

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 (TiCl<sub>4</sub>) and the commonly used ferric  
26 chloride (FeCl<sub>3</sub>) 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 (TiO<sub>2</sub>)  
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 TiCl<sub>4</sub> performed better than FeCl<sub>3</sub> in terms of  
31 turbidity, UV<sub>254</sub> 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 TiCl<sub>4</sub>  
34 treatment, sweep coagulation and bridging adsorption seemed to play a more important role for both  
35 PTC and FeCl<sub>3</sub> 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 TiCl<sub>4</sub>)

37 showed higher strength factor than  $\text{FeCl}_3$ , while  $\text{TiCl}_4$  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 ( $\text{FeCl}_3$ ) 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 ( $\text{TiCl}_4$ ), to circumvent the sludge disposal issue. The  $\text{TiCl}_4$  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  $\text{TiCl}_4$  coagulant lies on the possibility of recycling the generated sludge via  
68 a simple calcination method to produce titanium dioxide ( $\text{TiO}_2$ ) as a valuable by-product [11, 14, 15].  
69 In fact,  $\text{TiO}_2$  is a widely used metal oxide finding applications in paints, solar cells, cosmetics,  
70 photocatalysts or electronic papers [16, 17].

71 The use of  $\text{TiCl}_4$  has opened doors for a more cost-effective coagulation to sludge disposal approach.  
72 However, it was observed that the optimum coagulation efficiency of  $\text{TiCl}_4$  occur at low pH values  
73 ranging from 3.0 to 5.0, mainly due to the release of large amounts of  $\text{H}^+$  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  $\text{H}^+$  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  $\text{TiCl}_4$  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  $\text{TiCl}_4$  in  
92 terms of their removal efficiency on turbidity,  $\text{UV}_{254}$ , 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.  $\text{FeCl}_3$ ), 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  $\text{TiCl}_4$  (>> 99% purity, Sigma Aldrich, Australia) was prepared by slowly adding  
102 (i.e. drop by drop) 46.4 mL of concentrated  $\text{TiCl}_4$  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  $\text{TiCl}_4$  solution to obtain a final OH/Ti ratio of 1.5 using a slow alkaline  
106 titration method. The stock solution of  $\text{FeCl}_3$  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  $\mu\text{m}$  syringe filter before measuring the  
121 dissolved organic matter.  $\text{UV}_{254}$  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 FeCl<sub>3</sub>, TiCl<sub>4</sub> and PTC for the treatment of coal mining wastewater

##### 152 3.1.1 Floc zeta potential and removal efficiencies for turbidity, UV<sub>254</sub> and DOC

153 The coagulation performance of the three coagulants was assessed in terms of turbidity, UV<sub>254</sub> 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 FeCl<sub>3</sub>, TiCl<sub>4</sub> 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.,  $\text{TiCl}_4$  and PTC) obtained better  
161 performance than  $\text{FeCl}_3$  coagulant in reducing the turbidity and  $\text{UV}_{254}$  of CMWW; however, PTC  
162 showed the lowest DOC removal efficiency among the three coagulants.

163 The difference in DOC removal efficiency between  $\text{TiCl}_4$  and PTC may be explained by the  
164 difference in hydrolysed Ti species present in the solution. In fact, the dominant hydrolyzates of  $\text{TiCl}_4$   
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  $\text{TiCl}_4$  in terms of  
171 turbidity and  $\text{UV}_{254}$  removal by employing a much lower dose, which suggests that PTC could be  
172 potentially a more cost-effective coagulant than  $\text{TiCl}_4$ . Besides, the effluent pH after  $\text{TiCl}_4$   
173 flocculation decreased to 3.43 (Table 2) while the pH with both  $\text{FeCl}_3$  and PTC flocculation remained  
174 neutral (i.e. in the pH range 6-8). The difference in effluent pH between  $\text{TiCl}_4$  and PTC shows that the  
175 low pH after flocculation associated with  $\text{TiCl}_4$  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  $\text{FeCl}_3$ ,  $\text{TiCl}_4$  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  $\text{FeCl}_3$  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  $\text{FeCl}_3$  coagulant [29]. With the use of  $\text{TiCl}_4$ , 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.  $\text{TiCl}_4$  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  $\text{TiCl}_4$  not only completely removed the biopolymers but also showed higher performance (compared  
218 to  $\text{FeCl}_3$ ) for the removal of humics and LMW neutrals. In the present study, however,  $\text{FeCl}_3$  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  $\text{FeCl}_3$ . For instance, the iron removal efficiency was only 59.1% with  $\text{FeCl}_3$ , however, PTC and  $\text{TiCl}_4$   
230 achieved a removal efficiency of more than 90%. It has to be noted that the lower iron removal  
231 efficiency observed for  $\text{FeCl}_3$  can be biased due to the potential residual iron from the  $\text{FeCl}_3$  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.  $\text{Ti}(\text{OH})_3^+$ ,  $\text{Ti}(\text{OH})_2^{2+}$  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  $\text{FeCl}_3$ ,  $\text{TiCl}_4$   
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  $\text{TiCl}_4$  and PTC have the  
260 ability to form larger aggregates within a shorter retention time than  $\text{FeCl}_3$ . 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  $\text{FeCl}_3$  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  $\text{FeCl}_3$ , while  $\text{TiCl}_4$  obtained  
273 the highest RF from all the three coagulants (i.e. 18.3% against 11.1% and 10.9% for PTC and  $\text{FeCl}_3$ ,  
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  $\text{FeCl}_3$  and PTC while charge neutralisation  
277 might have played a more important role for  $\text{TiCl}_4$ . 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  $\text{TiCl}_4$  and conventional  $\text{FeCl}_3$  for the treatment of coal mining wastewater.  
294 Coagulation performances were evaluated in terms of four different water quality parameters (i.e.  
295 turbidity,  $\text{UV}_{254}$ , 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  $\text{TiCl}_4$ ) showed better efficiency in removing turbidity,  
298  $\text{UV}_{254}$  and inorganic compounds from CMWW compared to  $\text{FeCl}_3$ . 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  $\text{TiCl}_4$  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  $\mu\text{m}$ , 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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