



# Removal of Trace Thallium from Industrial Wastewater by Fe<sup>0</sup>-Electrocoagulation

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Abstract: As thallium (Tl) is a highly toxic heavy metal, there are compulsory environmental regulations in many countries on minimizing its release. This research investigated the treatment of real industrial wastewater with low Tl(I) concentration by Fe<sup>0</sup>-electrocoagulation (Fe<sup>0</sup>-EC) in a batch aeration-forced pump cycle reactor. The effects of pH (7–12), current density (8.3–33.3 mA/cm<sup>2</sup>), dissolved oxygen (DO) in wastewater, and initial Tl(I) concentration (66–165 µg/L) on Tl(I) removal efficiency were investigated. The removal efficiency of Tl(I) is pH-dependent, to be exact, it increases significantly with pH rising from 8 to 11. Initial pH of influent and DO concentration were the key operation parameters which strongly affect Tl(I) removal. After the water sample with initial Tl(I) concentration of 115 µg/L was treated for 12 min by a single-step process at pH of 11 and current density of 16.7 mA/cm<sup>2</sup>, the residual Tl(I) concentration was decreased to beneath the emission limit in China (2  $\mu$ g/L) with a low energy consumption of 0.82 kWh/m<sup>3</sup>. By prolonging the operation time, the concentration was further reduced to  $0.5 \,\mu\text{g/L}$  or even lower. The main composition of the flocculent sludges is iron oxyhydroxide, yet its crystal structure varies dependent on pH value which may result in different Tl(I) removal efficiency. Feroxyhyte nanosheets generate in situ by Fe<sup>0</sup>-EC, which contributes to the rapid and effective removal of Tl(I), while the speedy oxidation under DO-enriched conditions benefits the feroxyhyte formation. The mechanism of Tl(I) removal by Fe<sup>0</sup>-EC is attributed to the combination of electrostatic attraction and the formation of inner-sphere complexes. As shown in the technical and mechanical studies,  $Fe^0$ -EC technology is an effective method for low Tl concentration removal from wastewater.

**Keywords:** thallium; electrocoagulation; industrial wastewater; iron electrodes; dissolved oxygen; feroxyhyte

# 1. Introduction

Thallium (Tl) is a rare but widely dispersed element with high toxicity. Because of its high acute toxicity to living organisms and its irreversible biological toxicity and strong bioaccumulation [1,2], Tl and its compounds are considered as the main hazardous wastes by the World Health Organization [3]. It has been classified as a priority pollutant by the United States Environmental Protection Agency (USEPA) [4] and the European Union Water Framework Directive [5]. It has also been listed by China as one of the key heavy metal pollutants [6]. The concentration of Tl in the natural environment is



usually remarkably low, which makes it challenging to evaluate its quantity precisely [2] and to remove it effectively [7]. Because of this, Tl has been studied much less than other toxic elements such as Cr, As, or Cd. Owing to the increasing consumption of Tl and its compounds, Tl is now a new emerging element which has become an unneglectable burden on the environment [8–10].

Tl belongs to Group 13 of the periodic table of the elements sitting, and it can exist in aqueous solutions mainly in two oxidation states, Tl(III) and Tl(I) [11]. Tl(III) usually exists in water such as lake water or marsh water, which is rich in colloids and organic matter [12]. Yet, under normal circumstances, Tl(III) is converted to a monovalent state as it possesses a strong oxidizing tendency [13]. So, in most natural environments, thallous compounds are the dominant species [14]. Tl(I) is soluble as the species of Tl(I) cation or TlOH<sub>(aq)</sub> at a wide pH range of 0–14 [7], which suggests that the conventional approaches, such as co-precipitation to remove of heavy metals from wastewater might be invalid when processing Tl(I).

Currently available methods for Tl removal mainly include adsorption [15–18], oxidation-reduction precipitation [19,20], solvent extraction [21], and ion exchange processes [22]. Most of these studies were conducted at a higher Tl concentration using model water [7], which is not consistent with the actual circumstances, i.e., real wastewater, where Tl concentration therein generally ranges from only a few  $\mu$ g/L to a few mg/L [23], while rarely exceeding 10 mg/L [24]. Due to mass transfer limitations, the removal efficiency at low concentration may be worse. In this case, further research on the treatment of wastewater with lower Tl concentration (<1 mg/L) is essential. In their recent review of Tl removal processes, Xu et al. [7] highlighted that, until now, only a few studies, where strong oxidants [20,25] or advanced oxidation [19,26] methods were used, reported that the effluent Tl concentration can meet the Tl emission standards of industrial wastewater in China (5  $\mu$ g/L) and of some provincial standards (2  $\mu$ g/L). Therefore, it is crucial to introduce a cost-effective technology for deep purification of low Tl concentration industrial wastewater to meet the strict emission requirements and reduce the risk of Tl pollution.

Electrocoagulation (EC) is an effective electrochemical wastewater treatment technology [27]. During EC treatment, polymeric metal (usually Fe or Al) hydroxide species were derived in situ, while gas evolved at the cathode. As an easy-to-operate technique, it generates minimal sludge and requires no chemical additives, and it has received considerable attention in recent years as an environmentally friendly option [28,29]. It has been successfully applied to process organic [30–32] and inorganic [33–35] industrial wastewaters. Possessing an ability to thoroughly remove pollutants, EC has also been used in drinking water and surface water treatment [36–38].

In this study, iron electrodes have been used in the EC process. Fe<sup>0</sup>-electrocoagulation (Fe<sup>0</sup>-EC) products may form in situ monomeric ions, Fe(OH)<sub>n</sub> (n = 2 or 3), iron hydroxyl complexes with hydroxide iron ions, and polymeric species (hereafter collectively referred to as iron oxides/hydroxides) which strongly depend on the pH of the solution [27]. They have a strong affinity for heavy metals, colloidal solids and particles, as well as soluble inorganic pollutants [27,28]. The following equations describe the Fe<sup>0</sup>-EC process.

Anode:

$$Fe_{(s)} \to Fe_{(aq)}^{2+} + 2e^{-},$$
 (1)

$$Fe_{(aq)}^{2+} + H_2O + O_{2(g \text{ or } DO)} \to Fe(OH)_n + H_{(aq)}^+.$$
 (2)

Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-_{(aq)}.$$
 (3)

Iron oxides/hydroxides exist in wastewater in the form of a gelatinous suspension, which can remove the pollutants by complexation or electrostatic attraction, followed by coagulation [27]. Metal oxides/hydroxides generated in the EC process have much higher adsorption capacity than the pre-synthetized ones, which guaranteed the removal efficiency [28], especially in the treatment of heavy metals [33,34,39]. Although the affinity of Tl(I) cation to iron oxides/hydroxides is usually

expected to be weak because it has low  $\log K_{\text{MOH}}$  of  $10^{-13.2}$ , study [40] shows that Tl(I) can adsorb well on ferrihydrite in alkaline solutions (pH > 8). Therefore, besides the eight potential feasible technology schemes for different Tl industry wastewater recommended by Xu et al. [7], EC may be another feasible solution for low Tl concentration industrial wastewater treatment. However, there is still insufficient information available on Tl removal by EC technology. In our initial trial of Al<sup>0</sup>-EC treatment, the result of Tl removal was unfortunately not as good as expected. It performs much worse than the Fe<sup>0</sup>-EC approach (Figure S1). The problem may lie in the fact that Al<sup>0</sup>-EC can only exert its maximum performance in neutral conditions [29,41], yet the Tl adsorption performs better at alkaline pH.

Hence, a Fe<sup>0</sup>-EC treatment is proposed in this study for Tl containing wastewater. The effects of operational parameters, such as initial pH, current density, dissolved oxygen (DO) in wastewater, and initial Tl concentration, on Tl removal efficiency from real industrial wastewater were investigated. The flocculent sludge generated under different initial pH was investigated to reveal the mechanism of Tl removal. The specific energy consumption under optimized conditions was also calculated with effluent concentration of 5  $\mu$ g/L. The lab-scale batch aeration-forced pump cycle EC reaction system we used is easily converted to continuous mode, which can be easily amplified for a pilot-scale test to evaluate the industrial feasibility of Tl removal from wastewater with EC technology.

# 2. Materials and Methods

# 2.1. Wastewater Sampling

# 2.1.1. Real Industrial Wastewater

The wastewater was collected from a  $Mn_3O_4$  production plant located in Hunan province, China. Its initial pH value was adjusted in the workshop to c.a. 10 to recover manganese. The wastewater contains a variety of pollutants, among which Tl is derived from the raw manganese sheets. Because of the fluctuation of pollutant content in this real wastewater, the components therein were detected before each batch of experiments. Five main items were chosen to be measured, and their concentration ranges are shown in Table 1. The concentration range of elements is consistent with long-term industrial monitoring.

Table 1. Concentration ra	inge of main element	s in the industrial	wastewater.
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Components	Tl(μg/L)	Mn(mg/L)	Ca(mg/L)	Mg(mg/L)	Cl-(g/L)
Concentration range	66–165	0.1–0.3	1–5	30–50	2.0-2.2

The initial Tl concentration varied according to different manganese raw materials. Chloride salt was usually used as a supporting electrolyte to increase the electrical conductivity of wastewater and relieve electrode passivation in EC treatment [33,42]. There is no need to add supporting electrolytes additionally since the chloride ions therein amount to 2.0 g/L.

#### 2.1.2. Artificial Wastewater

To study the forms of Tl in flocculent sludges, it is necessary to ensure that Tl content therein is larger than the detectable lower limit of the analyzing apparatus. For this purpose, Tl content was intentionally adjusted. The artificial samples with high Tl concentration were prepared by dissolving the corresponding amount of  $TINO_3$  (99.9%, Sigma-Aldrich, USA) in the real wastewater to obtain suitable thallium-containing sludge.

#### 2.2. EC Operation Procedure

The experiments were carried out at room temperature with an aeration-forced pump cycling reaction system in batch mode. Connected by pipelines and valves, the EC reactor, direct current (DC)

power supply, iron electrode plates, circulating pump, and rotameter were assembled to construct this reaction system. The plexiglass reactor consisted of a reaction tank and an overflow tank with a total valid volume of 2.7 L. The reaction tank had dimensions of 101 mm  $\times$  150 mm  $\times$  100 mm. Vertical grooves with a depth of 2.5 mm and a groove space of 10 mm were carved on the side wall of the reaction tank, which stopped at 30 mm above the reaction tank bottom, for placing electrode plates. The iron (carbon steel, Q325) plates with dimensions of 103 mm  $\times$  140 mm  $\times$  2 mm (wide  $\times$  height  $\times$ thick) were used as sacrificial electrodes. Two electrodes were positioned vertically in the groove of the reaction tank with a minimum and maximum distance of 10 mm and 60 mm, respectively. Figure 1 shows the schematic diagram of the EC setup. The effective surface area immersed in wastewater of one single electrode was 121.2 cm<sup>2</sup>. The top ends of plates, located 20 mm above the wastewater surface, were connected to a DC power supply (Zhaoxin RXN-3010D, 0–10 A, 0–30 V, China) by an alligator clip. A pump (Mingling ML-200, 4 L/min, China) was used to provide cycle flow for the reaction system. An air pipe was installed at the inlet of the pump for inhaling air. The inhaled air volume was regulated by a valve and measured by a rotor flowmeter. A pH meter (Thermo, Orion star A211, USA) was used to measure the initial pH of the wastewater. The pH value was adjusted using diluted HCl or NaOH. The solution conductivity and DO concentration were measured by using a conductivity meter (REX, DDS-307, China) and RDO/DO meter (Thermo, Orion star A223, USA), respectively. The instant pH value, solution conductivity, and DO of the wastewater were continuously monitored during each experiment.



Figure 1. Schematic diagram of the electrocoagulation (EC) setup.

For every single experiment, the iron plates were pre-polished with abrasive paper (600 grit), and then cleaned quickly with diluted HCl (5 wt.%) and rinsed with water to eliminate the attachments on the surface. After each experiment, the plates were cleaned with water and stored in diluted HCl (1 wt.%). Water samples with a volume of 20 mL were taken at 2 min intervals during the pre-determined time, then filtrated using a microfiltration membrane (Xinya, mixed fiber film, 0.45  $\mu$ m, China). All experiments were triplicated, and the results were given as average. For the initial stage of electrolysis, the standard errors were no more than 5%, and this will be less than 1% with the prolongation of time. Filtrate was collected and analyzed. Flocculent sludge obtained in the experiment was separated and collected by filtration, dried in a vacuum drying oven (50 °C, vacuum degrees of -80 kPa) for 12 h before being sealed and stored in a refrigerator for further analyses.

The Tl percent removal efficiency was calculated by Equation (4):

$$\eta(\%) = \frac{C_0 - C}{C_0} \times 100,\tag{4}$$

where  $C_0$  and C are the concentrations of Tl in the original wastewater sample and in the EC processed one, respectively.

The energy consumption of the overall EC treatment was calculated using Equation (5):

$$E_{cons} = \frac{U \times I \times t}{V},\tag{5}$$

where  $E_{cons}$  is the energy consumption (kWh/m<sup>3</sup>), *U* is the operating voltage (V), *I* is the matching current (A), *t* is the EC operating time (h), *V* is the treated wastewater volume (L).

According to Faraday's law, the theoretical dissolved mass of sacrificial anodes was calculated with the following Equation (6):

$$m = \frac{I \times t \times M}{z \times F},\tag{6}$$

where *m* is the mass (g) of the dissolved anode material, *I* is the current density (A), *t* is the electrolysis operating time (s), *M* is the molecular weight of the anode material (g/mol), *z* is the number of electrons involved in the EC reaction, and *F* is Faraday's constant (96,485.33 C/mol).

In order to investigate the absorption capacity of different FeOOH obtained by the Fe<sup>0</sup>-EC process, the as-prepared FeOOH was added into 50 mL of centrifuge tubes with 30 mL Tl(I)-containing wastewater. The suspension was shaken at 100 rpm for 4 h in a shaker at room temperature. Then it was filtered through a microfiltration membrane (Xinya, mixed fiber film, 0.45  $\mu$ m, China) and the Tl concentration in the filtrates was determined.

# 2.3. Characterization

Tl concentration in the water sample was measured by inductively coupled plasma mass spectrometry (ICP-MS), using iCAP RQ (Thermo, Waltham, USA) with a lower detection limit of  $0.01 \mu g/L$ . Each group of contrast data was sampled at the same batch in order to reduce the impact of instrument errors. Concentrations of other metals or high Tl content (>1.0 mg/L) were determined by atomic absorption spectrometry (AAS) with spectrometer WYS2200 (Wayeal Co. Ltd., Hefei, China). The phase composition of flocculent sludges was determined by X-ray diffraction analysis (XRD) using D8 advance (Bruker, Berlin, Germany) with a Cu K $\alpha$  X-ray source. To investigate the morphology of the flocculent sludges, scanning electron microscopy (SEM) observation was conducted using JSM-7900F (JEOL, Akishima, Japan). X-ray photoelectron spectroscopy (XPS) study was conducted using ESCALAB 250Xi (Thermo, Waltham, USA) with a monochromatized Al  $K_{\alpha}$  source operated at 150 W. Fourier transform infrared spectroscopy (FT-IR) was adopted to characterize functional groups on flocculent sludges using Nexus 670 (Thermo Nicolet, Waltham, USA) over a wavenumber range from 400 to  $4000 \text{ cm}^{-1}$ . The specific surface area, average pore size and pore volume were measured by nitrogen adsorption using density functional theory (DFT) method with surface area and pore size analyzer Quadasorb SI-3 (Quantachrome Instruments, Boynton Beach, USA). The precise content of Tl, total Fe (TFe), and the proportion of different iron valence states in the flocculent sludge were measured by chemical analysis method.

#### 3. Results and Discussion

# 3.1. Effect of Initial pH

The pH value of the wastewater is a key factor affecting EC treatment efficiency. Solution conductivity, zeta potential, and electrode dissolution [29,43], especially the metal oxides/hydroxides species generated therein and the coagulation mechanism of EC treatment [44,45], are all influenced by

pH value. Since the pH value varies during EC processing [46,47], the initial pH of the solution was used to study the effect of pH on EC performance.

It is noteworthy that, like the artificial samples configured with TlNO<sub>3</sub> and NaCl, simply adjusting the pH value has little effect on Tl content in the real wastewater. It can be concluded that there is no co-precipitation occurring in the Fe<sup>0</sup>-EC treatment for Tl removal from the real wastewater. This testifies that Tl(I) is the dominate Tl component, so the Tl element in the target water is hereafter referred as Tl(I). Meanwhile, the microgram level Tl(I) content in the wastewater at room temperature is not a solubility-controlling phase owing to the high solubility of TlCl [48,49].

Studies have shown that there is a strong correlation between EC treatment effect and the initial pH, which is variable according to different pollutants [28,29]. The EC removal of Tl(I) from wastewater, especially that with low Tl(I) concentration, has been rarely studied. Besides, the Tl(I) sorption is appreciable at alkaline pH [40]. To evaluate EC treatment effects, a series of experiments were performed to treat low Tl(I) samples with a comparatively broader initial pH range of 7–12. The initial pH was adjusted by adding diluted HCl or NaOH. As can be seen from Figure 2, Tl(I) removal rates are 19.1%, 27.7%, and 70.9% at pH 7, 8, and 9, respectively, with applied current density 16.7 mA/cm<sup>2</sup>, after 20 min Fe<sup>0</sup>-EC treatment. Meanwhile, the Tl(I) removal efficiency increased significantly when the pH value increased from 9 to 10 or more. The best removal effect was achieved when the initial pH was 11, to be precise, after the water with feed concentration of 141 µg/L was processed by the EC treatment for 6 and 18 min at pH 11, the residual Tl(I) concentration was reduced respectively to be less than 5 µg/L and 2 µg/L. These results meet the national wastewater emission standards and some strictest provincial standards in China, respectively. They are also comparable with the maximum permissible Tl concentration for drinking water suggested by USEPA [50].



**Figure 2.** Effect of initial pH on (**a**) removal efficiency, (**b**) concentration of Tl(I) within a 20 min EC treatment under an applied current density of 16.7 mA/cm<sup>2</sup> with aeration of 0.2 L/min, using Fe–Fe electrodes at a distance of 2 cm.  $C_0 = 141 \mu g/L$ .

The effect of solution pH on ion adsorption can be achieved by changing the surface charge properties of the adsorbent. The Tl(I) removal capacity of EC treatment increased along with the initial pH, which may be due to the changes of pH-dependent electrostatic force existing between the iron oxides/hydroxides and Tl species. The point of zero charge (PZC) of synthetic Fe-oxides usually ranges between pH 7 and 9 [51]. For instance, the PZC of  $\delta$ -FeOOH is measured as 8.4 [52]. In the solution with a pH value higher than the PZC, the adsorption capacity of iron oxides/hydroxides increases as it can favor the electrostatic attraction between them and Tl(I) ions. This is consistent with the adsorption behavior of Tl(I) on ferrihydrite which is only appreciable at alkaline pH [40]. Since Tl(I) is converted to TlOH<sub>(aq)</sub> at high pH (11.7), as suggested by Lin and Nriagu [25], an excessive pH, i.e., intensified converting, will reduce the adsorption efficiency of Tl species.

It is noteworthy that when the initial pH value exceeded 12, less flocs formed and Tl(I) removal efficiency declined. The main reason for flocs' reduction may relate to the anodic passivation at higher

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pH, which inhibits the dissolution of the sacrificial anode [53]. The superposition factors for the flocs reduction can be attributed to the lower corrosion rate of iron, as can be seen from its corrosion rate-pH chart [30] and the formation of soluble  $Fe(OH)_4^-$  in alkaline pH [54]. In addition, when the initial pH value increased from 11 to 12, the specific surface area of the flocculent sludge decreased by 7.83% and the pore volume decreased by 17.6%, while the average pore diameter decreased slightly (Table S2). This change may lead to the decrease of active adsorption sites on the flocculent sludge and then the decrease of Tl(I) removal efficiency.

After treatment at different initial pH, flocculent sludges share a similar composition, but varied crystal structure. XRD patterns, FT-IR spectra, and SEM images of flocculent sludges generated under different initial pH are shown in Figure 3. As shown in Figure 3a, the main phase of the sludges generated under aeration is iron oxyhydroxide, which is in the form of lepidocrocite ( $\gamma$ -FeOOH) at initial pH 7 and 8, feroxyhyte with less ordered crystallinity ( $\delta'$ -FeOOH) [55] at an initial pH above 10, or a mixture of them at an initial pH of 9. Both FeOOH forms were supposed to be obtained under different reaction conditions in Fe<sup>2+</sup>-containing solution [56], which is consistent with the conclusion that Fe<sup>2+</sup> forms at the anode in the Fe<sup>0</sup>-EC process [54,57]. The inter-conversions between the various monomeric iron ions, iron oxides/hydroxides, and polymeric hydroxyl complexes are possible and often occur readily [56]. Both high pH and high DO concentration can enhance the oxidation rate of Fe<sup>2+</sup> to form feroxyhyte, while slow oxidation rate and neutral pH benefit the formation of lepidocrocite [55]. Further research shows that oxidation rate was greatly affected by DO concentration and is a key factor for formation of feroxyhyte. Detailed discussion on DO can be found in Section 3.2.

XRD patterns show that, with the increase of pH, the diffraction peak broadens while it declines in intensity (Figure 3a). This indicates that the flocs generated at high pH possessed less-ordered crystalline characteristics, which are possibly more favorable in offering reactive sites compared to the low pH ones. When the pH value exceeds 9, the characteristic peaks of lepidocrocite disappeared and feroxyhyte became the main phase. It can be clearly observed on the FT-IR spectra of the flocculent sludges (Figure 3b) that obvious differences exist in the structures and functional groups on flocculent sludges obtained at different initial pH values. The spectra obtained are similar to those reported in the literature [55,56,58]. Adsorption peaks located at 3383.28, 1624.58, 1067.29, and 680.37 cm<sup>-1</sup> on the spectra of flocculent sludges obtained at high pH correspond to the characteristic bands of feroxyhyte [55]. Meanwhile, the characteristic bands on the spectra of flocculent sludges obtained at low pH show that they are of lepidocrocite phase [58].

The morphology of flocculent sludges varied along with the initial pH value. As demonstrated in Figure 3c, sludges generated at a low pH value (pH = 7, 8) exhibited mainly honeycomb-like platelet structure with curls at the edge or stacked small platelets. Nanosheets c.a. 200–300 nm in length and 20 nm in thickness form a large flower-like structure by staggered accumulation create. The porosity of the samples increases as more pores and channels appeared. As the pH increases, the sludge is more likely to form a sheet stacking structure, which was also described by Chukhrov et al. [55]. Until the pH exceeds 9, instead of forming a honeycomb-like structure, the sludge looks like aggregates of smaller platelet nanosheets with a size of about 100–200 nm and thickness of 10–20 nm.

The effects of solution pH on the adsorption properties of the two FeOOH samples, which were obtained by electrolysis of salt water at initial pH of 7 and 11, were compared. According to the number of flocs produced by EC for 20 min, 13.2 mg FeOOH powder was added into 30 mL real wastewater. As illustrated in Figure S3, for the low Tl(I) concentration wastewater, feroxyhyte has better Tl(I) removal efficiency than that of lepidocrocite over the pH range of 7–11. Possessing higher specific surface area than lepidocrocite (Table S2), feroxyhyte can provide more active adsorption sites for Tl(I) and contribute to the increase of Tl(I) removal efficiency.



**Figure 3.** Effect of initial pH on flocculent sludge (**a**) crystal structure; (**b**) surface groups; (**c**) micromorphology, from a 20 min EC treatment applying a current density of 16.7 mA/cm<sup>2</sup> with aeration of 0.2 L/min, using Fe–Fe electrodes at a distance of 2 cm.

The variation of pH during the EC process is mainly a combined effect of OH<sup>-</sup> generation at the cathode (Equation (3)) and the hydrolysis reaction (Equation (2)) of equivalent amount of Fe<sup>2+</sup> formed at the anode. Furthermore, some Fe(OH)<sub>4</sub><sup>-</sup> is likely to form at alkaline pH and result in consumption of OH<sup>-</sup>, which can also explain the decrease of pH [54]. Generally, the effluent pH would increase for acidic influent, but can decrease for alkaline influent [29,47]. As shown in this study, after 20 min EC treatment with aeration, the effluent pH value from the influent pH of 9, 10, 11, and 12 decreased respectively to 8.68, 9.46, 10.43, and 11.76, while the effluent pH from influent pH of 7 increased to 7.85, and there was no obvious change for the influent pH of 8 at current density of 16.7 mA/cm<sup>2</sup>. It is noteworthy that the decrease of effluent pH has no visible negative effect on Tl(I) removal efficiency, because feroxyhyte will form continuously in a solution with pH above 10 under aeration. As illustrated in Figure 2a, the removal rate of Tl(I) increases steadily and slightly after the maximum removal efficiency stage.

The influence of coexisting ions such as Mg (Table 1) on Tl(I) removal efficiency, especially in wastewater with high pH value, is also neglectable. According to the removal efficiency data, in the presence of Mg under different initial pH (Figure S2), coprecipitation of Mg occurs at high pH and its competition with Tl(I) for active adsorption sites on the surface of iron oxides/hydroxides, may also be another reason causing the decrease of Tl(I) removal efficiency at pH = 12.

# 3.2. Effect of DO in Wastewater

Studies on the valence state of iron ions generated from the sacrificial anode during the EC process indicated that ferrous was the main form of anodic dissolution [54,57]. Generally, ferrous constituents are more soluble than ferric constituents [59], only when insoluble ferric oxide flocculate is formed by ferrous oxidation can pollutants in water be effectively removed. The spontaneous chemical oxidation of ferrous to ferric in solution is a complex process [60]. The rate and degree of oxidation depends on parameters such as pH, DO, solution composition and temperature, which affect the structure of flocculent sludge and the pollutant removal efficiency. Study showed that there is a second order relationship between the oxidation rate and the hydroxyl ion concentration at a pH range of 6.0–7.5 [59], which means that the reaction rate can be increased by more than 100-fold with an increase of one pH unit. Nevertheless, when pH exceeds 8.1, the rate appeared to be independent of pH value [60]. Furthermore, the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> was very fast with the presence of trace DO, especially in alkaline solutions, the rate of Fe<sup>2+</sup> oxidation by DO can be significantly promoted [54]. This indicates that DO, rather than the chemical reaction, determines the oxidation rate in alkaline environments. DO concentration in an alkaline solution is a major determinant of the rate and extent of ferrous oxidation, which has an important influence on the crystal structure of iron oxides/hydroxides [56].

As illustrated in Figure 4a, the DO concentration, near-saturated (7.5–8 mg/L) at room temperature in 2.7 L wastewater, can be maintained at around 4.7 mg/L based on the DO consumption rate during the EC process with forced aeration at a current density of 16.67 mA/cm<sup>2</sup> and a pH of 11. By contrast, the residual DO was less than 100  $\mu$ g/L in around 8 min of electrolysis without aeration under the same open atmospheric condition.

As shown in Figure 4b, the Tl(I) removal efficiency under non-aerated conditions was almost the same as that of aerated conditions before the DO was depleted, showing that the DO plays a role in promoting the hydrolysis reaction (Equation (2)). Along with the depletion of initial DO, the Tl(I) removal efficiency starts to decline after it had reached its summit. It may be that the lack of DO in wastewater inhibits the oxidation of ferrous, thereby slowing down or even stopping the deprotonation process according to Equation (2) [33], and resulting in the formation of green rust, which contains lot of ferrous ions (Figure 4b). Feroxyhyte formed in the first 8 min may partially transform to a new phase by the catalytic dissolution action of ferrous ions and reprecipitation process [61,62], meanwhile, some captured Tl(I) may re-release into the wastewater in the phase transition process.

DO concentration also has an important influence on the crystal structure of iron oxides/hydroxides, which then affects the removal efficiency of Tl(I) in wastewater. XRD patterns of flocculent sludges generated at different aerated conditions are shown in Figure 4c. It was found that no green rust formed under aerated conditions, while without aeration, the formation of green rust begins to increase with DO consumption (Figure 4a). This indicated that ferrous ions oxidized rapidly under forced aeration. Very rapid oxidation is essential for feroxyhyte formation. Unlike the direct formation of feroxyhyte by rapid oxidation, green rust prefers to be transformed into the final product by dissolution and recrystallization, then magnetite is formed at a lower oxidation rate under alkaline conditions [56,63].



**Figure 4.** Effect of aeration of 0.2 L/min and no aeration on (**a**) Tl(I) removal efficiency, (**b**) dissolved oxygen (DO) concentration, and (**c**) X-ray patterns of flocculent sludge within a 20 min EC treatment under an applied current density of 16.7 mA/cm<sup>2</sup> at initial pH of 11 ± 0.1, using Fe–Fe electrodes at a distance of 2 cm.  $C_0 = 109 \mu g/L$ .

It is feasible to maintain the DO concentration by forced aeration. The DO concentration plays an important role in Tl(I) removal as it affects the distribution of different valence iron in wastewater and the crystal structure of flocs. Feroxyhyte generated by aeration-forced Fe<sup>0</sup>-EC is a key factor for the rapid and thorough removal of Tl(I). Furthermore, an additional benefit of aeration is that the bubbles help to alleviate concentration polarization and flocculation separation. It is worth noting that it is not an essential condition to apply the aeration law in this work to all EC processes. For processes relying on the reducibility of ferrous, it is unnecessary to aerate while electrolyzing [33,42]. As an important parameter of the EC process, regulation by aeration can be adapted to the removal mechanism of different pollutants.

Amid the EC treatment of the wastewater with an initial pH of 11 under non-aerated conditions, the effluent pH decreased slightly to 10.94 after 8 min, namely, before the exhaustion of DO. Yet the effluent pH increased to 11.28 after 20 min of EC treatment. The degree of hydrolysis of ferrous bivalent decreases due to the decrease of DO concentration in solution, and the deprotonation (depending on Equation (2)) process almost stops when DO is depleted [33]. That means the cathodic reaction plays a leading role resulting the increase of effluent pH even in alkaline conditions. It indicates that the EC process will lose its pH buffering effect when the DO in wastewater is depleted.

# 3.3. Effect of Applied Current Density

Current density has been considered an important factor affecting EC performance [29]. For electrodes with equal area, the amount of ferrous released from iron electrodes, according to Faraday's law, is generally proportional to the current density. The number of flocs and the bubbles derived from the cathode augment with increasing current density [64,65]. The current density determines the coagulant dosage rate and the bubble production rate, which affects the mass transfer inside the reactor [66].

At an initial solution conductivity of 7.9 mS·cm<sup>-1</sup>, current densities of 8.3, 16.7, 25, and 33.3 mA/cm<sup>2</sup> were applied to EC processes with applied voltages of 3.6, 5.5, 7.8, and 9.9 V, respectively. Figure 5

shows the effect of current densities on the removal efficiencies and residual Tl(I) concentrations. It indicates that the removal rate climbs with the increase of current density, even though the increase is smaller stepwise. After 4 min EC treatment, the Tl(I) removal rates are 85.57%, 94.57%, 96.79%, and 98.31% at the current densities of 8.3, 16.7, 25, and 33.3 mA/cm<sup>2</sup>, respectively. The cumulative removal efficiencies of Tl(I) were continuing to increase as the electrolysis continued, as illustrated in Figure 5a. For the initial Tl(I) concentration of 115  $\mu$ g/L, as shown in Figure 5b, the residual concentrations were less than 5  $\mu$ g/L after operating for 12, 6, 4, and 4 min at the current densities of 8.3, 16.7, 25, and 33.3 mA/cm<sup>2</sup>, respectively. Longer operation time is needed to meet some Chinese provincial emission standards for industrial wastewater (2  $\mu$ g/L). The residual concentrations were less than 2  $\mu$ g/L after operation for 12, 8, and 6 min at the current densities of 16.7, 25, and 33.3 mA/cm<sup>2</sup>, respectively, based on the initial Tl(I) concentration of 115  $\mu$ g/L.

With a capacity for deep purification, EC treatment has been used for purification of surface water and drinking water [36,45,67]. This capacity displays in Tl(I) removal too, as after EC processing, the residual Tl(I) concentration can be reduced to  $0.5 \mu g/L$ , or even lower with a prolonged electrolysis time.



**Figure 5.** Effect of current density on (**a**) removal efficiency, (**b**) concentration of Tl(I) within 20 min EC treatment under initial pH of  $11 \pm 0.1$ , using Fe–Fe electrodes at a distance of 2 cm. Aeration of 0.2 L/min. C<sub>0</sub> = 115 µg/L.

Sodium chloride can increase solution conductivity while minimize the energy consumption [32,33]. Wastewater samples with 0.5, 1.0, 1.5, and 2.0 g/L Cl<sup>-</sup> as the supporting electrolyte were treated at current density of 16.7 mA/cm<sup>2</sup>. The results (Figure S4) show that, the Tl(I) removal efficiency increases with the increase of Cl<sup>-</sup> concentration. This increase is likely due to a combination of the faster ion migration under higher solution conductivity and the depassivation effect of the chloride ion [29,33,68]. Nonetheless, excessive supporting electrolytes increases the risk of infringing on the emission restrictions. Based on a consideration for both energy consumption and removal efficiency, a minimum concentration of supporting electrolyte can be determined.

Energy consumption is directly proportional to the current density applied at a certain solution conductivity. When treating the water sample with the initial Tl(I) concentration of 115  $\mu$ g/L at current densities of 8.3, 16.7, 25, and 33.3 mA/cm<sup>2</sup>, the energy consumption is 0.27, 0.41, 0.58, and 0.98 kWh/m<sup>3</sup>, respectively, to reduce the residual concentration of Tl(I) to less than 5  $\mu$ g/L. Applying a current density of 16.7 mA/cm<sup>2</sup>, the energy consumption to achieve a residual Tl(I) concentration of 2  $\mu$ g/L is doubled to 0.82 kWh/m<sup>3</sup>. Another factor related to the operating costs is the consumption of sacrificial iron anodes. the iron consumption was 154.3 g/m<sup>3</sup> to achieve a residual Tl(I) concentration of 2  $\mu$ g/L with the initial Tl(I) concentration of 115  $\mu$ g/L at a current density of 16.7 mA/cm<sup>2</sup>. However, due to the rapid removal of Tl(I), the consumption of the EC treatment is acceptable compared to traditional chemical precipitation methods. The Fe<sup>0</sup>-EC treatment is likely to be a potential economical industrial application for Tl(I) removal from industrial wastewater.

Fe<sup>0</sup>-EC treatment of wastewater samples with initial Tl(I) concentrations of 66, 115, 141, and 165  $\mu$ g/L, which are within the normal concentration range, was carried out at the current density of 16.7 mA/cm<sup>2</sup> (Figure S5). This showed that the Tl(I) removal processes exhibit a similar tendency for samples with different initial concentrations. Higher initial concentration brings higher removal efficiency, which is more pronounced in the early operation stage [64,68]. Nonetheless, longer EC operation time is required to achieve the same residual concentration when treating samples with higher initial concentration. The operation times obtained by interpolation were 4.43, 5.30, 5.86, and 6.13 min after the residual concentration reached 5  $\mu$ g/L at the initial concentrations of 66, 115, 141, and 165  $\mu$ g/L, respectively.

In order to evaluate the removal effect at higher Tl(I) concentration, solutions with initial Tl(I) concentrations of 0.66, 10, and 17.3 mg/L were concocted by replenishing TlNO<sub>3</sub> (99.9%, Sigma-Aldrich) into real wastewater for further EC treatment in the same reactor. Compared with treating wastewater with initial concentrations at the microgram level, the Fe<sup>0</sup>-EC removal of milligram Tl(I) concentrations from water samples observes the same removal rule (Figure S6).

# 3.5. Removal Mechanism

Generally, iron oxides/hydroxides can remove pollutants such as heavy metals, colloidal or solid particles, as well as soluble inorganic pollutants through either complexation or electrostatic attraction [27]. Due to its low hydration energy, Tl(I) is one of the few cations with specific adsorption capacity [69]. There is obvious Tl(I) sorption onto  $\alpha$ -FeOOH at pH values of less than 9.3, the PZC of  $\alpha$ -FeOOH [70] indicated that, besides deriving exospheric complexes induced by electrostatic attraction, Tl(I) is inclined to form stable inner-sphere complexes on iron oxides/hydroxides. In addition, studies have proved that the adsorption mechanism of Tl(I) on amorphous manganese oxide also fit the inner-sphere complexes model [71].

In order to investigate the mechanism of Tl(I) removal, the adsorption characteristics of different flocs at different pH values were studied using the suspension effluent as feed water. The suspension effluents were obtained after 20 min EC treatment at an initial pH of 7 and 11. The suspension pH was adjusted by adding concentrated HCl or NaOH. As shown in Figure S7, with the decrease of pH value, the Tl(I) concentration in the effluent increased gradually, indicating that the adsorption efficiency of feroxyhyte decreases with the decrease of the pH value. Nonetheless, 60.9% Tl(I) was captured when the solution pH was lower than the PZC, which may suggest that the formation of the ligand is possible in the process of Tl(I) removal by EC treatment. Similarly, by increasing the pH of the effluent, the adsorption efficiency of lepidocrocite increased, which can be partly attributed to the electrostatic attraction.

Figure 6 shows the XPS spectra of flocculent sludge from Fe<sup>0</sup>-EC treatment of Tl-containing wastewater and blank water samples. Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$  peaks appeared respectively at 724.39 eV and 710.99 eV on both spectra in Figure 6a, showing the characteristics of Fe<sup>3+</sup> [72]. This is consistent with our chemical analysis of different valence iron contents in flocculent sludges (Table S1). It can be concluded that, amid this Tl(I) adsorption process, the chemical state of Fe did not change as the Fe 2p peaks have almost identical shape and centroid. On the spectrum (Figure 6b) of flocculent sludge collected from Fe<sup>0</sup>-EC processed wastewater, two peaks of Tl 4f, i.e., 4f7/2 and 4f5/2, appeared at 118.69 and 123.09 eV. The XPS peaks show a characteristic of Tl(I) [71], which verified the chemical state of Tl in the processing circumstances is Tl(I). It can be concluded that there is no Tl(I) that was oxidized and thereby no surface precipitation effect on the Tl removal by the Fe<sup>0</sup>-EC treatment. Figure 6c shows the O 1s peak in the range of 527–534 eV. The O 1s peak at 529.89 eV is typical for oxygen bonded to transition metal [73], namely, Fe–O in this study. The second peak at 531.24 eV can be assigned to the -OH group with higher binding energy [73]. It is observed that after capturing Tl(I), the integral area of the -OH group increased significantly. This can be attributed to the decrease of electron cloud density on oxygen, since electrons surrounding the oxygen of the deprotonated

hydroxyl were attracted by Tl(I) cations. These XPS spectra indicate the successful capturing of Tl(I) by feroxyhyte owing to the interaction of surface hydroxyl and Tl(I).



**Figure 6.** X-ray photoelectron spectroscopy (XPS) spectra of flocculent sludge obtained under applied current density of 16.7 mA/cm<sup>2</sup> at initial pH of 11: (**a**) Fe 2p core level; (**b**) Tl 4f core level; (**c**) O 1s core level.

According to the above discussion, it can be concluded that the Fe<sup>0</sup>-EC removal of Tl(I) is actualized by the combined effect of two mechanisms. Figure 7 shows the schematic diagram of the possible removal pathways of Tl(I) during the Fe<sup>0</sup>-EC process. The Tl(I) removal efficiency of both feroxyhyte and lepidocrocite is pH-dependent when treating water samples with a pH higher than the PZC, which indicates that the adsorption of Tl(I) on negatively charged FeOOH is induced by electrostatic attraction. Meanwhile, both FeOOH samples can still absorb respectively 60.9% and 22.4% Tl(I) (Figure S7) at a pH of 7 (below PZC), showing the existence of inner-sphere complexes, as proved by the XPS results.



Figure 7. Schematic diagram of the removal pathways of Tl(I) during the Fe<sup>0</sup>-EC process.

# 4. Conclusions

The Fe<sup>0</sup>-EC process with aeration can be applied for effective Tl(I) removal from real industrial wastewater. Initial pH and DO concentration were indicated to be the key operation parameters for Tl(I) removal. Iron oxyhydroxides with different crystal structure were obtained from Fe<sup>0</sup>-EC processed water with different initial pH values. A slow oxidation rate and neutral pH benefit the forming of lepidocrocite, while rapid oxidation under DO-rich conditions is the key factor for feroxyhyte formation. Nanosheet-structured feroxyhyte with large specific surface area generated in situ is an important factor for rapid and effective Tl(I)removal. The mechanism for Tl(I) removal by Fe<sup>0</sup>-EC is attributed to the combination of exospheric complexes formed by electrostatic attraction under alkaline pH and the formation of inner-sphere complexes with active groups of iron oxides/hydroxides.

The lab-scaled batch aeration-forced pump cycle EC reaction system is easily converted to continuous reaction mode. A pilot scale experiment operating in continuous mode is already under way to evaluate the industrial feasibility of Tl(I) removal from wastewater by EC technology.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/12/1/163/s1. Figure S1: Effect of electrode material on Tl(I) removal efficiency within 20 min EC treatment under applied current density of 16.7 mA/cm<sup>2</sup> with initial pH of 11  $\pm$  0.1, electrodes distance of 2 cm,  $C_0 = 109 \mu g/L$ . Figure S2: Effect of pH on Mg removal efficiency within 20 min EC treatment under applied current density of 16.7 mA/cm<sup>2</sup>, using Fe-Fe electrodes at distance of 2 cm,  $C_0 = 41.5$  mg/L. Figure S3: Effect of pH on Tl(I) removal efficiency of the as-prepared FeOOH. Adsorbent dose 0.44 g/L, agitation speed at 100 rpm for 4 hours at room temperature (25 °C),  $C_0 = 141 \,\mu$ g/L. Figure S4: Effect of Cl<sup>-</sup> concentration on Tl(I) removal efficiency within 20 min EC treatment under applied current density of 16.7 mA/cm<sup>2</sup>, initial pH of 11 ± 0.1, using Fe-Fe electrodes at distance of 2 cm,  $C_0 = 95 \mu g/L$ . Figure S5: Effect of initial Tl(I) concentration on Tl(I) removal efficiency within 20 min EC treatment under initial pH of  $11 \pm 0.1$  with aeration of 0.2 L/min, using Fe-Fe electrodes at distance of 2 cm,  $C_0 = 66$ , 115, 141, 165 µg/L, respectively. Figure S6: Removal efficiency of high Tl(I) concentration within 60 min EC treatment under initial pH of  $11 \pm 0.1$  with aeration of 0.2 L/min, using Fe-Fe electrodes at distance of 2 cm, C<sub>0</sub> = 660, 10,000 and 17,300 µg/L, respectively. Figure S7: Effect of pH on Tl(I) removal efficiency of effluent after 20 min EC treatment under applied current density of 16.7 mA/cm<sup>2</sup> with aeration of 0.2 L/min. using Fe-Fe electrodes at distance of 2 cm. Initial pH of 7 and 11, respectively. Table S1: The content of  $Fe^{3+}$  and TFe (wt.%) in flocculent sludges obtained at vary initial pH. Table S2: The specific surface area, average pore size and pore volume of flocculent sludges obtained at vary initial pH.

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