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Short Communication

One-step removal of thallium (I) from groundwater by electrocoagulation using an aluminum anode

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Thallium (Tl) contamination in groundwater is a widespread issue, and the development of an efficient treatment process is of strong interest. We present, herein, a one-step Tl(I) removal method using electrocoagulation systems. Using this method, 86.4% ± 1.0% of total Tl was removed within 60 min by an aluminum anode, with an initial Tl(I) concentration of 10 mg/L and current density of 10 mA/cm^2. The Tl removal efficiency increased with increasing current density. However, Tl removal efficiency increased first and then decreased with increasing pH in alkaline pH range. Tl(I) was partly oxidized to Tl(III) and both species precipitated with function of synchronously produced coagulants. X-ray photoelectron spectroscopy was used to analyze the recovered precipitate as well as to confirm the generation of Tl(III) and simultaneous adsorption of Tl(I). This study provides an efficient alternative for one-step Tl removal from groundwater via electrocoagulation.

Keywords: Thallium; Electrocoagulation; Aluminum anode; Groundwater

1. INTRODUCTION

Thallium (Tl), a non-essential heavy metal with high toxicity, is persistent in the ecosystem as a by-product from the extraction of iron, cadmium and zinc [1], as well as from catalytic reactions of alloys, dyes pigments, optical lenses and semiconductors [2] Deep groundwater has high contamination levels of Tl (13-1100 μg/L) within the Tl-mineralized area in southwest Guizhou Province, China [3]. Tl exposure causes serious disorders and cancers and is a serious human health threat [4]. Tl exists in two main chemical states: Tl(I) and Tl(III). Tl(I) is the most commonly found state in nature, especially in the anoxic environment of groundwater [5]. Adsorption is often involved in the removal of Tl(I) from water [6]; however, this technique suffers from high cost and possible secondary pollution during disposal of spent adsorbents. Thus, a suitable and efficient method to remediate Tl-contaminated groundwater is urgently needed.

The oxidation of Tl(I) facilitates Tl removal from the environment, as Tl(I) has a higher mobility than Tl(III) [7]. Electrochemical oxidation is a promising method, as it is environmentally friendly and efficient [8]. Our previous research realized the electrochemical oxidation of Tl(I) using a boron-doped diamond anode [9]. Large amounts of acids and subsequent coagulation/precipitation are required for total Tl removal from groundwater. *In situ* electrocoagulation can oxidize ions in aqueous solution and generate hydrocolloids that form coagulants through anodic corrosion [10]. This is the strategy we chose for our one-step removal of toxic heavy metal ions from water [11]. This technique has advantages over chemical coagulation, which uses chemical salts to induce coagulation [12]. Strongly mobile metal ions, such as As(III), have been satisfactorily removed from water by electrocoagulation [13]. However, few studies have employed electrocoagulation for Tl(I) removal in contaminated groundwater.

In this study, the feasibility of Tl(I) removal by electrocoagulation, using common aluminum (Al) and iron (Fe) anodes, was evaluated. Operating factors as current density, pH and initial Tl(I) concentration were examined for selected anode. The mechanism of action was also studied by investigating the electrochemical oxidation processes and obtained precipitates. This study provides a new perspective and method for successful remediation of Tl-contaminated groundwater.

2. MATERIALS AND METHODS

2.1 Experimental apparatus and chemicals

The configuration of the proposed system consisted of a power supply and an electrolytic reactor with copper wires connected together during the experiment. The electrolytic reactor was fabricated from a glass beaker whose working volume was 200 mL. Anode was made of high purity Al or Fe (2.5 cm × 2 cm × 0.3 cm), and graphite plate (2.5 cm × 2 cm × 0.3 cm) served as cathode. The electrode spacing was 1.0 cm. The anodes were polished by sand paper and then rinsed in 1 M HNO_3 followed by ultrapure water before every operating cycle [14]. Freshly prepared solution containing Tl(I) in the form of $TlNO_3$ was added into the reactors, and its initial pH was adjusted to 9.0 by 1 M NaOH. The glass beaker was placed on a magnetic stirrer for sufficient mixing. All other chemicals were of analytical grade and utilized without further purification.

2.2 Experimental procedure

The performances of the Al and Fe anodes were comparatively studied first. Then, different current densities (5 mA/cm^2 and 15 mA/cm^2) and initial Tl(I) concentrations (5 mg/L and 15 mg/L) were tested with the selected anode, respectively. The electrochemical processes were investigated by cyclic voltammetry (CV) test and detecting the generated active species. The contributions of active species were also identified by employing an H_2O_2 scavenger consisting of 0.1 mM EDTA-Fe(II). The coagulants produced from the same electrochemical system were collected, and their functions were also examined individually as control, by adding them to 10 mg/L Tl(I) solutions. Finally, precipitates generated during experimental process were collected by a suction filter with 0.22 μm membrane and analyzed using X-ray photoelectron spectroscopy (XPS). All experiments were carried out at room temperature (22 ± 2 ºC). Each test was repeated three times and the mean results were reported.

2.3 Analytical methods

Total Tl was determined by graphite furnace atomic absorption spectrophotometry (ASC-990, Persee, China). The concentration of Tl(III) was measured as follows: 2.5 mL sample, 1 mL HCl (2 M), 1 mL NaCl (1 M) and 20.5 mL ultrapure water were put in a 25-mL volumetric flask, which was mixed and put into a separating funnel with10 mL methylbenzene and 1 mL crystal violet (0.1%) to extract the Tl(III). The supernatant was measured by an UV–Vis spectrophotometer (DR 5000, HACH, USA) at 605 nm [15]. pH was measured using a pH-201 meter (Hanna, Italy). Concentration of hydrogen peroxide (H_2O_2) was also measured by the spectrophotometer (DR 5000, HACH, USA) at 350 nm after the sample mixed with 0.1 M potassium iodide and 0.01 M ammonium heptamolybdate tetrahydrate [16]. CV test was conducted at the scan rate of 50 mV/s using an electrochemical workstation (VMP3, Bio-Logic Science Instruments, France). Element composition of the precipitates was analyzed by XPS (AXIS-Ultra, Kratos Analytical, UK).

3. RESULTS AND DISCUSSION

3.1 Tl removals

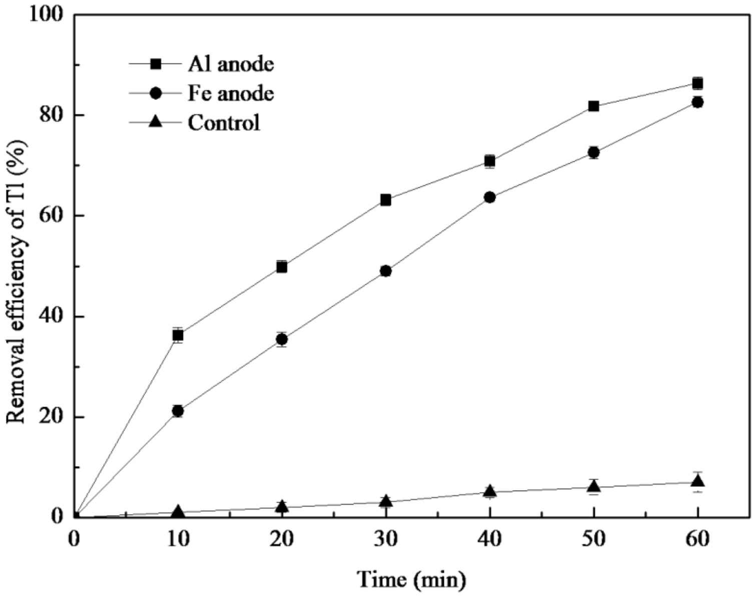
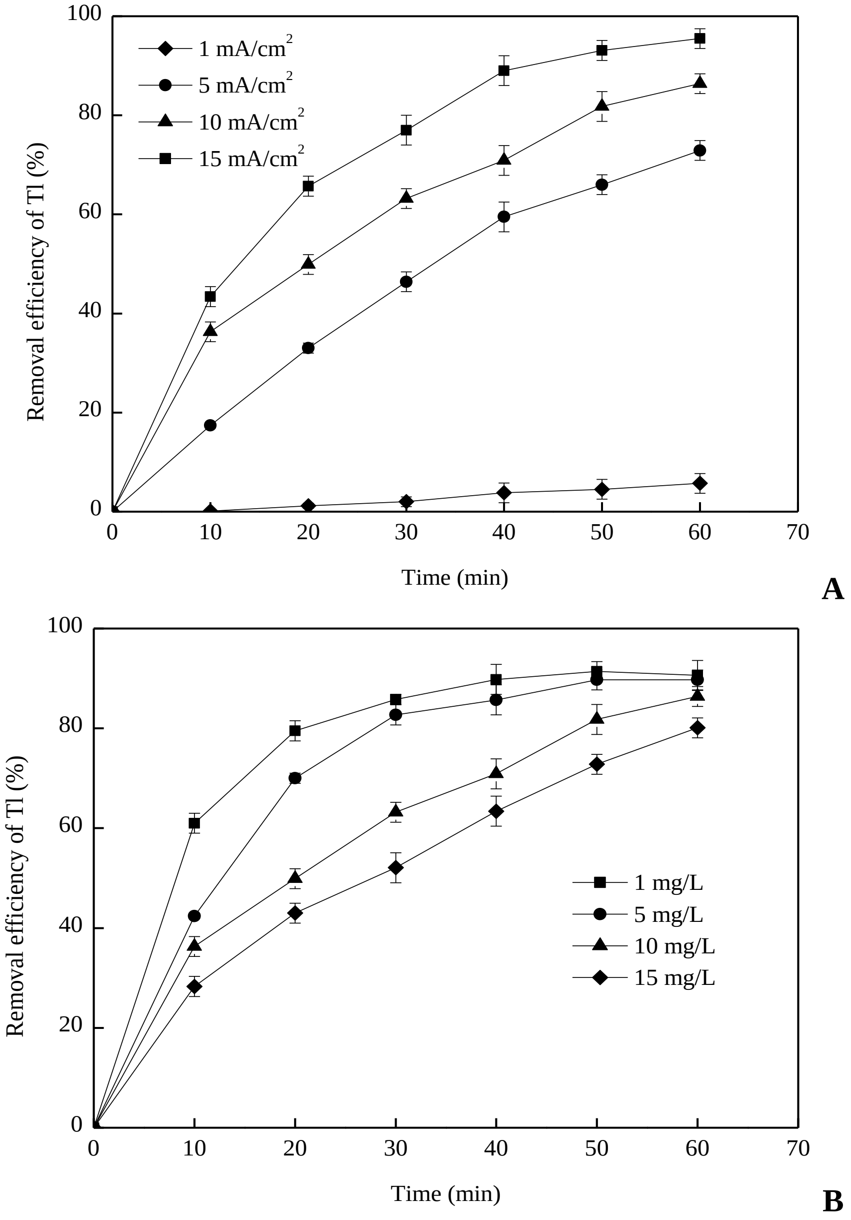


Figure 1. Tl removals with time in the electrocoagulation system with different anode materials (Al and Fe) and through coagulation by coagulants generated from the same system using Al anode with initial Tl(I) concentration of 10 mg/L and current density of 10 mA/cm^2.

With an initial Tl(I) concentration of 10 mg/L, pH of 9.0, and current density of 10 mA/cm^2, the total Tl removal was determined in the electrocoagulation system using the Al anode. After 60 min of operation, Tl removal efficiency peaked at 86.4 ± 1.0% (Fig. 1), which is higher than a study reporting Tl(I) removal using multiwalled carbon nanotubes (40% after 180 min) [17]. The anode material affected the performance of the electrocoagulation system, and the Al anode produced a higher Tl removal rate than the Fe anode (Fig. 1). This was likely because the Fe anode was partial shielded by metal deposits, decreasing the corrosion of the Fe anode surface [18]. In addition, aluminum hydroxide flocs were capable of binding more Tl, chemically or physically, than the iron hydroxide flocs [19]. Thus, the following experiments were conducted with the Al anode.



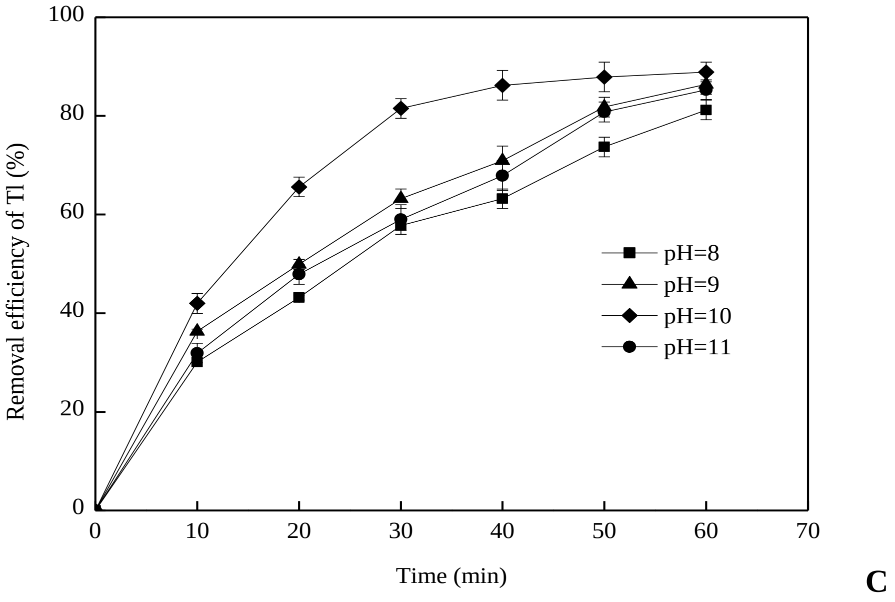


Figure 2. The influences of different operating factors on the Tl(I) removal efficiency in the electrocoagulation system with Al anode. (a) different current densities with Tl(I) concentration of 10 mg/L and pH of 9.0; (b) different initial Tl(I) concentrations with current density of 10 mA/cm^2 and pH of 9.0 and (c) different solution pH with Tl(I) concentration of 10 mg/L and current density of 10 mA/cm^2.

Tl removal efficiencies increased with increasing current densities (Fig. 2a), as higher current density resulted in a greater production of coagulants ($Al(OH)_3$), which was in favor of Tl removal [20]. Tl removal efficiencies decreased gradually with increasing initial Tl(I) concentration (Fig. 2b), as certain amounts of coagulants and oxidants were generated with the fixed current density. Tl removal efficiencies increased first and then decreased with increasing pH in the alkaline pH range (Fig. 2c). Tl(I) has a low cation hydrolysis constant, and Tl(I) adsorption will only occur under alkaline pH conditions [21]. Lower pH of the aqueous solution facilitated the generations of active species. When the pH was too high, the reaction resulted in the formation of soluble AlO_2^-, and the coagulant $Al(OH)_3$ flocs were not detected at pH >10 [22].

3.2 Mechanisms studies

After 60 min of operation, 1.22 mg/L of Tl(III) was detected in the exhausted electrolyte, with a total Tl concentration of 1.36 mg/L. This suggests the electrochemical oxidation of Tl(I) to Tl(III) took place in the electrocoagulation process. Current ranges of the CV curves for the electrocoagulation system gradually narrowed as the experiment progressed (Fig. 3), implying that the direct electrochemical oxidation did not proceed for Tl(I) oxidation. This result is consistent with that of a previous study [9].

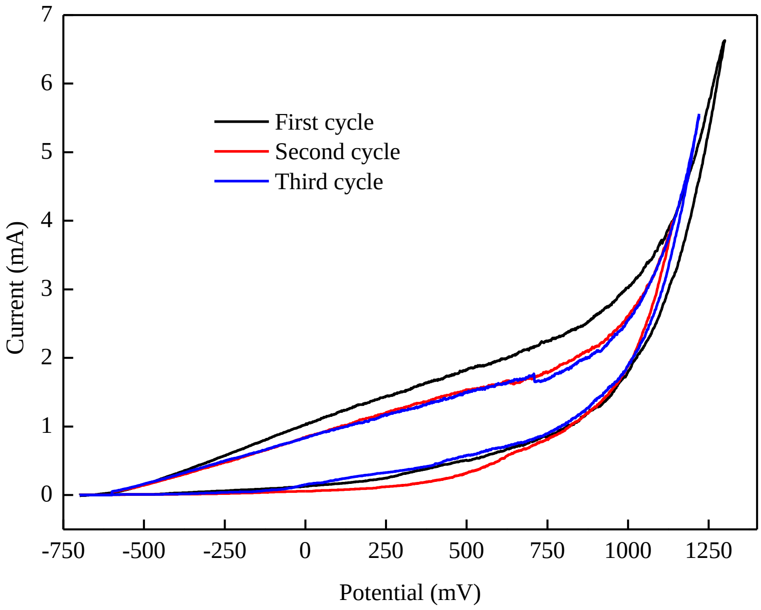


Figure 3. CV curves with Al anode in the electrocoagulation system at the scan rate of 50 mV s^{-1}.

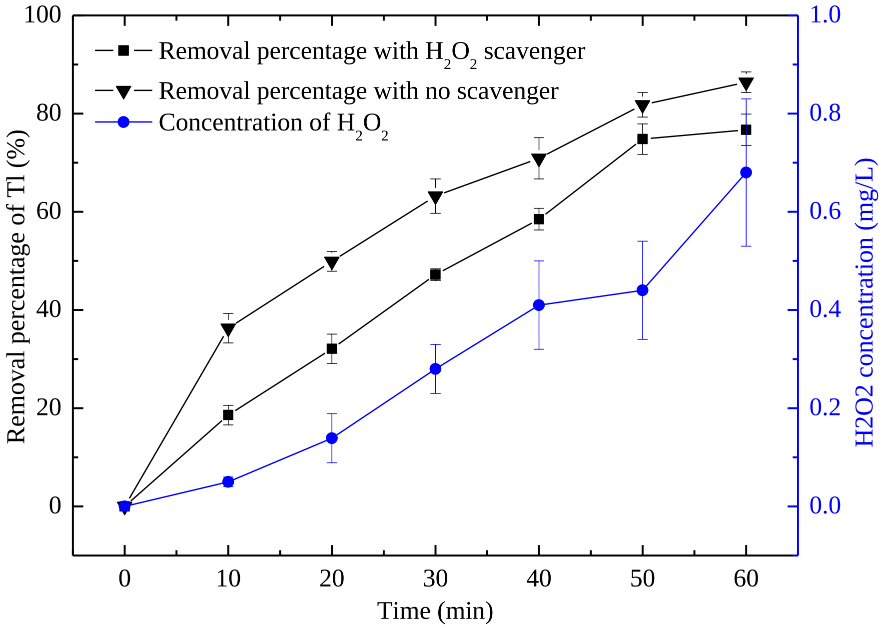


Figure 4. The concentration of H_2O_2 generated during the experiment and Tl removal efficiency with and without H_2O_2 scavenger in the electrocoagulation system with Al anode.

Active species, such as H_2O_2, were generated in the electrochemical process (Eq. 1) [23], and the concentrations of H_2O_2 increased with time in this study (Fig. 4), showing that indirect oxidation was the main pathway to oxidize Tl(I). A scavenger was also added to further specify the functions of H_2O_2 [24]. Compared to the results without the scavenger, Tl removal efficiencies decreased sharply with the addition of the H_2O_2 scavenger, indicating that H_2O_2 contributed significantly in the oxidation process (Fig. 4). The presence of Tl(I) in the electrolyte also resulted in a substantial catalytic effect on O_2 reduction, which promoted the generation of H_2O_2 in the basic solutions [25]. Similar observations were also reported for other heavy metal ion removal systems. For example, As(III) oxidation, followed by As(V) adsorption onto the metal hydroxides/oxyhydroxides, was achieved by electrocoagulation [26], and the oxidation rate was promoted by reactive intermediates, represented as H_2O_2, with air injection [27].

$$O_2 + 2e^- + H_2O \rightarrow HO_2^- + OH^- \qquad (1)$$

$$Tl^+ + HO_2^- + H_2O \rightarrow Tl(OH)_3 \qquad (2)$$

$$Al + 3OH^- \rightarrow Al(OH)_3 + 3e^- \qquad (3)$$

Moreover, the Al anode itself could also be electrochemically oxidized with the generation of coagulants (Eq. (3)). At the anode, aluminum ions are produced and then transformed to aluminum hydroxides [28]. After 6 h of operation, the pH increased from 9.0 to 9.6. The generated Tl(III) precipitated spontaneously under alkaline pH conditions [29] and simultaneously coagulated and swept by *in situ* formed $Al(OH)_3$ flocs. Some Tl(I) was also removed by the generated coagulants. These effects worked together, thus, realizing the one-step method of Tl removal from groundwater. Coagulation of Tl(I) by *in situ* generated coagulants from the same electrocoagulation system was also investigated individually as a control, and very little Tl removal occurred (Fig. 1). This further confirmed the benefits of transforming Tl(I) to Tl(III) for efficient Tl remediation.

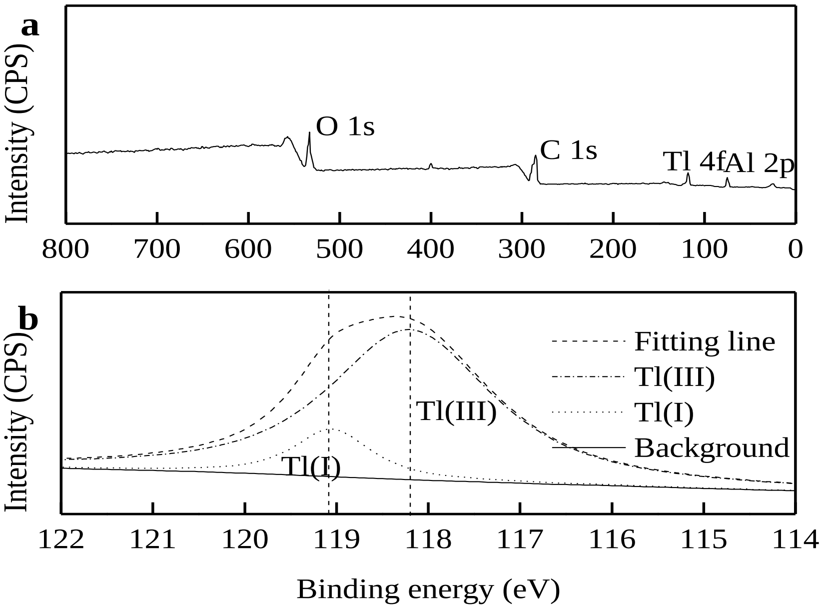


Figure 5. XPS spectra of the generated precipitate during the operation of electrocoagulation system with Al anode. (a) survey and (b) high resolution XPS spectra of Tl.

In addition, the precipitate collected from the electrocoagulation system was analyzed. The XPS spectrum showed the presence of O 1s and Al 2p, with peaks located at 531.1 eV and 74.4 eV (Fig. 5a), respectively. These peaks corresponded to $Al(OH)_3$ [30]. There was also a Tl 4f peak, with banding energy at 118.2 eV, which could be ascribed to Tl(III) [31]. High resolution of the Tl 4f peak indicated that Tl(III) was the main state of Tl in the precipitate (Fig. 5b). This suggests that Tl(I) was oxidized to Tl(III) and precipitated via the $Al(OH)_3$ flocs. The Tl 4f peak at 119.1 eV, corresponded to Tl(I), implying simultaneous Tl(I) adsorption and confirming the proposed mechanisms. As Tl(I) has higher mobility and solubility than Tl(III), with less adsorption capacity [32], pre-oxidation of Tl(I) and subsequent adsorption of Tl(III) is the most efficient means to remove Tl from groundwater [9]. This study realized Tl(I) oxidation and concomitant coagulation of oxidation products in one step; thus, the proposed electrocoagulation process shows great promise for the remediation of Tl-contaminated groundwater.

4. CONCLUSION

86.4 ± 1.0 % of Tl(I) was successfully removed in the electrolytic reactor with Al anode within 60 min. Tl removal efficiency was suppressed by the increase of initial Tl(I) concentration, while it was enhanced by the increase of current density. Tl removal efficiencies increased first and then decreased with the gradual increase of pH in alkaline pH ranges. Compared to the direct electrochemical oxidation, indirect effects by H_2O_2 played a key role for Tl(I) oxidation. The generated Tl(III) was removed by *in situ* formed coagulants $Al(OH)_3$ flocs. XPS analysis further confirmed the generation of Tl(III) and the simultaneous adsorption of Tl(I). An efficient, one-step method for the remediation of Tl-contaminated groundwater had therefore been proposed.

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