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1 # Efficient electrochemical oxidation of thallium (I) in

2 # groundwater using boron-doped diamond anode

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11 **Abstract**

12 Thallium (Tl) is a highly toxic element whose occurrence is widespread in soil

13 and groundwater. The present study investigates the oxidation of Tl(I) with

14 boron-doped diamond (BDD) anode in an electrochemical system, compared with

15 PbO_2 and carbon felt materials. Under initial conditions of Tl(I) of 10 mg L^{-1}, pH of

16 2.0, and current density of 5 mA cm^{-2}, $99.2 \pm 0.9\%$ of Tl(I) is oxidized to Tl(III)

17 within 15 min. This process is suppressed by the increase of initial Tl(I) concentration

18 and initial pH, respectively, while it is enhanced with the increase of current density.

19 Compared with direct electrochemical effect, indirect electrochemical oxidation with

20 the generated oxidants mainly contribute to the excellent performance and ·OH plays

21 a significant role. Subsequent coagulation/precipitation realizes the nearly complete

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22 removal of total Tl in the exhaust electrolyte and the quality of the effluent can meet

23 EPA drinking water standards. Analysis of the generated precipitate further indicates

24 that Tl(III) is the main oxidation state of Tl. This study offers a potentially attractive

25 method for remediation of Tl-polluted groundwater.

26 **Keywords:** Thallium; Electrochemical oxidation; Boron-doped diamond anode;

27 Groundwater

28 **1. Introduction**

29 Thallium (Tl), a bio-accumulative element, is commonly responsible for

30 environmental contamination [1,2]. Compared with other heavy metals such as Pb, Ni

31 and Zn, Tl is more toxic to mammals [3]. Though Tl and its compounds have many

32 applications, including in fiber (optical) glass manufacture, and as semiconductors

33 and lasers, fireworks, pigments and dyes [4,5], its excessive discharge is hazardous to

34 the eco-system and human health [6]. It enters soil and groundwater primarily through

35 metal-based mining, ore processing, smelting, and coal combustion. Ingestion of Tl

36 causes both chronic and acute poisoning [7,8]. There are two main oxidation states of

37 Tl, i.e. monovalent (Tl(I)) and trivalent (Tl(III)) cations, while the former is more

38 widespread in the natural environment and of stronger mobility than the latter [9].

39 Oxidation of Tl(I) facilitates Tl removal from environment. Over the past few years,

40 several different technologies have been employed for Tl removal, among which

41 adsorption is frequently employed [10-13], whereas it requires large amounts of

42 adsorbents which are very expensive and difficult to regeneration or disposal. Thus a

43　　simple, efficient way of treating Tl-contaminated groundwater is urgently needed.

44　　　　Nowadays, electrochemical oxidation technology is considered a green, efficient

45　　method for the removal of contaminants from soil and water, owing to the strong

46　　oxidative oxidants produced during electrolysis [14,15]. To date, electrochemical

47　　process has been widely used for remediation of metal-contaminated aqueous systems,

48　　with various metals as targets, including As, Pb, V, Cd [16-18], while few

49　　contributions are focused on Tl removal based on this technology. Additionally, anode

50　　materials, which determine the removal efficiency of target pollutants, are particularly

51　　important for the performance of electrochemical oxidation technology [19,20]. The

52　　boron-doped diamond (BDD) anode has become increasingly the electrode of choice

53　　in electrochemistry, noting its unique advantage in the complete mineralization of

54　　organic pollutants [21-23]. To date, hardly any investigations have been made into the

55　　treatment of Tl-contaminated groundwater with this particularly efficient electrode.

56　　　　The present study proposed an electrochemical oxidation system with a BDD

57　　anode for the effective oxidation of Tl(I) in simulated groundwater. A systematic

58　　program of tests was undertaken to enable selection of suitable material for the anode,

59　　with removal efficiency in mind. Operating factors affecting the performance as well

60　　as possible oxidation mechanisms were also examined. Exhausted electrolytes were

61　　subjected to subsequent coagulation/precipitation tests; and the precipitate was further

62　　analyzed. This work provided a promising alternative for treating Tl-contaminated

63　　groundwater.

64　　**2. Methods and Materials**

65 *2.1 Experimental apparatus and chemicals*

66   The configuration of the proposed system consisted of a power supply and an

67 electrolytic reactor with copper wires connected together during the experiment (Fig.

68 1). The electrolytic reactor was fabricated from a glass beaker (250 mL) whose

69 working volume was 200 mL. The BDD electrode with surface area of 5 cm^2,

70 provided by CONDIAS GmbH, Germany served as anode. Other two kinds of anode

71 materials, PbO_2, and carbon felt, prepared according to Li et al. [19], were also tested.

72 The cathode was made of graphite plate with surface area of 10 cm^2 during all the

73 experiments. The electrode spacing was 1.0 cm during the experiments [24]. Freshly

74 prepared solution with Tl(I) concentration of 10 mg L^{-1} was added to the reactors, in

75 the form of $TlNO_3$, and its initial pH was adjusted to 2.0 by 0.1 M HCl. All other

76 chemicals were of analytical grade and utilized without further purification.

77 *2.2 Experimental procedures*

78   The oxidation of Tl(I) with initial concentration of 10 mg L^{-1} was conducted in

79 the electrochemical system with a current density of 5 mA cm^{-2} within 15 min

80 operating cycle. The performance of BDD anode was comparatively evaluated with

81 PbO_2 and carbon felt anodes in the aspect of Tl(I) oxidation, by measuring the

82 production of Tl(III) as the generated Tl(III) was soluble under this condition.

83 Subsequently influencing factors affecting the performance of the system were

84 examined, including initial Tl(I) concentration (5 mg L^{-1}, 10 mg L^{-1}, 15 mg L^{-1}, 20 mg

85 L^{-1}), initial pH (1.5, 2.0, 2.5, 3.0) and current density (1 mA cm^{-2}, 5 mA cm^{-2}, 10 mA

86 cm^{-2}, 15 mA cm^{-2}). When one factor was examined, it changed while others kept

87   consistent with the condition in the first part of the experiment. The initial pH was

88   adjusted by 0.1 M HCl. After that, the oxidation process and its underlying

89   mechanism were investigated through electrochemical test and by synchronous

90   monitoring of active substances and the oxidation products. Subsequent

91   coagulation/precipitation with the exhausted electrolyte by two different coagulants

92   was performed to remove total Tl from the aqueous solution, i.e. addition of 2.5 g of

93   ferric chloride ($FeCl_3 \cdot 6H_2O$) or polymeric ferric sulfate (PFS) respectively with

94   magnetic stirring and pH of 9.0 by 1 M NaOH. Then the solution was filtered through

95   a suction filter with 0.22 μm membrane. Tl(III) and total Tl were examined in the

96   filtrate and the generated precipitate during that process was then analyzed using

97   X-ray photoelectron spectroscopy (XPS). All experiments were carried out at room

98   temperature (22 ± 2 ℃). Each test was repeated three times and the mean results were

99   reported.

100   *2.3 Analytical methods*

101   The concentration of Tl(III) was measured by a UV-vis spectrophotometer (DR

102   5000, HACH, USA) at 605 nm [25]. Total Tl was determined by graphite furnace

103   atomic absorption spectrophotometry (Zeenit700, Analytik Jena AG, Germany). pH

104   was measured using a pH-201 meter (Hanna, Italy). Cycle voltammetry (CV) was

105   performed at a scan rate of 50 mV s^{-1} using an electrochemical workstation (VMP3,

106   Bio-Logic Science Instruments, France) with saturated calomel electrode (SCE) as

107   reference electrode [26]. The concentration of total oxidizing species were monitored

108   by N,N-diethyl-p-phenylenediamine (DPD) colorimetric method [27]. The

109 concentration of hydrogen peroxide was also measured by the spectrophotometer (DR

110 5000, HACH, USA) at 350 nm, after the sample was mixed with 0.01 M ammonium

111 heptamolybdate tetrahydrate and 0.1 M potassium iodide [24,28]. Hydroxyl radical

112 was determined using dimethyl sulfoxide (DMSO) [27,29]. Element composition of

113 the precipitate was analyzed by XPS (AXIS-Ultra, Kratos Analytical, UK).

114 On the basis of measured Tl(III), current efficiency (CE) was calculated using

115 the following equation:

116 $$CE = \frac{[Tl(III)_t - Tl(III)_0]FV}{120It} \quad\quad\quad\quad (1)$$

117 where $Tl(III)_0$ and $Tl(III)_t$ are the concentration of Tl(III) (in g L^{-1}) at time 0 and t (in

118 s), respectively; F is Faraday constant (96 487 C mol^{-1}); V is the volume of electrolyte

119 (in L); I is the current (in A).

120 **3. Results and Discussion**

121 *3.1 Tl(I) oxidation behaviors with BDD anode*

122 Obvious Tl(I) removal was observed in the electrochemical system equipped

123 with BDD anode, under the initial conditions of Tl(I) of 10 mg L^{-1}, pH of 2.0, and

124 current density of 5 mA cm^{-2}, as shown in Fig. 2a. Tl(I) removal efficiency reached as

125 high as $99.2 \pm 0.9\%$ within 15 min operation, which represented a major improvement

126 on previous adsorption studies for Tl(I) using modified *Aspergillus niger* biomass [30]

127 and nano-sized manganese dioxide [31] with the same initial Tl(I) concentration. The

128 CE for the oxidation of Tl(I) with BDD anode was about $7.1 \pm 0.4\%$, comparable with

129 previous results using the same anode material [32]. Comparatively, Tl(I) removal

130   efficiencies achieved using the PbO_2 and carbon felt anode materials were $30 \pm 1.1\%$

131   and $11.3 \pm 0.8\%$, respectively, much lower than that obtained from BDD anode,

132   implying that electrochemical oxidation with BDD anode was efficient for Tl(I)

133   removal in groundwater.

134   Compared with the other two anode materials, BDD electrodes exhibited high

135   oxygen over-potentials when producing electrochemical oxidants in situ from water,

136   and the oxidants were short-lived free radical species such as $\cdot OH$, $O\cdot$, $HO_2\cdot$ [33] and

137   more stable substances such as H_2O_2, O_3, $S_2O_8^{2-}$, ClO^-, HClO [34-36]. BDD anodes

138   had previously been classified as non-active anodes having a weak interaction

139   between the anode surface and electro-generated hydroxyl radical [26,37,38].

140   Therefore, once hydroxyl radicals formed during the reaction procedure, they would

141   then fall from the BDD anode surface into the solution and so Tl(I) was rapidly

142   oxidized to Tl(III) [39,40]. In contrast with the BDD case, the hydroxyl radical

143   remained attached to the PbO_2 electrode surface in an adsorbed state because of the

144   strong adsorption properties of the electrode material [41], and thus such radicals

145   hardly entered the solution. Far fewer hydroxyl radicals formed on the carbon felt

146   electrode than on the other two electrodes. In short, the main advantages of BDD

147   electrodes were their relatively wide electrochemical potential window, chemical

148   inertness and thermal properties, and their stability under polarity inversion [36,42].

149   Four gradients of initial Tl(I) concentration were examined and Tl(I) removal

150   efficiencies decreased gradually with the increase of initial Tl(I) concentrations (Fig.

151   2b). After 15 min operating, Tl(I) was nearly completely removed when initial Tl(I)

152 concentrations were 5 mg L^{-1} and 10 mg L^{-1}. When they were increased to 15 mg L^{-1}

153 and 20 mg L^{-1}, the removal efficiency decreased to $76.4 \pm 1.2\%$ and $62.8 \pm 0.9\%$,

154 respectively. The amount of active substances generated in the system might be

155 constant, so as the Tl(I) that could be oxidized. Thus proper range of initial Tl(I)

156 concentrations with corresponding operating time should be chosen to ensure the

157 quality of groundwater after treatment in the proposed system.

158   Fig. 2c illustrated that the removal efficiency of Tl(I) decreased with the increase

159 of initial pH. Notably, increasing the pH from 2.5 to 3.0 resulted in the significant

160 decrease of Tl(I) removal. Acidic condition facilitated the formation of oxygen

161 containing active substances, which could be propitious to oxidation process [43,44].

162 Moreover, the adjustment of pH by HCl was also an important factor, as the addition

163 of chloride ion could easily form complex compounds with the generated Tl(III),

164 which was favorable to the oxidation of Tl(I) [45]. Additionally, chlorion-related

165 intermediate could also be generated during the electrolysis process, accelerating the

166 oxidation of Tl(I) during the test. Therefore, the removal efficiency of Tl(I) decreased

167 with the increase of pH due to the lack of hydrogen and chloride ions.

168   It could be seen from Fig. 2d that the efficiency of Tl(I) removal increased

169 gradually with the increase of current density. Higher current density could result in

170 stronger direct electrochemical oxidation, and more active substances could also be

171 produced, both of which could promote the removal of Tl(I) [46]. Though higher

172 current density the results achieved more quick Tl(I) removal, more energy would be

173 consumed. Appropriate current density should be selected for economical

174 consideration.

175 *3.2 Tl(I) oxidation mechanisms*

176   The two main electrochemical oxidation mechanisms comprised: (1) direct

177 electrochemical effects on the anode surface; and (2) indirect electrochemical effects

178 mediated by oxidants, such as hydroxyl radicals, hydrogen peroxide and active

179 chlorine generated during electrolysis [41,47]. The oxidation peaks in the CV with

180 BDD anode got weaker and weaker as the experiment progressed (Fig. 3) [26], while

181 the oxidation efficiency of Tl(I) increased during the experiments (Fig. 2a), implying

182 that the direct electrochemical oxidation was not the main effect for Tl(I) removal,

183 consistent with previous studies [48,49]. The hydrogen peroxide and hydroxyl

184 radicals were subject to further monitoring and both of them exhibited an increasing

185 tendency with time (Fig. 4), and so as the total oxidizing species with the maximum

186 value of 9.51 ± 1.3 mg L^{-1} and the concentration level was comparable with results

187 obtained from the exact system for treating *p*-substituted phenols [41]. This result

188 suggested that indirect oxidation pathway by oxidants generated in electrochemical

189 tests played a more important role for Tl(I) removal.

190   The main oxidants, hydrogen peroxide and hydroxyl radical, were generated as

191 follows: (i) oxygen captured electrons on the cathode readily, and reacted with

192 hydrogen ions to form hydrogen peroxide in the acid solution (Eq. (2)); (ii) hydroxyl

193 radical formed due to single-electron oxidation of water because of the high voltage

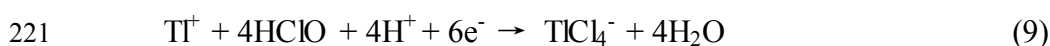194 on the anode (Eq. (3)) [33,50]. Moreover, active chlorine, such as Cl_2 and HClO,

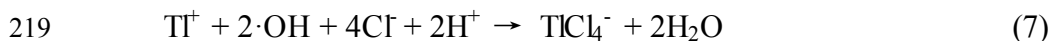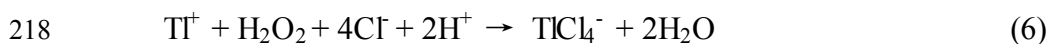195 could also be generated due to the addition of chloride ion according to Eq. (4), (5)

196 [46].

197 $$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad\qquad (2)$$

198 $$H_2O \rightarrow \cdot OH + H^+ + e^- \qquad\qquad (3)$$

199 $$2Cl^- \rightarrow Cl_2 + 2e^- \qquad\qquad (4)$$

200 $$Cl_2 + H_2O \rightarrow HClO + HCl \qquad\qquad (5)$$

201   To deeply investigate the exact roles of these active oxidative species during the

202 electrolysis process, different oxidant scavengers were added into electrolyte at the

203 beginning of tests according to previous studies [51,52]. Compared with the result

204 without scavenger in Fig. 2a, addition of isopropanol to remove ·OH solely

205 significantly inhibited the oxidation efficiency of Tl(I) (only about $8 \pm 0.4\%$) (Fig. 5),

206 suggesting that the Tl(I) oxidation pathway by ·OH was dominant, which coincided

207 with previous study [49]. While with the addition of FeSO$_4$-EDTA solely to remove

208 H_2O_2, the oxidation efficiency decreased slightly (about $86 \pm 1.5\%$), indicating H_2O_2

209 played a less significant role. Results from additions of both ·OH and H_2O_2

210 scavengers simultaneously indicated that the effect of active chlorine (Cl$_2$, HClO)

211 could be negligible [53]. Although some chemical reaction, for instance Fenton

212 reaction, could also produce oxidants as ·OH, other chemical reagents must be added

213 into the aqueous solution, probably resulting in higher cost and secondary pollution

214 [54].

215   With the aids of these oxidants, Tl(I) was oxidized satisfactorily to Tl(III) in a

216 current density of 5 mA cm^{-2} (Eq. (6), (7), (8), (9)) . The concentration of Tl(III)

217   increased accordingly as presented in Fig. 2a.

218    $$Tl^+ + H_2O_2 + 4Cl^- + 2H^+ \rightarrow TlCl_4^- + 2H_2O \qquad (6)$$

219    $$Tl^+ + 2\cdot OH + 4Cl^- + 2H^+ \rightarrow TlCl_4^- + 2H_2O \qquad (7)$$

220    $$Tl^+ + 2Cl_2 + 2e^- \rightarrow TlCl_4^- \qquad (8)$$

221    $$Tl^+ + 4HClO + 4H^+ + 6e^- \rightarrow TlCl_4^- + 4H_2O \qquad (9)$$

222   Additionally, the importance of HCl in achieving full removal of Tl(I) was

223   highlighted as the generated Tl(III) strongly binded to unidentate ligands with Cl⁻ to

224   form stable charged anionic species $TlCl_4^-$, which was the main final product of Tl(III)

225   [55,56]. Given that the pairing of Tl(III) and Tl(I) had high redox potential (+1.25 V),

226   Tl(I) could, in principle, be easily oxidized to Tl(III) in acidic condition [45]. It should

227   be noted that Tl(III) generally occurred in a strong oxidizing environment and was

228   easily hydrolyzed in solution [31]. Therefore, the presence of chloride ion prevented

229   Tl(III) from becoming hydrolyzed; this was a very satisfactory finding in the context

230   of the present study as Tl(III) in the form of $TlCl_4^-$ could precipitate more readily than

231   hydrolyzed on during coagulation/precipitation process [56]. As should be found from

232   Fig. 2a, most generated Tl(III) was still in the aqueous solution and the concentration

233   of total Tl kept steady after electrochemical treatment, with slight increase of pH

234   (from 2.00 to 2.07), thus subsequent treatment was necessary to achieve total Tl

235   removal and ensure groundwater security.

236   *3.3 Subsequent treatment for total Tl removal*

237   After electrolysis, subsequent treatment was performed for the exhausted

238   electrolyte. When its pH was adjusted to 9.0, spontaneous precipitation was hardly

239   observed as strongly steady $TlCl_4^-$ was the main form of Tl(III). It was tetrahedral

240   with all the coordination sites of Tl(III) were fully occupied by chloride and hydroxyl

241   ions lost the chance to combine with Tl(III) [57]. When the two coagulants were

242   added separately, significant removals of total Tl were realized through the bridge

243   formation and catching-sweeping mechanism in flocculating process (Fig. 6). The

244   quality of the treated effluent could meet EPA drinking water standards (less than 2 µg

245   L^{-1}) [58]. The foregoing results demonstrated that the proposed process i.e. oxidation

246   in the electrolytic reactor and subsequent coagulation/precipitation was capable of

247   remediation of Tl-polluted groundwater efficiently.

248   Precipitates from the coagulation/precipitation with different coagulants were

249   further analyzed by XPS (Fig. 7a). The spectrum had a peak corresponding to Tl 4f

250   and measured banding energy located at 118.2 eV, which could be ascribed to Tl(III)

251   [59,60]. The high resolution of Tl 4f was shown in Fig. 7b, which indicated that about

252   99% and 92% of Tl(III) was removed from the solution in coagulation/precipitation

253   with $FeCl_3$ and PFS, respectively. The lack of a peak corresponding to Tl(I) indicated

254   that scarcely any Tl(I) remained in the precipitate. These results showed that Tl(I) was

255   almost completely oxidized to Tl(III) and deposited on the $Fe(OH)_3$ surface.

256   Moreover, the XPS spectrum also indicated the presence of O 1s and Fe 2p with the

257   respective peaks located at approximately 531.1eV and 711.0 eV. Given that the two

258   peaks correspond to nucleophilic oxygen (O^{2-}) and Fe^{3+}, the oxides were inferred to

259 be Fe_2O_3, due to slow decomposition of the weak base ($Fe(OH)_3$) [61,62]. The

260 foregoing discussion had explained the chemistry of the processes behind Tl removal

261 using the technology presented herein.

262 **4. Conclusions**

263 99.2 ± 0.9% of Tl(I) was successfully oxidized to Tl(III) in the electrolytic

264 reactor with BDD anode within 15 min. Tl(I) oxidation was suppressed by the

265 increase of initial Tl(I) concentration and initial pH, respectively, while it was

266 enhanced with the increase of current density. Compared with direct electrochemical,

267 indirect oxidation reaction with ·OH played a significant role. Subsequent

268 coagulation/precipitation with $FeCl_3$ realized the satisfactory of total Tl removal and

269 the quality of the effluent could meet EPA drinking water standards. XPS analysis

270 further confirmed that Tl(III) was the primary oxidation state of Tl. An efficient

271 alternative had therefore been proposed for remediation of Tl-contaminated

272 groundwater.

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453

454 **Figure Captions**

455 **Fig. 1.** Schematic diagram of the electrolysis system used in the present study.

456 **Fig. 2.** The removal efficiency of Tl(I) with different anode materials (a) as well as

457 operating factors studies. (b) initial Tl(I) concentration; (c) initial pH; (d) current

458 density.

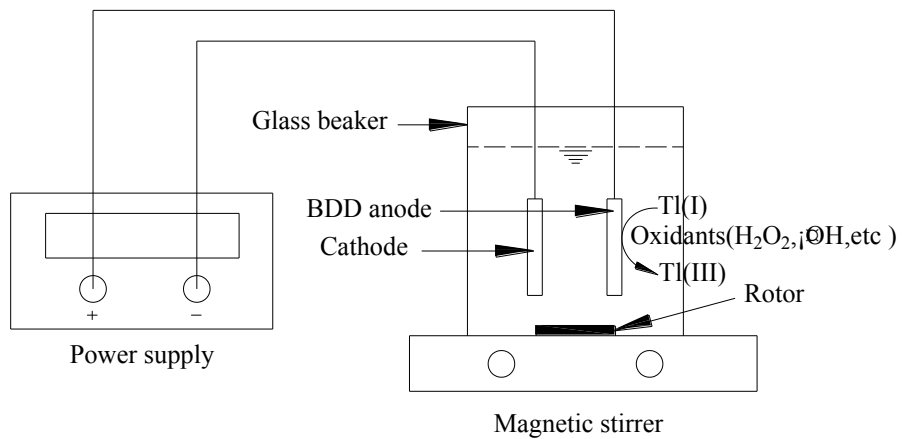459 **Fig. 3.** CV curves with the BDD anode at the scan rate of 50 mV s^{-1}.

460 **Fig. 4.** Concentration evolution of hydrogen peroxide and hydroxyl radical produced

461 on BDD anode during the experiment.

462 **Fig. 5.** The oxidation efficiency of Tl(I) with different scavengers in the electrolytic

463 reactor.

464 **Fig. 6.** Histogram showing concentrations of total Tl and Tl(III) at initial conditions

465 for FeCl$_3$ and PFS used in the coagulant tests.

466 **Fig. 7.** XPS spectra for precipitate from the coagulant test with FeCl$_3$ and PFS: (a)

467 survey; and (b) high resolution plot in vicinity of Tl 4f.

468

Glass beaker

BDD anode
Cathode

Tl(I)
Oxidants(H_2O_2,¡OH,etc)
Tl(III)
Rotor

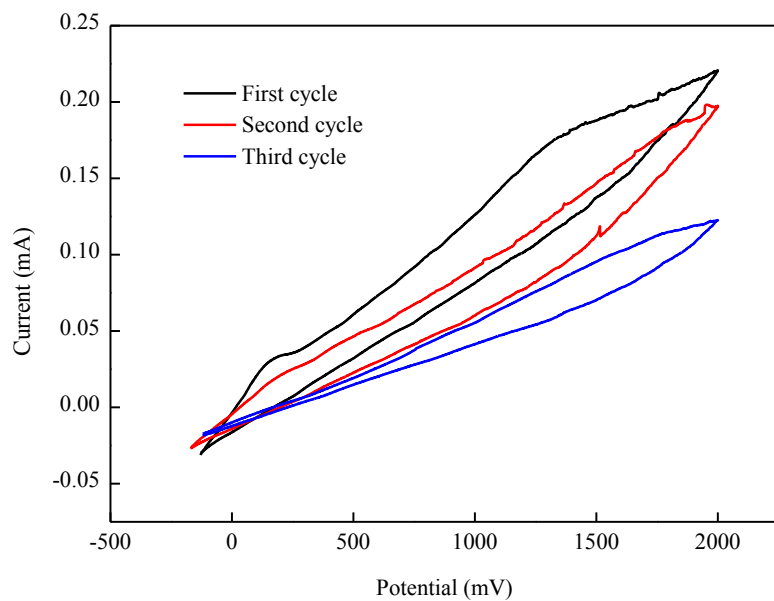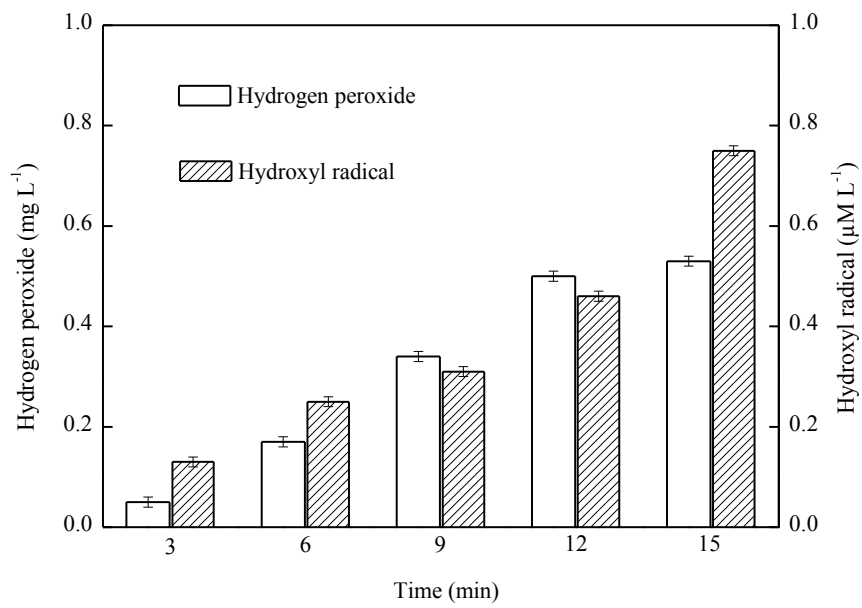Power supply

Magnetic stirrer

469

470 **Figure 1**
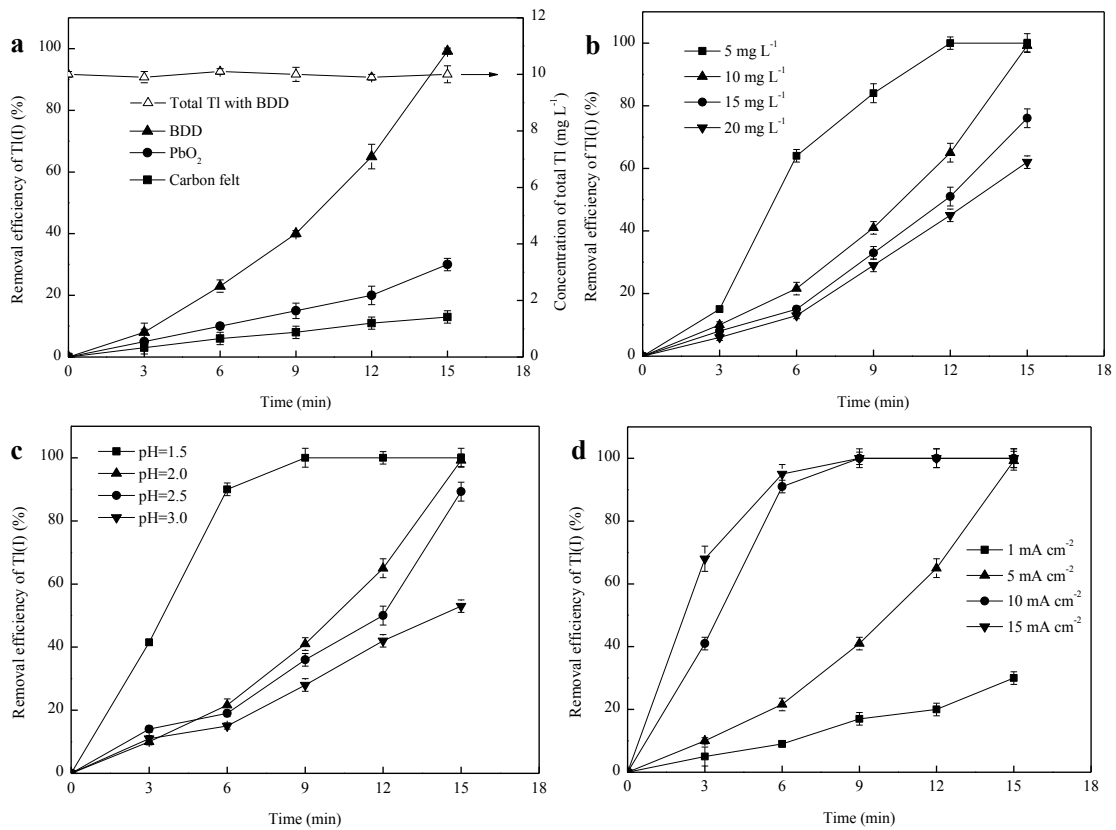
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472

473   **Figure 2**
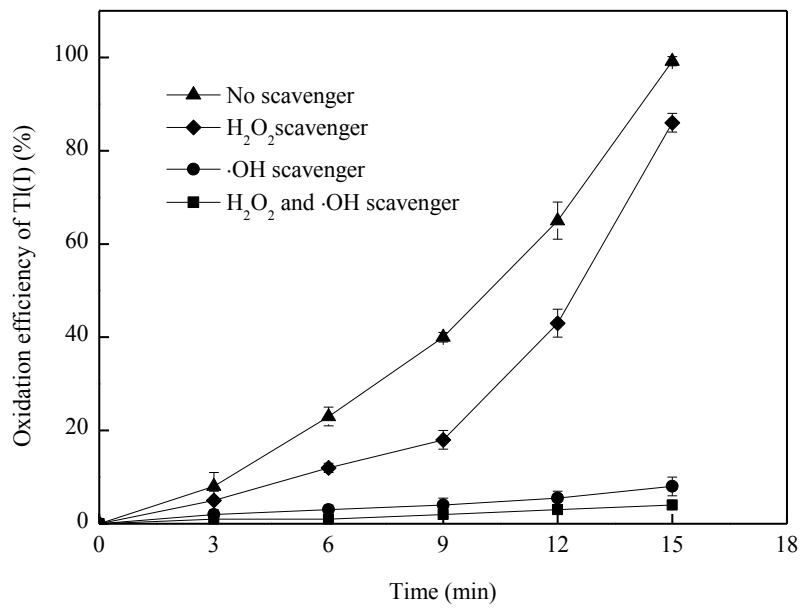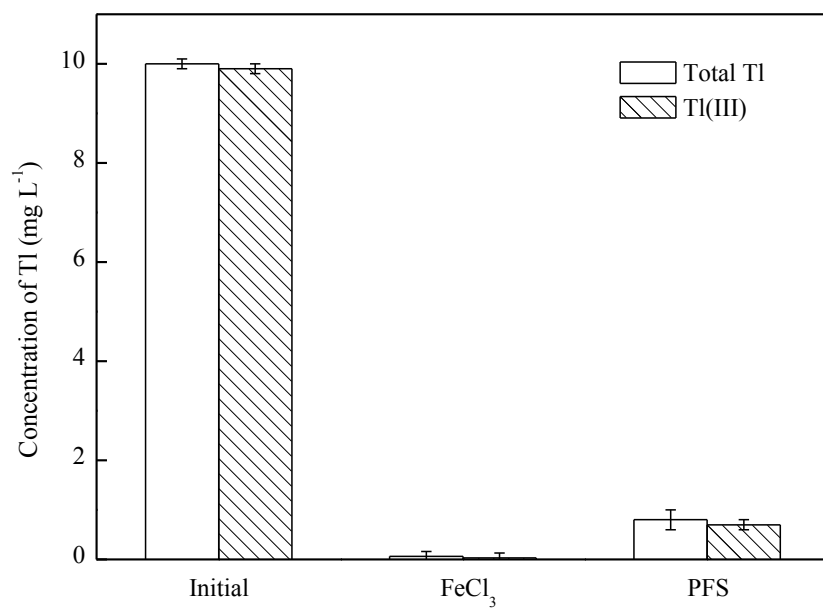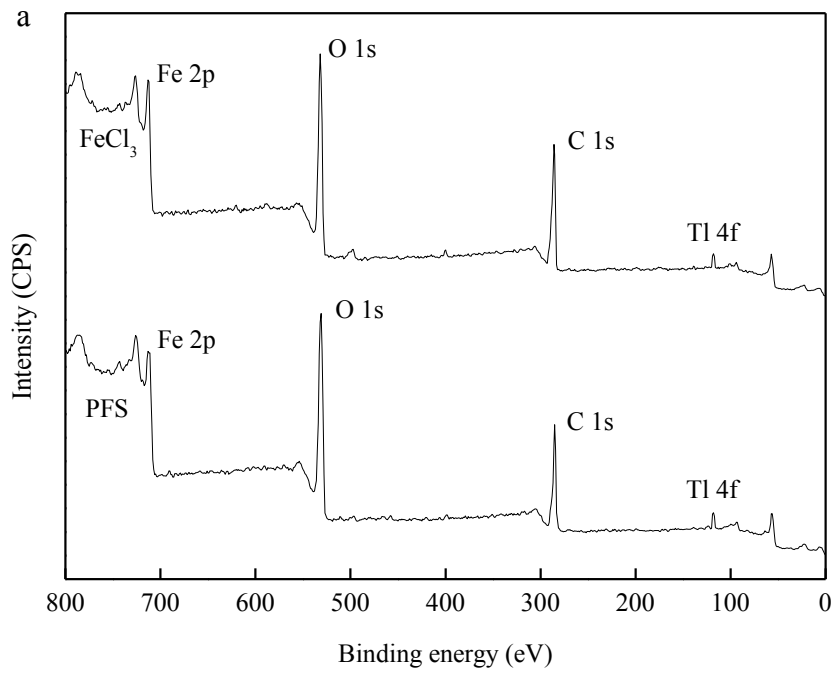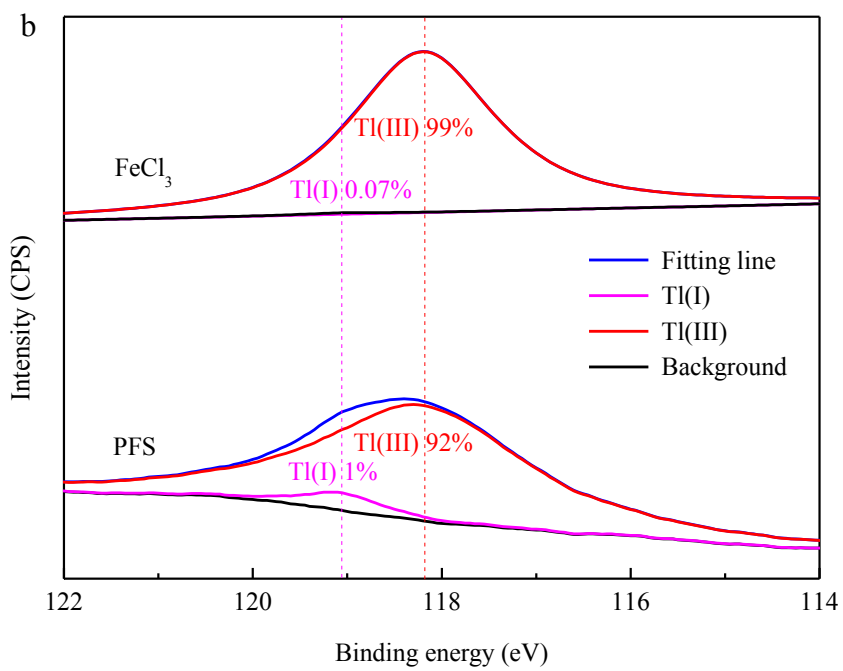
474

475   **Figure 3**

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478   **Figure 4**

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480 **Figure 5**

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482   **Figure 6**

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Figure 7

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