Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23805

154 (2019) 166–176
June

Efficient removal of thallium and EDTA from aqueous solution via the Fenton process

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Received 28 July 2018; Accepted 17 January 2019

ABSTRACT

As a common chelating agent, ethylenediaminetetraacetic acid (EDTA) can form stable chelates with toxic metals. Such metal–EDTA complexes are of chemical stability, which poses a challenge to their removal from contaminated water/wastewater. In this study, simultaneous removal of toxic heavy metal thallium (Tl) and EDTA using the Fenton process was investigated for the first time. Influencing factors including the molar ratio of $[Fe^{2+}]/[H_2O_2]$, H_2O_2 dosage, pH and reaction time on the removal performance of Tl and EDTA were examined. Over 98% of Tl and 62% of total organic carbon (TOC) can be removed under optimized conditions: $[Fe^{2+}]$ of 21.6 mM, $[H_2O_2]$ of 54.0 mM, reaction pH of 2.5, reaction time of 5 h and flocculation pH of 10.0. After treatment, an increase in ammonium nitrogen was clearly observed, which was mainly due to the cleavage of C–N and N–N bonds of EDTA. The single-factor experiments and the analyses of FT-IR, SEM-EDS and X-ray photoelectron spectroscopy spectra reveal that the removal of Tl and EDTA was mainly attributed to the synergistic effects of Fenton oxidation, surface complexation, coagulation, precipitation and co-precipitation. The findings of this study indicate that the Fenton process is a facile, effective and promising technique for Tl and EDTA removal from water/wastewater.

Keywords: Thallium; EDTA; Fenton; Heavy metals; Advanced oxidation process

1. Introduction

Water contamination due to the release of metal ions and organic contaminants from industries has become a worldwide environmental problem. Thallium (Tl) is well known to be an extremely toxic heavy metal [1,2], and it is more poisonous than many other heavy metals such as cadmium (Cd), zinc (Zn) and lead (Pb) [3,4]. Exposure to Tl could result in hair loss, muscle atrophy, kidney damage and even death [5]. The toxicity of Tl on the organisms is substantially remarkable even at a low concentration [6,7]. Wastewater containing Tl was mainly generated from alloy manufacturing, mining process [8] and the industrial application of pigments and dyes [1,9]. The release of Tl-containing wastewater into the natural environment poses significant risks to human health. To minimize Tl pollution impacts, China adopts a stringent maximum contaminant level for drinking

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water, namely 0.1 μg L^{-1}, which is 20 times lower than that established by the U.S. Environmental Protection Agency [9,10]. However, the removal technology of Tl is much less studied in comparison with the As, Cd, Hg and Pb [11,12]. It is urgent to develop effective Tl removal techniques for water/wastewater [13].

Ethylenediaminetetraacetic acid (EDTA) is a strong chelating agent widely used in many industries such as metallurgy, mining and electroplating [14–16]. EDTA becomes a potential danger when it forms extremely stable complexes with toxic heavy metals, and such metal–EDTA chelates are commonly of high mobility, chemical stability and recalcitrant nature. Once wastewater is polluted with both Tl and EDTA, it may cause significant environmental problems. In addition, metal–EDTA chelates would complicate the treatment of contaminated waters by reducing the removal efficiency of heavy metals [17,18]. Simultaneous removal of heavy metals and organic pollutants in wastewater stream can not only protect the environment but also prevent the exposure of toxic contaminants to human. Therefore, the effective removal of both Tl and EDTA prior to discharge is of vital importance.

Currently, common methods such as ion exchange and precipitation [19] are invalid in treating metal–EDTA due to its high stability and mobility. A number of techniques such as photocatalysis [20], microelectrolysis [21], ozonation [16] and other combined technologies have been developed to remove metal–organic chelates from aqueous medium. Although these treatment methods are effective in some cases, they are largely hindered due to relatively high cost, complex process, chemical toxicity and poor selectivity. Advanced oxidation processes (AOPs) using strong oxidants have potential to reliably and effectively remove EDTA and its metallic complexes from aqueous solution [22]. Among the AOPs, the Fenton process has attracted growing attention because of its high efficiency in degradation of refractory organic pollutants in aqueous media [22–24]. Fenton's reagents can generate strong oxidants such as hydroxyl radical ($^{\bullet}OH$), which can degrade a wide variety of organic and inorganic contaminants [25,26] (Eq. (1)). Hydroxyl radical is well known to be a strong oxidant with a standard oxidation potential of 2.8 V, which can effectively destroy organics and eventually degrade them into CO_2 and H_2O (Eqs. (2) and (3)) [27].

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

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \tag{2}$$

$$R^{\bullet} + O_2 \rightarrow ROO^{+} \rightarrow CO_2 + H_2O \tag{3}$$

The Fenton process is a mature wastewater treatment technique showing the advantages of simple operation, strong oxidability and high efficiency [28,29]. The Fenton process has been widely employed in the treatment of various types of wastewater streams, such as landfill leachate [30], phenol wastewater [31] and dyeing effluents [32–35]. The strong oxidant of $^{\bullet}OH$ is non-selective reactive oxygen species for the rapid degradation of organic contaminants [18], thus it might have potential to degrade the Tl–EDTA complexes via Fenton process. Additionally, the coagulation process that occurs in the latter phase of the Fenton process, may probably contribute to an enhanced removal of Tl. It is known that Tl(III) is much more easily precipitated and then removed from aqueous medium than Tl(I) [36]. The key in this study is to break down the bonds between metals and organics in the complexes, after that, aqueous Tl can be oxidized and precipitated and then removed via the coagulation by iron hydroxide; while EDTA can be degraded via oxidation by $^{\bullet}OH$. Researchers have used the Fenton's reagents to successfully achieve effective treatment of metal–organic complexes [20,21]. However, to the best of our knowledge, little information is available on using the Fenton process for the treatment of Tl–EDTA. The feasibility and mechanism of the Fenton process for simultaneous removal of Tl and EDTA from wastewater stream are of great interest.

In this study, we first and successfully applied the Fenton process to effectively remove Tl and EDTA from aqueous solution. The removal performance of Tl and EDTA was studied under different experimental conditions (e.g., the molar ratio of $[Fe^{2+}]/[H_2O_2]$, H_2O_2 dosage, pH, EDTA/Tl molar ratio and reaction time). Scanning electron microscope equipped-energy dispersive spectrum (SEM-EDS), Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) were used to unravel the mechanism of efficient removal of Tl and EDTA via the Fenton process.

2. Materials and methods

2.1. Reagents and solutions

All reagents used were of analytical grade and used as received from the suppliers. The $TlNO_3$ was purchased from Sigma-Aldrich, USA. The other reagents were purchased from Guangzhou chemical reagent factory, China. All the solutions were prepared with deionized water. Aqueous stock solutions of Tl(I) and EDTA of 1,000 mg L^{-1} were prepared by dissolving the appropriate amount of $TlNO_3$ and EDTA($C_{10}H_{14}N_2O_8Na_2{\cdot}2H_2O$) in deionized water, respectively. The working solutions of 50 μM Tl(I) and 500 μM EDTA were prepared daily by serial dilution.

2.2. Experimental procedures

All the Fenton reactions were performed in a series of 50 mL beakers with 40 mL mimic wastewater stream containing Tl(I) and EDTA. The typical Fenton treatment includes two stages, namely, the initial oxidation and the latter coagulation. In the oxidation stage, a given amount of Fe^{2+} and H_2O_2 were added into the mimic wastewater under continuous magnetic stirring for a given reaction time. Then in the coagulation stage, after oxidation, the solution pH was adjusted to a designated value and was sustained for another 30 min. Take the experiments on the effect of dosage of Fenton's reagents, for example, first, a designated amount of Fe^{2+} and H_2O_2 were added, then the initial pH for the reaction was adjusted to 3.5 with diluted H_2SO_4 or NaOH aqueous solution. After 2 h reaction, the value of final pH was adjusted to 11.0 by adding a certain amount of $Ca(OH)_2$.

Then the solution was stirred for 30 min to maintain the final pH at 11.0. At the end, 10 mL supernatant was withdrawn and filtrated with 0.45 μm pore size filter. Finally, 0.1 mL HNO_3 solution was added for preservation and made ready for analysis. The experiments on other influencing factors were almost analogous to the above example. All the experiments were repeated three times under identical conditions and the data are presented as the mean values and standard deviation of the as-obtained results. For all the samples, the removal performance of Tl and total organic carbon (TOC) was examined.

To gain more insights into the role of various factors in the oxidation/coagulation for simultaneous removal of Tl and EDTA, a batch of single-factor tests (seven runs in total) in which the reaction pH, Fe^{2+} dose, H_2O_2 dose and coagulation pH was deliberately designed. Reaction pH of 3.5 and reaction time of 2 h were used. Other factors such as Fe^{2+} dose, H_2O_2 dose and flocculation pH were considered or not to confirm their role in the removal of Tl and organics. The details on the reaction conditions and experimental results are given in Table 1.

2.3. Analytical methods

The concentration of Tl was measured by a flame atomic absorption spectrometry (Thermo Scientific, USA). A TOC analyzer (liqui TOC II, Elementar) was used to determine the concentration of TOC in the aqueous solution. The removal efficiency η (%) of Tl and TOC was calculated from the following equation:

$$\eta = \frac{\left(C_0 - C_e\right)}{C_0} \times 100\% \tag{4}$$

where C_0 and C_e (mg L^{-1}) are Tl (or TOC) concentrations at initial and at equilibrium, respectively.

The concentration of NO_3–N and NH_3–N was determined by an UV–Vis spectrophotometer (UV 752, China) to understand the fate of nitrogen species during the Fenton process. FT-IR spectra were recorded on a Tensor27 FT-IR meter (Bruker, Germany) to obtain the information of chemical bonds of the precipitates. For FT-IR test, the precipitates were pelletized with an appropriate amount of dried KBr powder. SEM images and EDS analyses were taken by a JSM-7001F (JEOL, Japan) microscope to observe the microstructures and morphologies of the precipitates. XPS was conducted using a monochromatic Al Kα radiation (1,486.6 eV) to provide chemical state information of the elements of the collected precipitates. All binding energies were referenced to C 1s peak at 284.6 eV [37]. The software XPSPEAK4.1 was used to fit all the XPS spectra.

3. Results and discussion

3.1. Dosage of the Fenton's reagents ($[Fe^{2+}]/[H_2O_2]$)

In the Fenton process, the dosage of H_2O_2 and Fe^{2+} is one of the most critical parameters that significantly affect the operation cost as well as the efficacy [28]. As can be seen from Fig. 1a, by increasing the dosage of Fe^{2+} (fixed molar ratio of $[Fe^{2+}]/[H_2O_2]$ is 0.4) from 3.6 to 7.2 mM, the removal efficiency of Tl increased from 76.4% to 93.4%. When the dosage of Fe^{2+} reached 21.6 mM, the Tl removal was 99.2%, which is 6% higher than that of Fe^{2+} dosage at 7.2 mM. Upon the Fe^{2+} dosage exceeding 21.6 mM, the Tl removal remains at a high level (≥99.2%), indicating that the Fenton process can effectively remove Tl from aqueous solution when a suitable dosage of Fenton's reagents was used. It is noted that some TOC removal (i.e., 31%–45%) can also be achieved, implying that organic pollutants were partially degraded due to the generation of •OH. Furthermore, sufficient iron hydroxide would be generated in-situ [38] so that Tl was able to be effectively removed by coagulation process. Tl is reported to be captured by iron hydroxides when the solution pH is above 10 [39]. Our experimental results are in line with that report. The obtained desirable results demonstrate the effectiveness of the Fenton process to remove both Tl and EDTA from aqueous solutions. It should be noted that excess addition of the Fenton's reagents will generate a great amount of Fe-bearing sludge [40]. Therefore, from the economic and environmental aspects, the Fe^{2+} dosage of 21.6 mM and H_2O_2 concentration of 54.0 mM were considered as optimum dosage for the treatment of Tl and EDTA in the wastewater stream in this study.

3.2. Effect of H_2O_2 dosage

Fig. 1b shows the removal of Tl and TOC by the Fenton process with the addition of different amounts of H_2O_2. The

Table 1
Results of the single-factor tests on the Fenton process for Tl and EDTA removal

Group	Tl (μM)	EDTA (μM)	Fe^{2+} (mM)	H_2O_2 (mM)	Reaction pH	Flocculation pH	Tl removal (%)	TOC removal (%)
1	50	500	0	0	3.5	Unadjusted	2.12	0.63
2	50	500	0	54.0	3.5	Unadjusted	10.75	5.25
3	50	500	21.6	0	3.5	Unadjusted	12.30	2.92
4	50	500	0	0	3.5	11.0	44.73	2.03
5	50	500	0	54.0	3.5	11.0	48.20	6.25
6	50	500	21.6	54.0	3.5	Unadjusted	60.86	78.14
7	50	500	21.6	54.0	3.5	11.0	98.99	39.37

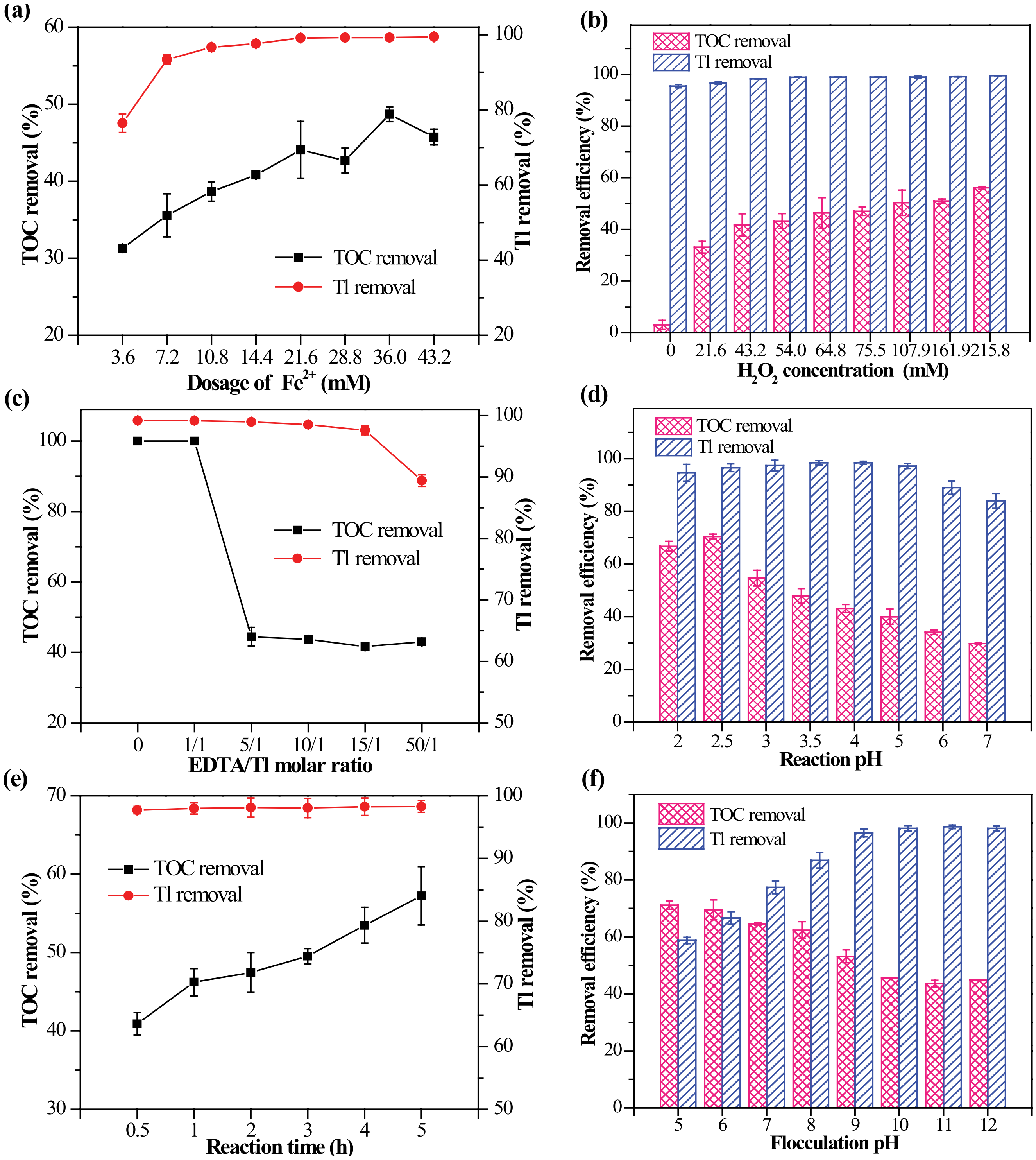

Fig. 1. Removal of Tl and EDTA by the Fenton process: effects of (a) Fe^{2+} dosage, (b) H_2O_2 concentration, (c) EDTA/Tl molar ratio, (d) reaction pH, (e) reaction time and (f) flocculation pH. Error bars represent standard deviation value (n = 3).

variation in the dosage of H_2O_2 was of little effect on the removal of Tl. In the absence of H_2O_2, the iron hydroxides exhibited strong affinity to Tl(I), which is consistent with the previous report [36]. Upon the increase in H_2O_2 dosage from 0.0 to 215.8 mM, the Tl removal efficiency only increased 4% (from 95.5% to 99.5%; Fig. 1b). This implies that the removal of Tl is mainly due to surface complexation, followed by the oxidation, precipitation, coagulation and co-precipitation [39]. On the other hand, the dosage of H_2O_2 shows a great impact on the degradation of TOC [41], as evidenced by substantial increases in the removal of TOC (Fig. 1b). The higher amount of H_2O_2 dosed, the more •OH generated.

Such that the organic contaminants were more effectively oxidized and then degraded [42]. At high dosage of H_2O_2, the excess H_2O_2 in the system acted as a scavenger of $^\bullet OH$ [29], producing $HO_2^\bullet$ (Eqs. (5) and (6)) which is less reactive than $^\bullet OH$ [43,44], thus lowering the oxidation efficiency. The highest TOC removal efficiency was only 56.1% even the H_2O_2 dosage was as high as to 215.8 mM, suggesting that overdose of H_2O_2 is unnecessary.

$$^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{5}$$

$$^\bullet OH + HO_2^\bullet \rightarrow H_2O + O_2 \tag{6}$$

3.3. Effect of EDTA/Tl molar ratio

The effect of EDTA/Tl molar ratio on the decomplexation of Tl complexes by the Fenton process was investigated. When the molar ratio of EDTA/Tl was lower than 1, nearly complete removal of Tl and TOC was achieved (Fig. 1c). The variation in the Tl removal was insignificant when the molar ratio of EDTA/Tl was below 15, suggesting that the organic matter concentration was of little impact on Tl removal at this range of EDTA/Tl molar ratio. When the molar ratio of EDTA/Tl increased from 15 to 50, the Tl removal efficiency only declined by 10%. The effective removal of Tl is ascribed to the synergistic effects of surface complexation, oxidation, precipitation and coagulation [36]. The TOC removal just slightly decreased by 1.5% (from 44.5% to 43.0%) when the molar ratio of EDTA/Tl increased from 5 to 50, further implying that an acceptable degradation efficiency of TOC by the Fenton process can be maintained [29]. To fully degrade the target organic pollutants, it generally requires more input of oxidants or extension of reaction time because most of organic macromolecular compounds were first decomposed into small-molecule intermediate products. The TOC removal efficiency cannot be efficiently removed at high molar ratios of EDTA/Tl likely due to insufficient $^\bullet OH$ for oxidation of the excess amount of EDTA in the reaction system.

3.4. Effect of reaction pH

The reaction pH is one of the most important processing parameters for the Fenton process [45] since it can significantly affect the decomposition rate of H_2O_2 and the speciation of Fe in aqueous solution, as well as the activities of the substrates and oxidants [28]. The pH directly affects the production rate of $^\bullet OH$ and the oxidation mechanism. As can be seen from Fig. 1d, the reaction pH exerts significant effects on the removal of TOC. At low pH (from 2.0 to 3.0), the generation of $^\bullet OH$ is favorable and therefore the oxidation of Tl and degradation of EDTA are of effectiveness. A maximum TOC removal efficiency of 70.4% was observed at pH 2.5, which is in good agreement with the results of other studies on the oxidation of organic compounds in wastewater stream [28,46]. However, with the increase in the reaction pH value, the generation of $^\bullet OH$ tended to be inhibited markedly because of the less effective interaction between Fe^{2+} and H_2O_2. When the reaction pH was higher than 3.5, more Fe^{2+} would get converted into Fe^{3+} and then react with OH^- to form $Fe(OH)_3$ precipitate, which would reduce the catalytic activity of the Fenton system [38]. While the pH was higher than 5.0, H_2O_2 would decompose into H_2O and O_2 and therefore produce less amount of $^\bullet OH$. As a result, it could further impair the efficacy of the Fenton system [29,47]. The standard redox potential of $^\bullet OH$ was reported to be 2.8 V in acid solution and 1.8 V in neutral solution [48], suggesting the reaction rate of the Fenton process was much more rapid in acidic medium than in neutral or in alkaline medium. The increment in TOC removal efficiency observed as pH decreased further provides the evidence on the enhanced TOC removal under classic acidic pH conditions.

3.5. Effect of reaction time

Fig. 1e shows the effect of reaction time on the removal efficiencies of Tl and TOC in the reaction system. About 97.7% of Tl was removed at a reaction time of 0.5 h. By prolonging the reaction time, the removal efficiency of Tl remained at a high level (Fig. 1e), indicating that the Fenton process is efficient on the removal of Tl from aqueous solution even within a short treatment time. The enhancement due to extending reaction time was very limited, as the surface complexation and oxidation have nearly reached a saturation point. Nonetheless, for the removal of EDTA, the reaction time should be extended as an increase in TOC removal was observed. The removal efficiency of TOC increased from 40.9% to 57.2% when the reaction time prolonged from 0.5 to 5 h, indicating that the intermediates of EDTA were further degraded as reaction time was extended [28]. In order to achieve a higher degree of mineralization of organic pollutants, extending the reaction time is an alternative. It should be noted that the degradation of TOC by the Fenton process can be well described by pseudo-first-order kinetic model (R^2 of 0.96, shown in Fig. S1), which is consistent with previous study [49].

3.6. Effect of flocculation pH

As shown in Fig. 1f, the flocculation pH affects remarkably on the removal of Tl and TOC. As the flocculation pH increased, Tl was increasingly removed while the TOC removal progressively decreased. It has been reported that iron hydroxides can strongly adsorb Tl under alkaline conditions (pH > 10) [36,39], which has been further confirmed in our study. Theoretical calculation has implied that only a combination of strong oxidation and high pH can lead to oxidation of Tl(I) to Tl_2O_3 [50]. The observation of enhanced removal performance of Tl at a higher pH in this study is consistent with the aforementioned theoretical calculation. However, when the flocculation pH was increased from 2 to 12, the removal efficiency of TOC decreased by 26.2%. It is likely that the inhibition of $^\bullet OH$ generation under high pH levels resulted in the decline in TOC removal (by ~40%). Another explanation is that the intermediates of the EDTA is negatively charged, which is effectively adsorbed at acidic conditions but poorly adsorbed at alkaline environment to the iron hydroxide colloids.

3.7. Roles of single-factor on Tl and EDTA removal

A series of experiments were performed to examine the roles of single-factor on the removal of Tl and EDTA

(Table 1). In Groups 1, 2 and 3, the removal of Tl and TOC were poor, because Tl and EDTA cannot be well removed without hydroxyl radicals formed via the Fenton's reagents. Furthermore, the pH in these three groups was not adjusted for coagulation. The small amount of TOC removed in Group 2 was most likely due to the limited oxidative degradation by H_2O_2 itself, the small amount of Tl removed in Group 3 might be due to the coagulation and surface complexation by Fe(II)/Fe(III) colloids [51]. In Groups 4 and 5, the Fenton reaction was not successfully triggered because of the lack of Fenton's reagents, the resulted removal of Tl was more than 40%. This is because that the elevation of pH and the addition of $Ca(OH)_2$ powder can contribute to a low removal of Tl via coagulation or precipitation. Compared with the high Tl removal under high pH with iron hydroxides, the $Ca(OH)_2$ colloids have much lower affinity to Tl than the Fe(III) colloids. In Groups 6 and 7, conventional Fenton process was applied. However, the flocculation pH was adjusted to alkaline only in Group 7. The TOC removal efficiency of Group 6 (78.1%) was much superior in comparison with that of Group 7 (39.4%). While the removal efficiency of Tl is much lower in Group 6 than that in Group 7. Such phenomenon is consistent with the results obtained in the experiment about the effect of flocculation pH (Section 3.6). These tests can provide important information in the Fenton process that the iron hydroxides and alkaline condition (pH > 10) are vital for Tl removal, and that the addition of H_2O_2 is essentially important to the oxidation and degradation of EDTA. In addition, the results from Group 6 further indicate that most of the intermediates of the EDTA might be negatively charged, which is effectively adsorbed at acidic conditions.

3.8. Fenton degradation of organic pollutant

In the blank group, the content of ammonia nitrogen was 0.36 mg L^{-1}, while a much higher content of 14.8 mg L^{-1} (1.06 mmol L^{-1}) in the experimental group was observed. The concentration of EDTA in the system was 0.5 mM and the theoretical concentration of ammonia nitrogen should be 1 mM. The detected concentration of ammonia nitrogen was very close to the theoretical value, suggesting that almost all the nitrogen bonds have been broken down. Most of the organic macromolecular compounds tended to be oxidized into small-molecule organic compounds by the Fenton reaction. The $^{\bullet}OH$ generated in the Fenton process can lead to the breakdown of the bonds between EDTA and Tl, leading to the breakage and degradation of EDTA [38]. The C–C and C–N bonds of the main chain of EDTA were destroyed and dehydrogenated to produce small-molecule intermediates (Fig. 2). After that, due to the instability of these intermediates and strong oxidizing property of $^{\bullet}OH$, some of them could be further oxidized and eventually converted into CO_2 and H_2O [52,53]. In the early stage of the Fenton process, the oxidative oxygen species such as H_2O_2, $^{\bullet}O_2$ and $^{\bullet}OH$ were produced and present in a high concentration, thus the oxidation rate was generally very fast. However, the amount of these oxidative components would gradually decrease as the reaction proceeded. As a result, the oxidation capacity of the reaction system tended to decline, resulting in incomplete degradation of large-molecular organic matters in the reaction system. The incomplete degradation would produce a number of intermediates such as formic acid, oxalic acid and other small-molecules organic matter in the solution [49]. Previous study shows that the $^{\bullet}OH$ is relatively difficult to degrade the small-molecules organic including organic acids [54], which explains the high residual TOC concentration in the effluent.

3.9. Mechanism of Tl and TOC removal by Fenton process

The morphology and composition of the precipitates were examined, in order to gain more insights into the degradation mechanism. The blank group (Fig. 3a) shows that the resulted precipitates of the Fenton process were nanoparticles of irregular spheres, and the XRD results confirm that the mineral phase of these precipitates is FeOOH (PDF no. 29–3713), shown in Fig. S2. The surface structure of the precipitates in blank group was porous. While after Fenton reaction with Tl–EDTA, the voids between the particles were filled up and the surface became quite smooth (Fig. 3b). It is most likely because the Tl is adsorbed onto the iron hydroxides and oxidatively precipitated under the alkaline condition [55]. Meanwhile, EDTA was degraded into small-molecule organic compounds. Some of these small-molecule organic compounds interacted with flocculation precipitates and were finally removed via coagulation and adsorption [56]. Others were further degraded into H_2O and CO_2. The EDS spectra show that Tl was successfully adsorbed onto the precipitates since the Tl content remarkably increased in the experimental group (Fig. 4). In addition, the elemental mapping of the precipitates of the Fenton system has been provided (Fig. S3), and Tl can be obviously found after Fenton reaction (Fig. S3e).

Compared with the blank group, the experimental group showed a significant change in the FT-IR spectra (Fig. 5a). The wide (3,810–3,315 cm^{-1}) and maximum adsorption

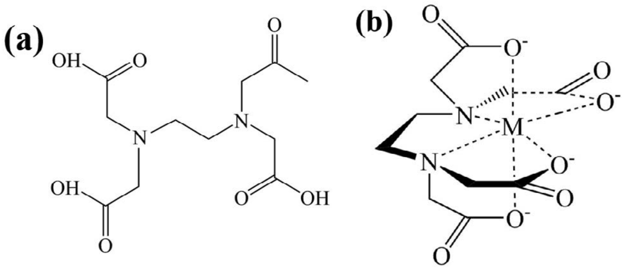

Fig. 2. Structure of (a) EDTA and (b) metal–EDTA complex.

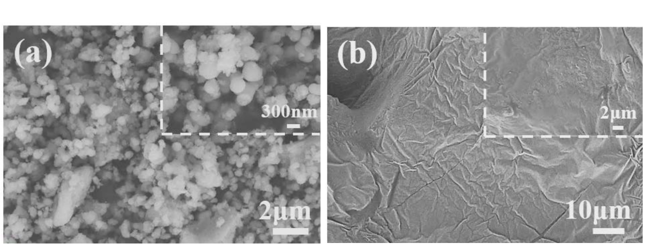

Fig. 3. SEM images for the precipitates of the Fenton process (Insets are the enlargement for the samples with higher magnification): (a) the blank and (b) experimental group.

peaks at 3,437 cm^{-1} might indicate the presence of adsorption H_2O onto the precipitates and the O–H group stretching vibration in water molecules [57]. The absorption peaks of O–H bonds around 2,361 cm^{-1} suggest that the interstitial H atoms were bonded with oxygen atoms for the O–H stretch modes [58]. A broad peak was observed at 1,400 cm^{-1}, which was ascribed to CO_3^{2-} ions, showing the presence of carbonate [59]. The weak band at 1,127 cm^{-1} was assigned to the FeOOH. The peak at 916 cm^{-1} was related to the C–O stretching vibration. The peak at 615 cm^{-1} was attributed to –COO groups [60], indicating that the low molecular weight acids onto the precipitates.

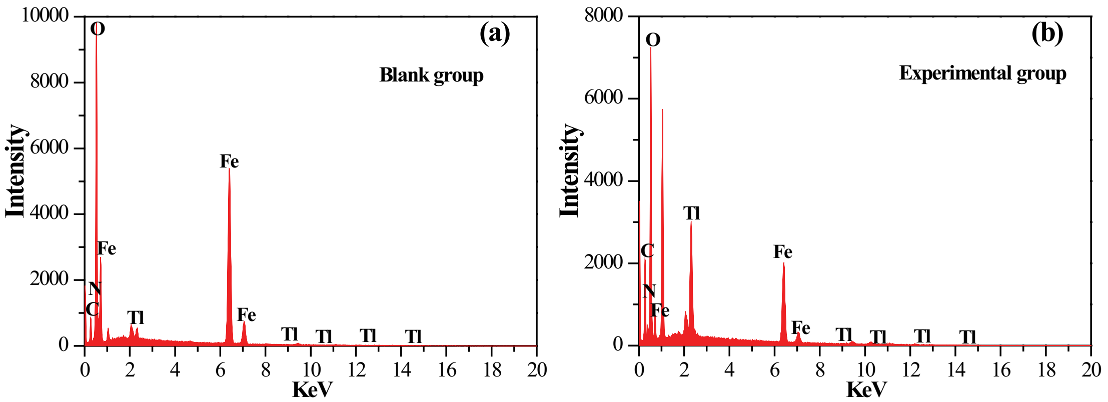

Fig. 4. EDS spectra for the precipitates of the Fenton process: (a) the blank and (b) the experimental group.

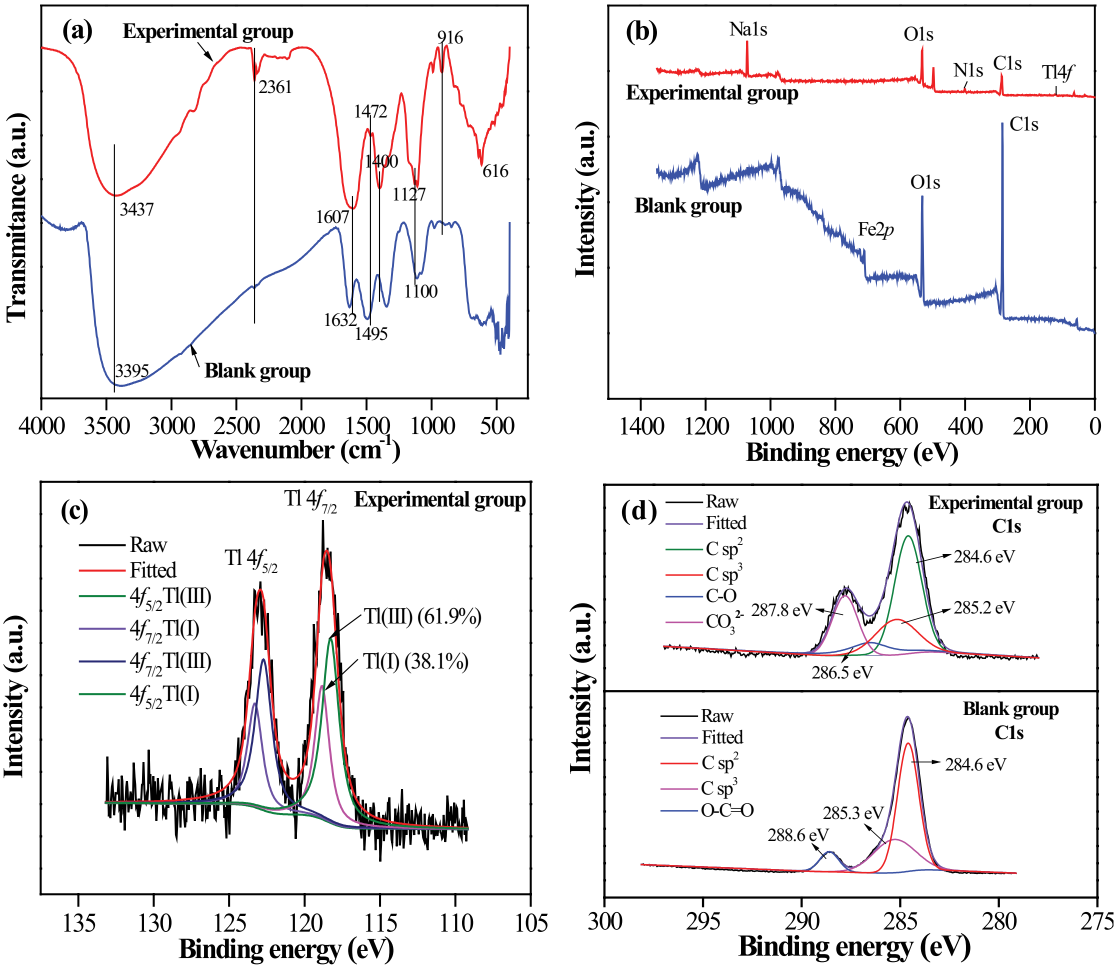

Fig. 5. (a) FT-IR spectra of resulted precipitates after the Fenton reaction. The XPS spectra of the precipitates: (b) survey, (c) Tl 4f core level after the Fenton reaction and (d) C 1s core level.

In the XPS spectra (Fig. 5b), the Tl absorption peaks appeared after the Fenton reaction, confirming that Tl was successfully captured onto the precipitates. After the Fenton treatment, the peaks of Tl 4f appeared (Fig. 5c). According to the method reported by Young et al. [61], the proportion of Tl(I) to Tl(III) in this study was 1.00:1.61 which indicates that 61.9% of Tl(I) was oxidized. Therefore, Tl(I) partially oxidized to Tl(III) and then precipitated as Tl_2O_3, this is one of the main mechanisms for Tl removal [3]. Because Tl(III) is unstable and prone to be slowly reduced to Tl(I) [62], the proportion of Tl(III) formed after the reaction was likely higher than the values revealed by the XPS analyses [36]. For the C1s XPS spectra, compared with the control group, the experimental group contained four sub-peaks (Fig. 5d). The first peak from sp^2 hybridized carbons centered at 284.6 eV coincided with that of elemental carbon species. The peaks located at 285.2 and 285.3 eV were attributed to sp^3 hybridized diamond-like carbons and associated with the presence of C–C/C–H groups [63]. A peak near 288.6 eV in blank group was attributed to –O–C=O [64]. The other peaks at 286.5 and 287.8 eV were indicative of oxygen-bonded carbon [63] and a carbonate (CO_3^{2-}) species [65], respectively. It can be verified that the degradation intermediates of EDTA were adsorbed on the precipitates after oxidative degradation in the Fenton system.

The degradation of Tl–EDTA was sketched in Figs. 6 and Eq. (7). Under the oxidation by $^{\bullet}OH$, Tl–EDTA was destroyed to be Tl and EDTA. Afterward, the chemical bonds (C–C and C–N) of EDTA were prone to cleave, producing low molecular weight (LMW) acids which were not qualitatively and quantitatively determined in this study. The derivatives for EDTA degradation in effluent are of interest and need further investigation. Due to the strong oxidability of $^{\bullet}OH$, some of them are finally degrading into CO_2 and H_2O, which is consistent with the findings of the previous reports [16,49,66]. Most Tl(I) was oxidized into Tl(III), which is then tensely precipitated as Tl_2O_3 or adsorbed onto the iron hydroxides [67]. As a result, Tl is effectively removed from wastewater through the synergistic effects of surface complexation, oxidation, coagulation, precipitation and co-precipitation. The Fe(III) species of $Fe(OH)_3$ and FeOOH may also capture the Tl precipitates and the organic intermediates from aqueous solution [68].

$$\mathrm{Tl^{I/III}EDTA} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{LMW\ acids} + \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{Tl^{III}} \quad (7)$$

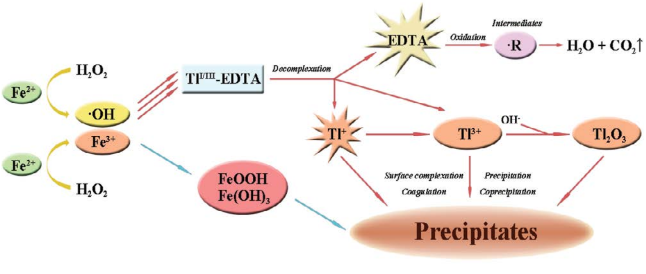

Fig. 6. Schematic of the removal of Tl–EDTA by the Fenton process.

Note that the LMW acids represent oxalic, propionic and iminodiacetic acids [49].

4. Conclusions

This study is the first report to demonstrate the effective treatment of Tl–EDTA complexes from wastewater using the Fenton process. The Fenton process can effectively and simultaneously remove Tl and the EDTA. Under the studied conditions, the optimum experimental conditions are [Fe^{2+}] of 21.6 mM, [H_2O_2] of 54.0 mM, reaction pH of 2.5, reaction time of 5 h and flocculation pH of 10.0. Hydroxyl radicals are responsible for the degradation of Tl–EDTA complexes, and the liberated Tl ions are efficiently removed via oxidation, surface complexation, coagulation, precipitation and co-precipitation. TOC removal is mainly attributed to the strong oxidation capability of hydroxyl radicals. The degradation pathway of ETDA by hydroxyl radical is interesting and additional investigations are needed to further identify the intermediates. The Fenton process could be a promising technology for the effective removal of both ETDA and toxic Tl from wastewater.

Acknowledgments

The research was supported by the National Natural Science Foundation of China (51708143, 51808144), the Guangzhou Education Bureau (1201630390), the Department of Education of Guangdong Province (2015KQNCX115), the Foundation for Fostering the Scientific and Technical Innovation of Guangzhou University, the Science and Technology Program of Guangzhou, China (201804010366), Guangzhou University's Training Program for Excellent New-recruited Doctors (YB201710), Scientific Research Foundation for the Returned High-level Overseas Talents (2018).

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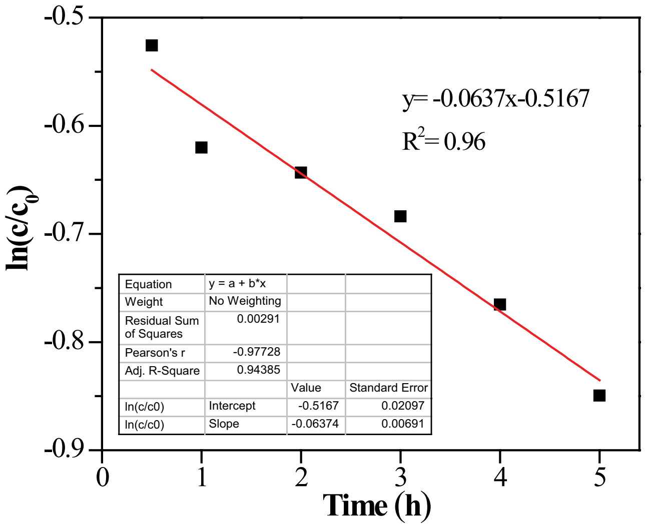
Supplementary Information



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.00291		
Pearson's r	-0.97728		
Adj. R-Square	0.94385		
		Value	Standard Error
ln(c/c0)	Intercept	-0.5167	0.02097
ln(c/c0)	Slope	-0.06374	0.00691

Fig. S1. Pseudo-first-order plot showing linearity for EDTA degradation from 1 to 5 h.

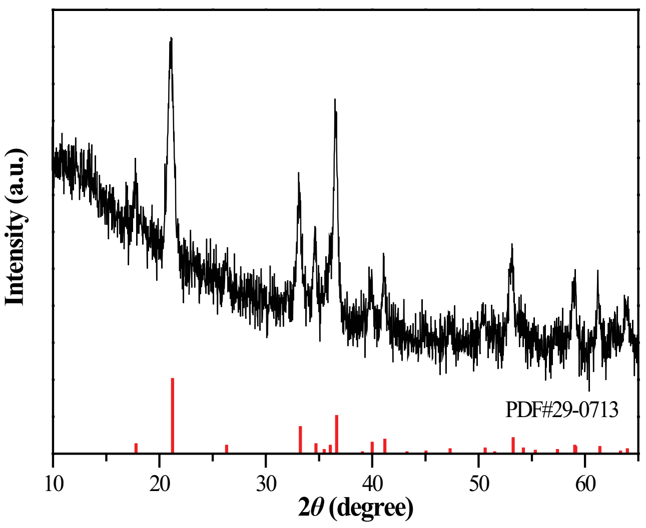


Fig. S2. XRD pattern of the precipitates (blank group: Fenton reaction without pollutant of Tl–EDTA).

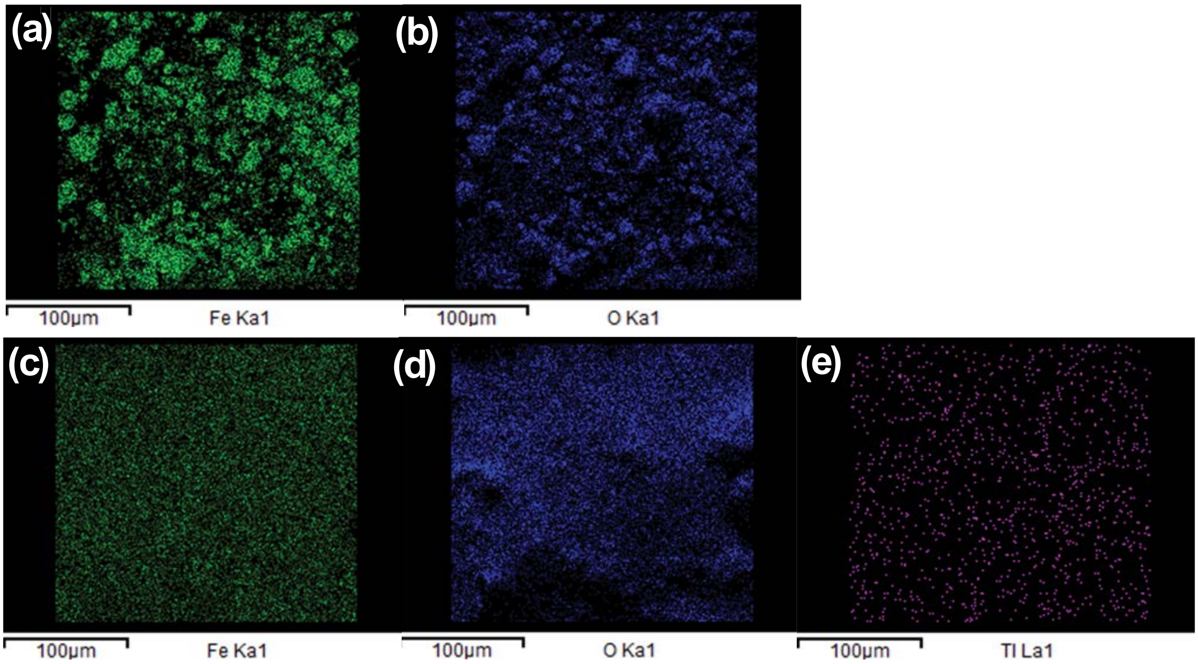


Fig. S3. Elemental mapping of the precipitates of the Fenton system: ((a) and (b)) Fe and O elemental mapping of blank group, ((c)–(e)) Fe, O and Tl elemental mapping of experimental group.