

1 **Coagulation performance and floc characteristics of polytitanium**
2 **tetrachloride and titanium tetrachloride compared with ferric chloride for**
3 **coal mining wastewater treatment**
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19 **Abstract:**

20
21 The production and discharge of large volumes of wastewater during coal mining activities are one of
22 the major environmental issues in Australia. Therefore, it is crucial to develop and optimise effective
23 treatment processes for the safe disposal of coal mining wastewater (CMWW). In this study, we
24 investigated the performance of a recently developed polytitanium tetrachloride (PTC) coagulant and
25 compared with the performance of titanium tetrachloride (TiCl₄) and the commonly used ferric
26 chloride (FeCl₃) coagulant for the treatment of CMWW from one of the coal mining sites in Australia.
27 The use of Ti-based coagulants is particularly attractive for the CMWW treatment due to the
28 advantage of being able to recycle the sludge to produce functional titanium dioxide (TiO₂)
29 photocatalyst; unlike the flocs formed using conventional coagulants, which need to be disposed in
30 landfill sites. The results showed that both PTC and TiCl₄ performed better than FeCl₃ in terms of
31 turbidity, UV₂₅₄ and inorganic compounds (e.g. aluminium, copper or zinc) removal, however, PTC
32 performed poorly in terms of dissolved organic carbon removal (i.e. less than 10%). While charge
33 neutralisation and bridging adsorption were the main coagulation mechanisms identified for TiCl₄
34 treatment, sweep coagulation and bridging adsorption seemed to play a more important role for both
35 PTC and FeCl₃ treatments. The flocs formed by PTC coagulation achieved the largest floc size of
36 around 900 µm with the highest floc growth rate. Both Ti-based coagulants (i.e., PTC and TiCl₄)

37 showed higher strength factor than FeCl_3 , while TiCl_4 coagulant yielded the flocs with the highest
38 recovery factor. This study indicates that Ti-based coagulants are effective and promising coagulants
39 for the treatment of CMWW.

40 **Keywords:** Coagulation; Coal mining wastewater; Polytitanium tetrachloride; Titanium tetrachloride.

41 **1 Introduction**

42 The coal mining industry is one of the major industries in Australia, which contributes largely to its
43 economy reaching a revenue of AUS\$ 39.8 billion in 2013 [1]. However, the activities associated with
44 coal mining have significant environmental concerns, especially on the production and discharge of
45 impaired mining water directly into the surrounding surface waters [2]. Coal mining wastewaters
46 (CMWW) are generally saline, and contain very high concentration of suspended solids and variable
47 concentrations of iron, aluminium and dissolved organic matter [3]. The most commonly employed
48 treatment of CMWW is through a coagulation/flocculation process [4] although membrane processes
49 such as microfiltration have also been adopted. Passive treatments such as the use of lagoons and
50 wetlands are also quite common in Australia, however, ponding is restricted in the state of
51 Queensland [5, 6].

52 Coagulation/flocculation is the most commonly employed treatment process for the removal of
53 colloidal particles and organic matter in wastewater [7]. Both iron (Fe) and aluminium (Al) based
54 salts have been widely used as coagulants since they have demonstrated high performance for the
55 removal of a wide range of pollutants found in wastewaters [8]. As an example, in the Centennial
56 Coal Mining site located in Fassifern, New South Wales, Australia, the currently-used method of
57 CMWW treatment is through a coagulation/flocculation process using ferric chloride (FeCl_3) along
58 with a cationic polymer. This site generates an average of 12-15 ML/d of CMWW. Though, there are
59 successes in the use of both Fe and Al-salts as coagulants, however, its major drawback is the
60 production of large quantities of coagulated sludge after the CMWW treatment process. Proper
61 disposal of the sludge generated from coagulation/flocculation treatment presents a very costly and
62 environmentally-problematic challenge of the CMWW treatment [9, 10]. Thus, the development of
63 new coagulants as well as advanced processes for sludge disposal and treatment has been sought out
64 in the past years. Recently, Shon et al. [11] developed a novel titanium (Ti) based coagulant, namely
65 titanium tetrachloride (TiCl_4), to circumvent the sludge disposal issue. The TiCl_4 coagulant was found

66 to have comparable performance as with those of the conventional Al and Fe-salts [12, 13], but the
67 main novelty of the use of TiCl_4 coagulant lies on the possibility of recycling the generated sludge via
68 a simple calcination method to produce titanium dioxide (TiO_2) as a valuable by-product [11, 14, 15].
69 In fact, TiO_2 is a widely used metal oxide finding applications in paints, solar cells, cosmetics,
70 photocatalysts or electronic papers [16, 17].

71 The use of TiCl_4 has opened doors for a more cost-effective coagulation to sludge disposal approach.
72 However, it was observed that the optimum coagulation efficiency of TiCl_4 occur at low pH values
73 ranging from 3.0 to 5.0, mainly due to the release of large amounts of H^+ during the titanium
74 hydrolysis [11, 13]. Thus, some approaches were undertaken to address this issue so as to enable the
75 Ti-based coagulant to be used at a wider pH range. A recent study resolved this issue by developing
76 polytitanium salts which minimises the release of H^+ through prehydrolysis of titanium salt [18]. In
77 their study [18], polytitanium tetrachloride (PTC) was synthesised by a slow alkaline titration method
78 at different basicity values (i.e., at different OH/Ti molar ratios in PTC solution) and used as a
79 coagulant. Their results showed higher or comparable treatment performance of PTC compared to
80 TiCl_4 in terms of removal efficiency for turbidity and organic matter. Additionally, improved floc
81 characteristics such as flocs size, growth rate and structure were also observed with the use of PTC.
82 Earlier studies on inorganic polymeric coagulants such as polyaluminum sulphate or polyferric
83 chloride [19-21] have suggested better performance compared to inorganic salts in terms of the
84 removal of organic matter and various pollutants, and also for pH dependence.

85 Floc characteristics such as floc size, strength factor and recoverability are important factors for
86 evaluating the performance of the coagulation process. For example, larger flocs settle faster than
87 smaller flocs of similar density [22], which leads to not only higher removal efficiency but also faster
88 floc settling time, thereby only requiring smaller sedimentation tanks. The ability of the floc to not
89 only resist breakage but also its ability to recover after breakage will have a significant impact on
90 water treatment processes and its capital and operation costs [23].

91 In the present study, we investigated and compared the coagulation performance of PTC and TiCl_4 in
92 terms of their removal efficiency on turbidity, UV_{254} , dissolved organic carbon (DOC), and inorganic
93 compounds from CMWW. Floc characteristics were studied by measuring the zeta potential, floc
94 sizes, as well as the floc recoverability. The results for the Ti-based coagulants were then compared
95 to those of the Fe-salt coagulant (i.e. FeCl_3), which is currently used to treat the CMWW from the
96 Centennial Coal Mining site located in Fassifern (NSW, Australia). A detailed flocs characterisation
97 was also undertaken to better understand the growth, breakage and re-growth of flocs formed by all
98 three coagulants.

99 **2 Materials and Methods**

100 2.1 Coagulants and coal mining wastewater

101 A stock solution of TiCl_4 (>> 99% purity, Sigma Aldrich, Australia) was prepared by slowly adding
102 (i.e. drop by drop) 46.4 mL of concentrated TiCl_4 to frozen cubes of deionised water under continuous
103 stirring to obtain the final concentration of 20% w/w. The detailed method for the preparation of PTC
104 solution can be found in Zhao et al. [18]. In brief, 63.3 mL of sodium hydroxide (NaOH) was added to
105 200 mL of the prepared TiCl_4 solution to obtain a final OH/Ti ratio of 1.5 using a slow alkaline
106 titration method. The stock solution of FeCl_3 was prepared by simply dissolving 2 g of powder in 200
107 mL of deionised water to obtain the final concentration of 10 g/L.

108 CMWW was collected from the Centennial Coal Mining site at Newstan Colliery located near
109 Fassifern in NSW, Australia. The detailed characteristics of the present CMWW are shown in Table
110 1.

111 **Table 1**

112 2.2 Jar-test

113 Jar-test experiments were carried out using a programmable jar-tester (PB-900TM, Phipps and Bird,
114 USA). Several preliminary tests were first carried out to determine the optimum coagulant dose. After

115 optimisation, the predetermined (i.e. optimised) amount of coagulant was then added to 500 mL of
116 CMWW. Rapid mixing at 200 rpm was first applied for 1.5 minutes followed by 20 minutes of slow
117 mixing at 40 rpm, and finally 20 minutes of quiescent settling. Water samples were then collected
118 from 2 cm below the surface for further analysis. Turbidity and floc zeta potential were directly
119 measured using 2100P turbidity meter (Hach, USA) and Zetasizer (Malvern Instruments, UK),
120 respectively. Water samples were pre-filtered using 0.45 μm syringe filter before measuring the
121 dissolved organic matter. UV_{254} absorbance was measured using UV-754 UV/VIS spectrophotometer
122 (Shimadzu, Japan) while the detailed organic matter characterisation was performed using liquid
123 chromatography-organic carbon detection or LC-OCD (DOC-Labor, Germany) as per the procedure
124 described elsewhere [24]. Inorganic elements such as Al, Fe, Cu, Mn and Zn were analysed using
125 inductively coupled plasma - mass spectrometry or ICP-MS at the Environmental Analysis
126 Laboratory of the Southern Cross University (Australia).

127 2.3 Floc characterisation

128 The dynamic floc size was measured online when the coagulation/flocculation was in progress, by
129 connecting the flocculating water to a laser diffraction instrument (Malvern 2000, Malvern, UK). The
130 schematic of the on-line floc measurement system used in this study is presented in Figure 1.

131 **Figure 1**

132 The strength and recoverability factors of the flocs formed during the coagulation process were
133 determined by subjecting the flocs to initial growth, breakage and regrowth cycle. The initial floc
134 growth phase was carried out at a slow mixing speed of 40 rpm for 15 minutes, then the aggregated
135 flocs were subjected to a high mechanical shear force by rapid mixing at 200 rpm for one minute.
136 After this breakage phase, slow mixing at 40 rpm was then proceeded for 20 minutes to allow
137 regrowth of flocs. The floc strength factor (SF) and recovery factor (RF) were then calculated as
138 follows [7, 25]:

139 $SF = \frac{d_2}{d_1} \times 100$ (1)

140 $RF = \frac{d_3 - d_2}{d_1 - d_2} \times 100$ (2)

141 where d_1 , d_2 , and d_3 are the average aggregate size of the floc at the plateau before applying the shear
142 force, the average aggregate floc size after aggregate breakage, and the average aggregate floc size
143 after regrowth to a new plateau, respectively.

144 High SF values indicate strong floc strength, i.e., the floc does not easily break at increased shear
145 force. Thus, the higher the SF values, the better ability of the flocs to resist shear forces and breakage.
146 Similarly, high RF value indicates the ability of the flocs to regrow after exposure to high shear force.
147 The floc growth rate was calculated by determining the slope of the rapid growth region [26] as
148 follows:

149 $Growth\ rate = \frac{\Delta size}{\Delta time}$ (3)

150 **3 Results and discussion**

151 3.1 Coagulation performance of FeCl₃, TiCl₄ and PTC for the treatment of coal mining wastewater

152 3.1.1 Floc zeta potential and removal efficiencies for turbidity, UV₂₅₄ and DOC

153 The coagulation performance of the three coagulants was assessed in terms of turbidity, UV₂₅₄ and
154 DOC removal efficiency and the results are presented in Table 2. Prior to the test proper, we initially
155 conducted preliminary tests (data not shown) in order to determine the optimum coagulant dose (i.e.,
156 coagulant dose at which 95% turbidity removal is achieved). In this study, the optimal dosages for
157 FeCl₃, TiCl₄ and PTC coagulants were determined to be 0.13 mmol Fe/L, 0.40 mmol Ti/L and 0.15
158 mmol Ti/L, respectively.

159 **Table 2**

160 The results in Table 2 show that both Ti-based coagulants (i.e., TiCl_4 and PTC) obtained better
161 performance than FeCl_3 coagulant in reducing the turbidity and UV_{254} of CMWW; however, PTC
162 showed the lowest DOC removal efficiency among the three coagulants.

163 The difference in DOC removal efficiency between TiCl_4 and PTC may be explained by the
164 difference in hydrolysed Ti species present in the solution. In fact, the dominant hydrolyzates of TiCl_4
165 were most likely $\text{Ti}(\text{OH})^{3+}$ or $\text{Ti}(\text{OH})_2^{2+}$ which then formed complex with negatively charged NOM
166 via charge neutralization [27]. For PTC however, the low DOC removal efficiency might be explained
167 by the formation of $\text{Ti}_n(\text{OH})_m^{4n-m}$ complexes with high m value, such as $\text{Ti}(\text{OH})_3^+$, $\text{Ti}(\text{OH})_4^0$, or even
168 negative ions ($\text{Ti}(\text{OH})_5^-$ and $\text{Ti}(\text{OH})_6^{2-}$) which led to unfavorable complexation with negatively
169 charged NOM macromolecules resulting in a low DOC removal efficiency [18].

170 It should be noted though that PTC achieved higher or comparable performance than TiCl_4 in terms of
171 turbidity and UV_{254} removal by employing a much lower dose, which suggests that PTC could be
172 potentially a more cost-effective coagulant than TiCl_4 . Besides, the effluent pH after TiCl_4
173 flocculation decreased to 3.43 (Table 2) while the pH with both FeCl_3 and PTC flocculation remained
174 neutral (i.e. in the pH range 6-8). The difference in effluent pH between TiCl_4 and PTC shows that the
175 low pH after flocculation associated with TiCl_4 can be managed to a certain degree by developing
176 PTC which minimised the release of hydrogen ions through the prehydrolysis of the Ti-species [18].

177 To assess the destabilisation potential of the coagulants, we investigated the changes in floc zeta
178 potential, which is also often employed as a tool to evaluate the coagulation mechanism involved, and
179 is usually explained in terms of charge neutralisation and sweep flocculation [28]. Under the optimum
180 coagulant dose conditions, the floc zeta potential after flocculation for FeCl_3 , TiCl_4 and PTC was -5.3
181 mV, -3.7 mV and -3.2 mV (Table 2), respectively. This suggests that charge neutralisation could play
182 an important role during the flocculation process of all three coagulants as the initial zeta potential of
183 the CMWW was -30.9 mV. In a previous study by Cheng [20], it was mentioned that the possible

184 mechanisms involved in the coagulation of humic acid (HA) by FeCl_3 was charge neutralisation and
185 bridging adsorption. Additionally, it was found that the fraction removed by bridging adsorption was
186 higher than that removed by charge neutralisation in the pH range of 7.5-9. In the present study, the
187 initial pH of the CMWW was about 7.3, which is close to this pH range and may therefore suggest
188 that, bridging adsorption together with charge neutralisation could be the main coagulation
189 mechanisms using FeCl_3 coagulant [29]. With the use of TiCl_4 , several studies [30-32] have
190 demonstrated that the main coagulation mechanisms was charge neutralisation. While for the PTC
191 coagulant, a recent study by Zhao et al. [18] indicated that charge neutralisation may be the
192 predominant coagulation mechanism as the zeta potential was close to zero after flocculation.

193 In the present study, complete charge neutralisation was not achieved with all three coagulants and
194 this is evident from the presence of negative surface charges after flocculation. These results therefore
195 indicate that charge neutralisation is not the only mechanism involved during the
196 coagulation/flocculation of the coagulants tested, but other mechanisms such as sweep coagulation
197 and/or bridging adsorption might also have played a role facilitating the floc aggregation.

198 3.1.2 Organic matter removal based on LC-OCD characterisation

199 In order to study further details about the nature of the organic species before and after
200 coagulation/flocculation, LC-OCD characterisation was used and the results are presented both in
201 Figure 2 and Table 3. LC-OCD characterisation results indicate that the CMWW is mainly composed
202 of humic substances and low molecular weight (LMW) neutrals with a small amount of biopolymers
203 and building blocks (i.e. less than 1%). Table 3 shows the percentage of organic fractions as a
204 function of the total DOC and it can be noted that, CMWW is predominantly composed of hydrophilic
205 compounds accounting to about 87% of the total DOC.

206 **Figure 2**

207 As shown in Figure 2, the reduction in the humic substances for the three coagulants was found to be
208 not quite significant after the coagulation process. A new peak appeared at about 70 minutes for PTC,

209 which can be attributed to the break-down of the high molecular weight (HMW) humics to LMW
210 humics and building blocks. Table 3 shows that for all three coagulants, the DOC removal was quite
211 low (i.e., less than 25%), however, considering the composition of the CMWW, this result is not
212 surprising. In fact, it has been already demonstrated before that flocculation preferentially removes the
213 hydrophobic natural organic matter (NOM) fraction [33]. Besides, it has also been demonstrated that
214 coagulation is mostly effective for HMW organics like biopolymers and the CMWW used in this
215 study had very low HMW compounds concentration. TiCl_4 was used in a study by Jeong et al. [34] to
216 remove the organic matter in seawater as a pretreatment to reduce membrane fouling. They found that
217 TiCl_4 not only completely removed the biopolymers but also showed higher performance (compared
218 to FeCl_3) for the removal of humics and LMW neutrals. In the present study, however, FeCl_3 showed
219 higher performance for the removal of both humic substances and LMW neutrals than the Ti-based
220 coagulants.

221 **Table 3**

222 3.1.3 Removal of multivalent metals based on ICP-MS analysis

223 The CMWW used in this study contains variable concentration of multivalent metals from 0.247
224 mg/L for aluminium to 0.024 mg/L for zinc. ICP-MS analyses were performed before and after
225 flocculation to determine the removal efficiency of these multivalent metals for all three coagulants
226 and their results are presented in Figure 3.

227 **Figure 3**

228 Figure 3 shows that the Ti-based coagulants achieved better multivalent metal removal efficiency than
229 FeCl_3 . For instance, the iron removal efficiency was only 59.1% with FeCl_3 , however, PTC and TiCl_4
230 achieved a removal efficiency of more than 90%. It has to be noted that the lower iron removal
231 efficiency observed for FeCl_3 can be biased due to the potential residual iron from the FeCl_3 coagulant
232 itself.

233 One possible mechanism for the removal of multivalent metals by titanium coagulants could be due to
234 the formation of metal-NOM complex [35]. The monomer Ti species (i.e. $\text{Ti}(\text{OH})_3^{3+}$, $\text{Ti}(\text{OH})_2^{2+}$ or
235 $\text{Ti}(\text{OH})_3^+$ might be the dominant hydrolyzates [27]) could firstly adsorb (i.e., physically through
236 charge neutralisation or chemically through chemical bridging adsorption) NOM containing
237 negatively-charged functional groups to form $\text{NOM-Ti}(\text{OH})_x^{(4-x)}$ complexes, which will then confer
238 the flocs with a negative surface charge. These negatively-charged flocs could then attract and adsorb
239 the positively-charged multivalent metal ions present in the solution to form other complexes such as
240 metal-NOM- $\text{Ti}(\text{OH})_x^{(4-x)}$. Another possible removal mechanism could be the precipitation of insoluble
241 metal compounds (i.e., Al, Cu, Fe, Mn and Zn) followed by bridging adsorption onto suspended
242 colloids since all three coagulants demonstrated both high turbidity and multivalent removal
243 efficiencies. It is expected that the formed colloids will become enmeshed in the settling sweep floc
244 and be removed from the suspension [36].

245 3.2 Dynamic variation of floc size during flocculation

246 Floc formation, breakage and regrowth during the coagulation-flocculation process using FeCl_3 , TiCl_4
247 and PTC under optimum coagulant dose condition were monitored online using Mastersizer 2000 and
248 the results are displayed in Figure 4.

249 **Figure 4**

250 The introduction of slow mixing at 40 rpm resulted to a rapid increase in floc sizes reaching a plateau
251 (i.e., a balance between floc growth rate and floc breakage rate) for all coagulants tested (Figure 4).
252 When the high speed mixing was introduced at 200 rpm, the floc size immediately decreased up to
253 60% of the original floc sizes, primarily due to the higher applied shear forces to the flocs resulting to
254 their breakage. Upon the reintroduction of slow mixing, the flocs sizes began to regrow, however,
255 none of the flocs could recover back to their initial floc size before breakage, for all three coagulants.

256 Table 4 shows the floc size at the different stages (i.e. before breakage, after breakage, and after
257 regrowth), the floc growth rate and the calculated SF and RF based on equations 1 and 2. It can be
258 seen that all three tested coagulants showed different floc sizes and growth rates. Ti-based coagulants
259 showed a faster floc growth rate with larger floc sizes indicating that both TiCl_4 and PTC have the
260 ability to form larger aggregates within a shorter retention time than FeCl_3 . This is a significant
261 advantage as a shorter retention time coupled with larger floc size will ultimately lead to smaller and
262 more compact flocculation and sedimentation tanks as larger particles generally settled down more
263 rapidly than smaller particles of comparable density [22]. Both the floc growth rate and floc size
264 during the coagulation process varied in the following order: $\text{PTC} > \text{TiCl}_4 > \text{FeCl}_3$ (Table 4). This
265 shows the obvious benefits of using Ti-based coagulants over Fe-based coagulant since the resultant
266 flocs present larger size regardless of floc growth, breakage and regrowth process. Finer flocs are
267 generally more prone to suspend in the supernatant, thus larger flocs will achieve better removal
268 efficiency by settling. This may also explain the lower turbidity removal efficiency of FeCl_3 compared
269 to Ti-based coagulants.

270 **Table 4**

271 3.3 Floc breakage and recovery

272 As summarised in Table 4, Ti-based coagulants showed higher SF than FeCl_3 , while TiCl_4 obtained
273 the highest RF from all the three coagulants (i.e. 18.3% against 11.1% and 10.9% for PTC and FeCl_3 ,
274 respectively). Previous studies reported that flocs formed by sweep flocculation have generally
275 weaker RF after breakage than those formed by charge neutralisation [37]. This may indicate that
276 sweep flocculation could be the main mechanism for both FeCl_3 and PTC while charge neutralisation
277 might have played a more important role for TiCl_4 . However, the poor recoverability of all the three
278 tested coagulants (i.e. $\text{RF} < 20\%$) suggests that besides charge neutralisation and sweep flocculation,
279 bridging adsorption of NOM could also be another major removal mechanism involved in the
280 coagulation-flocculation process. In fact, Gregor et al. [38] explained that the main removal route of

281 HA via coagulation varies depending on the pH conditions as follows: precipitation by forming
282 insoluble complexes at $\text{pH} < 6$, and bridging adsorption of HA onto hydroxide solid at $\text{pH} > 6$.

283 Figure 5 shows the particle size distribution (PSD) of the three tested coagulants before breakage,
284 after breakage and after regrowth. Results indicated that for all the three coagulants, the floc size after
285 breakage was about half the initial floc sizes. After regrowth, there was a slight shift in the peak
286 towards the larger sizes which indicated the floc reformation. The results in Table 4 show that the
287 increase in floc size after breakage was about 10-15% for all coagulants. Analysis of PSD also clearly
288 indicates the poor recoverability of all three coagulants as the difference in floc size before breakage
289 and after regrowth is significant.

290 **Figure 5**

291 **Conclusions**

292 In the present study, the performance of a recently developed PTC coagulant was assessed and
293 compared with TiCl_4 and conventional FeCl_3 for the treatment of coal mining wastewater.
294 Coagulation performances were evaluated in terms of four different water quality parameters (i.e.
295 turbidity, UV_{254} , DOC and inorganic compounds) and flocs characteristics (i.e. floc size, strength and
296 recoverability). The following conclusions are drawn from this study:

- 297 1. Both Ti-based coagulants (PTC and TiCl_4) showed better efficiency in removing turbidity,
298 UV_{254} and inorganic compounds from CMWW compared to FeCl_3 . However, the much
299 smaller coagulant dose of PTC used under optimum conditions, which still resulted to similar
300 or even higher removal efficiency than TiCl_4 makes PTC a more cost-effective coagulant.
- 301 2. During the initial floc growth period, PTC showed the fastest floc growth rate (i.e. 285.3
302 $\mu\text{m}/\text{min}$) combined with the largest floc size of 899.5 μm , indicating significant advantages
303 offered by PTC in terms of compact (smaller size) mixing and sedimentation units.

- 304 3. Both PTC and $TiCl_4$ showed higher strength factors than that of $FeCl_3$, however, between the
305 two, PTC had lower recovery factor than $TiCl_4$, suggesting that PTC floc may require more
306 careful handling during the separation process.
- 307 4. Charge neutralisation and bridging adsorption were the main mechanisms involved in $TiCl_4$
308 coagulation while sweep coagulation and bridging adsorption were found to be the main
309 mechanisms for both PTC and $FeCl_3$ coagulations.

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