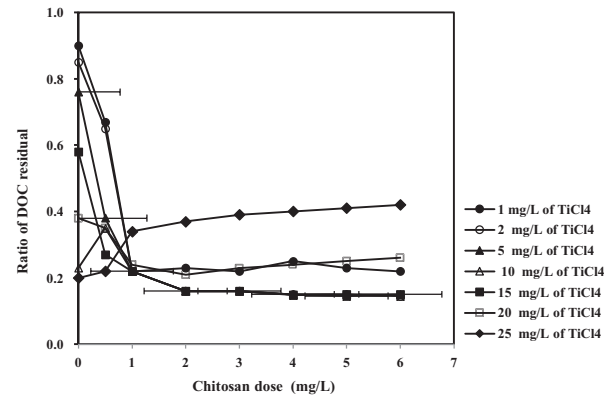


Fig. 5. Effect of the addition of chitosan doses on the residual DOC of TiCl_4 flocculation. Horizontal error bars are shown.

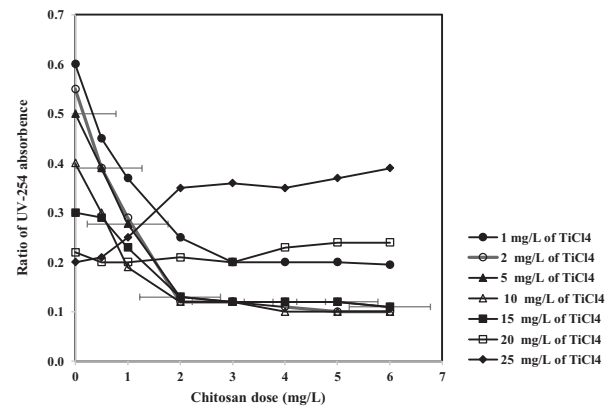


Fig. 6. Effect of the addition of chitosan doses on the UV-254 absorbance of TiCl_4 flocculation. Horizontal error bars are shown.

2009). According to Figs. 3 to 4, turbidity test is the master test for selecting the optimum dose as the turbidity test had a narrow dose range for Ti-chitosan flocculation. Doses of 2–10 mg/L of Ti salt and 2–5 of chitosan are considered to yield maximum removal of turbidity and organic matter to have good flocculation. Selecting any dose within the range showed the same Ti-chitosan flocculation performance. The average doses of Tichitosan flocculation (5 mg/L of Ti salt and 4 mg/L of chitosan) rather than the minimum doses (2 mg/L of Ti salt and 2 mg/L of chitosan) were chosen as they have a safe flocculation range below and above the optimum doses due to experimental or man-made error. Any dose below minimum doses means system destabilisation and bad flocculation.

Mechanism of Ti-chitosan flocculation

Adsorption and charge neutralisation mechanisms were found to be the predominant mechanisms for TiCl_4 and

chitosan flocculation. However, using $TiCl_4$ as a primary coagulant and chitosan as a coagulant aid would have a different impact on the negatively charged compositions of SWW to determine the proper coagulation mechanism.

On the one hand, Ti–chitosan flocculation system worked well when the addition of chitosan was directly after the $TiCl_4$. According to the surface charge interaction, the use of low doses of 2–10 mg/L of $TiCl_4$ coagulant would reduce the surface charge of the negatively suspended matter and colloids of SWW on adsorption, but still the optimum conditions were not achieved due to insufficient availability of Ti-hydroxide species to neutralise and then completely destabilise the SWW particles. When cationic chitosan was added, part of the protonated amine groups of chitosan completely neutralised the remaining anionic charges of SWW. Simultaneously, the other part of the chitosan chain segments were bridged to the neutralised SWW particles by hydrophobic interactions through hydrogen bridges to link the particles together and settled down indicating a bridging mechanism (Rinaudo *et al.*, 1999; Szygula *et al.*, 2009).

The removal rate reached its maximum when the protonated amine groups had completely neutralised the anionic charges of SWW and had effectively bridged between the SWW particles. When the amount of chitosan added to the SWW solution was further increased above the optimum doses, the excess protonated amine groups restabilised the SWW particles and decreased the efficiency of the flocculation. Likewise, when $TiCl_4$ doses were above the optimum doses of 2–10 mg/L, the Ti–chitosan flocculation system showed a low removal rate, regardless of the chitosan doses added. The reason behind this could be explained due to the predominance of positively charged $TiCl_4$ hydroxide species. Adding chitosan with positively charged amino groups tended to inhibit the adsorption process and consequently reduced the removal rate. Thus, Ti–chitosan flocculation system was involved in a dual mechanism of coagulation by charge neutralisation and flocculation by bridging.

On the other hand, Ti–chitosan flocculation system had a very low flocculation performance when the addition of chitosan was simultaneous with or before $TiCl_4$. When the addition of chitosan was before $TiCl_4$, the surface charge of some negatively suspended matter and colloids of SWW particles would be reduced on adsorption and/or bridging by positively charged chitosan species while other SWW particles would remain stable. When positively charged $TiCl_4$ hydroxide species were added after chitosan, part of $TiCl_4$ hydroxide species would neutralise the remaining anionic charge of SWW. However, the remaining part of $TiCl_4$ hydroxide species does not have the ability to

bridge the neutralised SWW particles and tended to restabilise SWW particles to decrease the efficiency of flocculation. Therefore, we believed that the inability of $TiCl_4$ hydroxide species to form hydrogen bridges through hydrophobic interactions to link the SWW and/or the neutralised SWW species together could be the main reason behind the low flocculation performance of using chitosan simultaneously with or before $TiCl_4$ in the rapid mixing process.

Floc characteristics of Ti–chitosan flocculation

The characteristics of the flocs in terms of floc formation and settling speed are very important parameters that affect directly the efficiency of the wastewater treatment process.

In $TiCl_4$ flocculation, the formation of the flocs was faster compared with Ti–chitosan flocculation which resulted in higher settling speed due to predominant adsorption and charge neutralisation mechanisms.

However, during the flocculation process of Ti–chitosan flocculation, it was noticed that the floc formation was required a double slow mixing time. As the time for slow mixing increased, the aggregated flocs of Ti–chitosan flocculation became bigger, tighter and finally formed a round shape at the bottom of the jar tester beaker. These flocs showed more resistance to break-up compared to the more fractal nature of $TiCl_4$ and chitosan flocs separately. The slow floc formation could be related to the double mechanism as Ti–chitosan flocculation was involved in coagulation by charge neutralisation and flocculation by bridging. It seemed that the bridging mechanism required extra time for chitosan chain coils to combine with SWW species to form dense particle aggregations with high strength that could easily settle down.

Sludge reduction by Ti–chitosan flocculation

Sludge handling and treatment are considered important parameters that affect directly the overall cost of the wastewater treatment process. Applying $TiCl_4$ flocculation for wastewater treatment solved the problem of the produced sludge by producing titania nanoparticles through an incineration process (Okour *et al.*, 2009; Shon *et al.*, 2009).

The sludge produced from Ti salt flocculation of SWW consisted of different amounts of organic matter, total dissolved and suspended solids and the compounds formed from $TiCl_4$. However, using chitosan as a coagulant aid after $TiCl_4$ flocculation is expected to further reduce the volume of the sludge formed as the optimum dose for $TiCl_4$ was remarkably reduced from 25 to 5 mg/L

and a small amount of chitosan (4 mg/L) was used as a coagulant aid. Applying optimum doses for TiCl_4 flocculation alone and dual flocculation for Ti–chitosan, we found that the amount of the wet sludge formed for TiCl_4 and Ti–chitosan flocculation was 7.90 and 4.80 mL per 500 mL of flocculated SWW solution. The dried sludge was just about 40 and 24 mg, respectively. This indicated that sludge reduction by Ti–chitosan flocculation was very effective and a small amount was produced. Thus, the flocculation process using Ti–chitosan flocculation had a better advantage over TiCl_4 flocculation by producing approximately 60% of TiCl_4 flocculation sludge which means sludge reduction of 40% of TiCl_4 flocculation. The sludge reduction helped in decreasing the cost of sludge handling and treatment. This sludge could be reused in the same way as TiCl_4 flocculation sludge to produce titania nanoparticles by incineration (Shon *et al.*, 2007).

Conclusions

Our findings confirmed that TiCl_4 doses resulted in a negative impact on flocculated SWW pH. TiCl_4 flocculation exhibited maximum turbidity and DOC removal of 80 and 70%, respectively, at low pH of flocculated SWW of 3.2 with a dose of 25 mg/L. Chitosan addition after TiCl_4 had a slight impact on the pH of flocculated SWW and also greatly improved TiCl_4 flocculation. The pH of Ti–chitosan flocculation remained within the neutral range below 25 mg/L of TiCl_4 dose, regardless of the chitosan doses applied. Turbidity and DOC removal reached over 85% at the optimum doses of 5 mg/L for TiCl_4 and 4 mg/L for chitosan. Ti–chitosan flocculation flocs were more resistant to break-up compared to the more fractal nature of TiCl_4 and chitosan flocs separately. Besides, the sludge produced from Ti–chitosan flocculation was about 60% of TiCl_4 flocculation sludge. Thus, Ti–chitosan flocculation not only adjusted the pH of flocculated SWW but also benefits in reducing the cost of sludge handling and treatment for titania nanoparticles' production. The work introduced in this paper is one step towards conducting environmental assessment of Sudair industrial site in KSA including the treatment of its wastewater.

Acknowledgement

The authors are thankful to Engineering and Applied Science Research Centre, MU for funding and supporting this project number (37/56)-2016.

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