Simultaneous Removal of Thallium and EDTA by Fenton Process

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Abstract. The wastewater containing heavy metals and organic pollutants is widely discharged from industries. Because of the coexistence of heavy metals and organic pollutants, the treatment of such wastewater is very difficult. Fenton process is considered to be one of the most effective approaches for the degradation of organic pollutants in aqueous solution due to the strong oxidative ability of hydroxyl radical which generated from the Fenton process. Apart from this, heavy metals are able to be removed during Fenton process owning to the synergic effect of coagulation and precipitation. In this work, pollutants of thallium and EDTA were successfully removed via the Fenton process. A series of single-factor experiments were designed and performed to achieve an optimal reaction conditions for the removal of both thallium and EDTA. Results showed that the removal efficiencies of thallium and TOC could be as high as 96.54% and 70.42%, respectively. The outcomes from our study demonstrate that Fenton process is a promising method for the purification of wastewater containing thallium and EDTA.
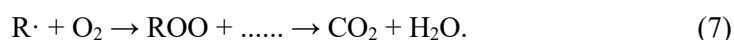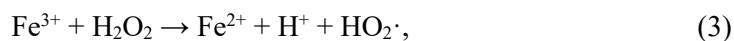
1. Introduction

Thallium (Tl) is an extremely toxic heavy metal [1, 2]. Its toxicity is known to be greatly higher than that of lead (Pb), cadmium (Cd) and mercury (Hg) [3]. Even if at low concentration, the toxic effect of thallium on the organisms is still significant, posing substantial risks to ecosystem and human health [4, 5]. A standard from US Environmental Protection Agency (USEPA) requires that the maximum contaminant level of Tl in drinking water is 2 μg/L, while a more stringent limit of 0.1 μg/L is adopted in China [6]. The release of Tl from industries (e.g., electrician industry, metallurgical industry and paper industry, etc.) often accompanied by organic pollutants, such as ethylenediamine tetraacetic acid (EDTA). In a wastewater stream, the complex of EDTA-chelated thallium exhibits much higher toxicity to environment and human because of its high mobility and recalcitrant feature [7, 8].

To remove metal-organic complex from wastewater stream, a number of techniques, such as electrolysis, photocatalysis, ion exchange and reverse osmosis [9-11], have been developed. Though these techniques have some positive outcomes, a number of significant drawbacks inevitably displayed, including poor treatment capability for organic wastewater with high concentration, high processing costs, and potential secondary pollution. Recently, Fenton's reagent method has been attracted an increasing attention in the degradation of organic contaminants in aqueous medium. The reaction mechanism of Fenton's reagent system generally involves a series of complex reactions (1)-(7)

forming hydroxyl radical ($\cdot$OH) which can effectively degrade organics and finally convert these organics into carbon dioxide (CO_2) and water (H_2O) [12].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-, \tag{1}$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH\text{-}, \tag{2}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2\cdot, \tag{3}$$

$$O_2\cdot + H_2O_2 \rightarrow O_2 + H_2O + \cdot OH, \tag{4}$$

$$H + \cdot OH \rightarrow R\cdot + H_2O, \tag{5}$$

$$R\cdot + Fe^{3+} \rightarrow R^+ + Fe^{2+}, \tag{6}$$

$$R\cdot + O_2 \rightarrow ROO + ... \rightarrow CO_2 + H_2O. \tag{7}$$

Fenton's reagent method is considered to be a reliable wastewater treatment method with many outstanding properties, such as fast reaction speed, easy to operate and environmentally friendly [13]. Fenton's reagent method has been successfully applied in treating different types of industrial wastewater, for instance, landfill leachate, dyeing wastewater, alkyl benzene and phenol wastewater [10, 14, and 15]. Owning to the strong oxidation capability of hydroxyl radical, it can be expected that Tl (I) is able to be oxidized into Tl (Ⅲ). Compared with Tl (I), Tl (Ⅲ) is much easily precipitated and thus finally removed from aqueous solution. Many efforts on the application of Fenton's reagent method to treat organic matters and generic heavy metal-organic complex have been conducted. However, to our best knowledge, the study on the simultaneous removal of both Tl and EDTA is very rare.

In the present work, we successfully employed Fenton's reagent method to eliminate both Tl and EDTA from aqueous solution. The removal efficiency of Tl and EDTA was studied under different treatment conditions such as various H_2O_2 concentration and reaction pH.

2. Materials and experimental methods

2.1. Materials
All the reagents used in this study were analytical grade and used without further purification. Thallium nitrate ($TlNO_3$) was purchased from National iron & steel research institute, China. Others were purchased from Guangzhou chemical reagent factory, China. The stock solution of (1000 mg/L) Tl (I) was obtained by dissolving $TlNO_3$ with deionized water. As to 1000 mg/L EDTA stock solution for the Fenton reaction, certain amount of $C_{10}H_{14}N_2O_8Na_2\cdot 2H_2O$ was dissolved into deionized water. The Tl (I) working solution (50 μM) and EDTA working solution (500 μM) were prepared daily by serial dilution in 40 ml solution.

2.2. Fenton reaction
All the Fenton reactions were performed in 50 ml beakers while each beaker's experimental solution was 40 ml in total. The Fenton reaction system was kept stirring on temperature-controlled stirrers and the reaction temperature was maintained at 298 K. The detailed experimental conditions of influencing factors of H_2O_2 concentration and reaction pH were described in the following sections.

2.2.1. Effect of H_2O_2 concentration
The tests were carried out in 50 ml beakers that contained 0.409 ml Tl(I) stock solution and 7.445 ml EDTA stock solution (final concentration of 50 μM and 500 μM after dilution in 40 ml solution, respectively), and then deionized water was added to 40 ml to form the synthetic wastewater. 0.24 g

$FeSO_4 \cdot 7H_2O$ (21.58 mM) was dissolved into the synthetic wastewater under continuous stirring. For the variation of molar ratio of H_2O_2/Fe^{2+} (0:1-10:1), certain amount of H_2O_2 was added. Afterward, using HNO_3 and NaOH solutions (in various concentrations) to adjust the reaction pH to be 3.5. After 2 h reaction, the final pH was adjusted to be 11 by adding Ca (OH)$_2$ powder. 10 mL final reaction solution was withdrawn by syringes and filtrated with 0.45 μm PDVF filter. Finally, 0.2 mL HNO_3 solution (50%, v/v) was added into the filtrate for preservation and further analysis.

2.2.2. Effect of reaction pH

As to the tests to study the effect of reaction pH, most of the experimental procedures were identical with those for the effect of H_2O_2 concentration. 0.24 g $FeSO_4 \cdot 7H_2O$ (21.58 mM) and 0.220ml H_2O_2 (53.96 mM) were dissolved into the synthetic wastewater. For the variation of pH, we used HNO_3 and NaOH solutions (in various concentrations) to adjust reaction pH values in the range of 2.0-7.0.

2.3. Evaluation of removal efficiency

Tl concentration was determined by an atomic absorption spectrometer (Thermo Scientific, USA). The content of EDTA is expressed by measuring the concentration of TOC. The TOC was determined by a liqui TOCII spectrometer (Elementar, Germany). The removal rate η (%) of Tl and TOC was calculated by the following equation:

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\% \qquad (8)$$

Where C_0 and C_e (mg/L) are the initial and equilibrium Tl (or TOC) concentrations of the working solutions, respectively.

3. Results and discussion

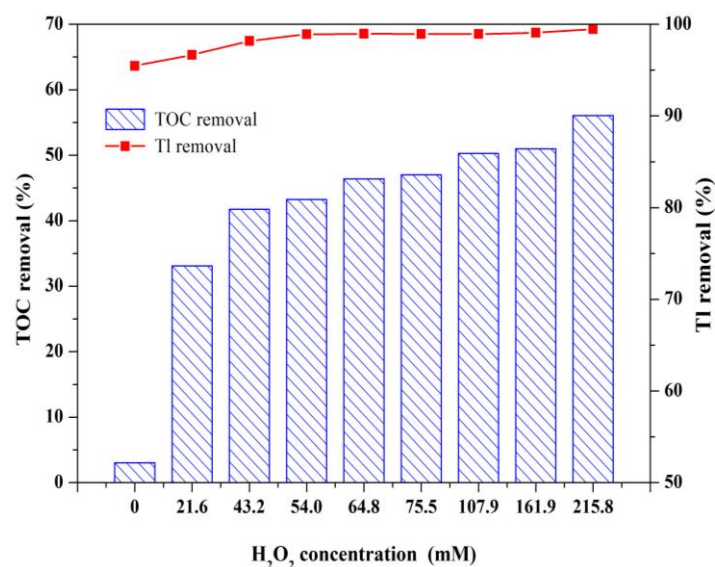### 3.1. Effect of H_2O_2 concentration on Tl and EDTA removal

Fig.3-1 showed the effect of H_2O_2 concentration on the removal rate of Tl and EDTA via Fenton process. It can be seen that H_2O_2 concentration was of little effect on the Tl removal rate, as only 4% removal rate of Tl increased (from 95.5% to 99.5%) when the dosage of H_2O_2 concentration increased from 0 to 215.8 mM. The removal of Tl is most likely due to the processes of precipitation, adsorption and coagulation. With a certain amount of Fe^{2+} in the solution, Ca (OH)$_2$ was employed to adjust the flocculation pH so that Tl was effectively removed via adsorption and coagulation. On the other hand, as for the removal rate of TOC, by increasing H_2O_2 concentration, the removal rate of TOC tended to increase rapidly but slow down under the conditions with high H_2O_2 concentrations (Fig. 3-1). With a high amount of H_2O_2 in the solution, more $\cdot OH$ will be generated because of the combination of H_2O_2 and Fe^{2+}. Thus, the organic matter can be oxidized and degraded effectively, achieving a higher removal rate of TOC. The amount of H_2O_2 significantly affects the oxidation effectiveness of Fenton process. In the case of with very high concentration of H_2O_2, the excess H_2O_2 in the system would react with $\cdot OH$ to produce $HO_2\cdot$, shown as the following equations (9)-(10). These reactions would result in invalid decomposition of H_2O_2 [16] thus inhibiting the generation of $\cdot OH$ and reducing the oxidation efficiency.

$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O, \qquad (9)$$

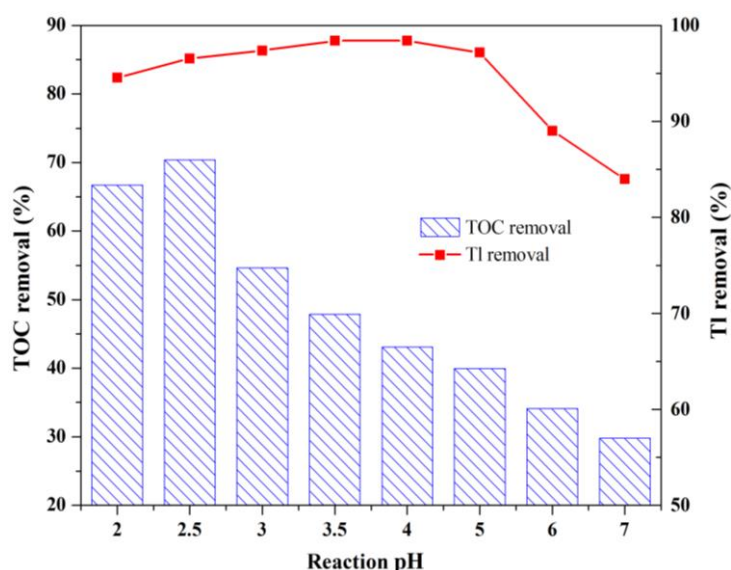$$\cdot OH + HO_2\cdot \rightarrow H_2O + O_2. \qquad (10)$$

3.2. Effect of reaction pH on Tl and EDTA removal

Fig.3-2. showed the effect of reaction pH on the removal rate of Tl and EDTA via Fenton process. Reaction pH affected directly the mechanism of oxidation and was remarkably influenced Tl and EDTA removal. When there was a change in the pH of the solution, the rate of production of hydroxyl

radical would be influenced. At low pH, the generation of ·OH is favored and thus the degradation of EDTA and the removal of Tl are effective. When pH=2.5, TOC got a maximum removal rate of 70.42% and Tl removal rate of 96.54%. However, with reaction pH increased, the generation of ·OH is tended to be inhibited due to the interaction between Fe^{2+} and H_2O_2. When pH is larger than 3.5, a portion of Fe^{2+} would convert into Fe^{3+} and then reacted with OH^- to form Fe $(OH)_3$. This process would invalidate the catalytic actives of Fenton system [17]. While pH is above 5.0, H_2O_2 would decompose into H_2O and O_2, which further impeded the Fenton reaction [18]. The reaction rates of Fenton process were much faster in acidic medium than that in alkaline medium.

Figure.3-1. Effect of H_2O_2 concentration on the removal rate of Tl and EDTA by Fenton process (Reaction conditions: initial Tl concentration: 50 μM, initial EDTA concentration: 500 μM, Fe^{2+} dosage: 21.58 mM, reaction pH: 3.5, reaction time: 2 h, flocculation pH: 11.0).

Figure.3-2. Effect of reaction pH on the removal rate of Tl and EDTA by Fenton process (Reaction conditions: initial Tl concentration: 50 μM, initial EDTA concentration: 500 μM, Fe^{2+} dosage: 21.58 mM, H_2O_2 dosage: 53.96 mM, reaction time: 2 h, flocculation pH: 11.0)

4. Conclusions

This study successfully demonstrated that both Tl and EDTA were effectively removed by a Fenton process. The optimum processing conditions for Tl and EDTA removal was 53.96 mM H_2O_2 and reaction pH of 2.5. The removal efficiencies of Tl and TOC were 96.54% and 70.42%, respectively. The removal mechanism of Tl is mainly due to the oxidation, adsorption, coagulation and precipitation process and the removal mechanism of EDTA is mainly ascribed to the strong oxidation capability of newly generated hydroxyl radical in the Fenton process.

5. Acknowledgment

6. References

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