Competitive removal of Cu–EDTA and Ni–EDTA via microwave-enhanced Fenton oxidation with hydroxide precipitation

Qintie Lin, Hanping Pan, Kun Yao, Yonggang Pan and Wei Long

ABSTRACT

Ethylenediaminetetraacetic acid (EDTA) can form very stable complexes with heavy metal ions, greatly inhibiting conventional metal-removal technologies used in water treatment. Both the oxidation of EDTA and the reduction of metal ions in metal–EDTA systems via the microwave-enhanced Fenton reaction followed by hydroxide precipitation were investigated. The Cu(II)–Ni(II)–EDTA, Cu(II)–EDTA and Ni(II)–EDTA exhibited widely different decomplexation efficiencies under equivalent conditions. When the reaction reached equilibrium, the chemical oxygen demand was reduced by a precipitation microwave-enhanced Fenton oxidation with hydroxide and surface treatment industries (Walsh & Reade 1994; Pitter & Sykora 2001; Gislaine et al. 2004; Salama & Berk 2005). EDTA can form a highly soluble complex with a wide variety of metal ions in an aqueous solution and can greatly reduce the efficiency of metal removal by conventional chemical precipitation, such as hydroxide and sulfide precipitations (Juang & Wang 2000).

Many technologies, such as interior microelectrolysis (Lan et al. 2012), photocatalysis (Park et al. 2006), electrochlorination (Khelifa et al. 2009), photoelectrocatalysis (Zhao et al. 2013), Fe2+ replacement and precipitation (Jiang et al. 2010), electro-coagulation and deposition (Yeh et al. 1995; Oztekin & Yazicigil 2006; Kabdasli et al. 2009), ultrasound-enhanced Fenton (Chitra et al. 2004; Fu et al. 2010) and Fenton-like oxidation (Gislaine et al. 2004) have been employed to treat wastewater containing metal–EDTA complexes. However, these technologies have some limitations, such as poor EDTA treatment efficiency, high energy consumption, chemical toxicity and excessive iron sludge.

Recently, a microwave-enhanced Fenton or Fenton-like (MF) process has been demonstrated as a promising technology for the efficient removal of aqueous pollutants (Homem et al. 2015; Liu et al. 2015). Compared to the sole Fenton reaction, MF has many advantages including: (1) increased reaction selectivity, (2) increased hydroxyl radical (OH•) formation, (3) reduced reaction time, (4) decreased activation energy, (5) ease of control, (6) increased high polymeric ferric species and facilitated coagulation process, and (7) formed compact floc and improved settling (Yang et al. 2009, 2010; Wang et al. 2014). MF stimulates free radical generation from the oxidants and rapid polarization of the pollutant molecule, which improves the degradation rate of various pollutants by at least 50 times compared to the Fenton and Fenton-like processes without microwave (MW) (Gromboni et al. 2007; Zhang et al. 2007; Remya & Lin 2011).
Industrial wastewater often contains EDTA complexes with several types of heavy metal ions, such as copper, nickel, cadmium and lead, and the reduction of metal–EDTA complexes depends on the relative concentrations of each metal species and the stability constant of each metal–EDTA complex. In a competitive oxidation environment, multiple metal species will compete for a limited amount of oxidant and alter the oxidation products and reaction pathways (Yang & Davis 2001; Fu et al. 2009).

However, the reduction of metal–EDTA complexes by MF, especially in mixed metal–EDTA systems, has not been previously reported. To appropriately employ MF technologies for environmental benefit, an understanding of the behaviors of these compounds within complex competitive environments is required.

In this study, to explore the competitive mechanisms of different metal–EDTA complexes in a microwave-enhanced Fenton reaction followed by hydroxide precipitation (MF-HP), the removal efficiencies of EDTA and metal ions as Cu(II)–EDTA and Ni(II)–EDTA complexes in single and binary systems were investigated and compared. The oxidation metal–EDTA complexes and the degradation pathway of EDTA are discussed.

MATERIALS AND METHODS

Materials

Copper nitrate, nickel nitrate and disodium ethylenediaminetetraacetic acid (Na2EDTA) were purchased from Merck (Darmstadt, Germany), and the 30% hydrogen peroxide (H2O2) aqueous solution, FeSO4·7H2O, NaOH and HNO3 were obtained from the Tianjin Fuchen Chemical Reagents Factory, Tianjin, China. The FeSO4 solution was prepared daily. All of these reagents were analytical grade and used without further purification. The pH regulation was adjusted using either NaOH or HNO3. Cu–EDTA, Ni–EDTA and mixtures of Cu–Ni–EDTA (molar ratio of Cu/Ni is 1:1) solutions were prepared by dissolving the metal nitrates and equimolar Na2EDTA (5 mM) in deionized water, to make sure the EDTA concentration was 5 mM, and the ratio of total metal and EDTA was 1:1. The characteristics of the simulated wastewater are provided in Table 1.

Table 1 | Characteristics of the simulated wastewater

<table>
<thead>
<tr>
<th></th>
<th>C10H16N2O8Na2 (mmol/L)</th>
<th>Cu(NO3)2 (mmol/L)</th>
<th>Ni(NO3)2 (mmol/L)</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>Cu2+ (mg/L)</th>
<th>Ni2+ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA</td>
<td>5</td>
<td>–</td>
<td>–</td>
<td>2.7</td>
<td>1050</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>EDTA-Cu</td>
<td>5</td>
<td>5</td>
<td>–</td>
<td>2.5</td>
<td>1050</td>
<td>300</td>
<td>–</td>
</tr>
<tr>
<td>EDTA-Ni</td>
<td>5</td>
<td>–</td>
<td>5</td>
<td>2.3</td>
<td>1050</td>
<td>–</td>
<td>250</td>
</tr>
<tr>
<td>EDTA-Cu-Ni</td>
<td>5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.4</td>
<td>1050</td>
<td>150</td>
<td>125</td>
</tr>
</tbody>
</table>

Methods

One millilitre of 0.125 M FeSO4 was added to a flask containing 250 mL of the metal–EDTA solution, and the pH value was adjusted to 2.5. The flask was placed in a microwave chemical reactor (MCR-3, Henan, China) with a frequency of 2450 MHz and a nominative maximum output power of 800 W. Thereafter, 4.8 mL of 30% H2O2 (W/W) was added to ensure an appropriate molar ratio for EDTA:Fe(II):H2O2, which was close to the optimum values (Pan et al. 2014). After the addition of H2O2, there was a small change of pH (<0.05). Next, the MF reaction was carried out for 20 min at 80 °C under microwave control, and the mean power during the reaction was about 240 W. During the experimental run, aliquots were withdrawn from the reactor at selected intervals, and the pH value was adjusted to 9.0 using 10% NaOH. Next, the solid precipitates were allowed to settle for 30 min. The effluents were withdrawn and filtered through a 0.45 μm membrane. The filtrate was analyzed for residual metal concentrations, chemical oxygen demand (COD), EDTA and its intermediate products. The removal efficiency of a pollutant by the MF-HP processes was calculated according to the following equation:

Removal (%) = \( \frac{C_0 - C_t}{C_0} \times 100 \)  \hspace{1cm} (1)

where \( C_0 \) and \( C_t \) are the concentrations of EDTA, COD and metal at reaction times 0 and \( t \), respectively.

To explore the effect of microwave on the reactions, the water bath heating was used as the reference experiment. Flasks containing 250 mL of the Cu–Ni–EDTA solution and Fenton were placed in a water-bath shaker and a microwave reactor, respectively, and the reaction temperature was...
set at 50, 60, 70 and 80 °C. When the temperature reached the set value, time was counted. At selected intervals, the COD was measured.

Analysis

The COD was determined using the potassium dichromate spectrophotometry method: 2 mL samples were digested with potassium dichromate and H₂SO₄–Ag₂SO₄ solution in the HACH digester (DR200 spectrophotometer, Loveland, CO, USA) and the absorbance read at 597 nm with the HACH spectrophotometer. The aqueous concentrations of copper and nickel were measured with an atomic absorption spectrophotometer (HitachZ-2000, Tokyo, Japan). EDTA was analyzed by a high performance liquid chromatography (HPLC) system (Shimadzu LC-20AT, Kyoto, Japan), and its oxidation products were determined with a Hewlett-Packard (HP) 5890 GC with HP 5970 Mass Selective MS system slowly increased. Even after completion of the reaction, the removal efficiency only reached a maximum of 67.5% (residual Ni²⁺ concentration was 95.3 mg/L). Therefore, the removal rate and efficiency of Ni²⁺ in the Cu–Ni–EDTA wastewater system was much higher than that in the Ni–EDTA system.

For Cu²⁺, the removal efficiency in the Cu–EDTA wastewater at 0 min was significantly higher than in the Cu–Ni–EDTA wastewater (P < 0.05), but after 2.5 min, the removal efficiency in the Cu–Ni–EDTA wastewater was significantly higher than in the Cu–EDTA wastewater (P < 0.05). These differences are primarily due to microwave thermal degradation and ligand exchange of the EDTA from Ni²⁺ to Cu²⁺. Nickel ion has an EDTA log stability constant that is similar to copper ion (18.62 versus 18.80, respectively). The rate of EDTA ligand exchange from Ni²⁺ to Cu²⁺ is normally slow (Equation (2)) (Madden et al. 1997). However, the microwave promotes ligand exchange, and

RESULTS AND DISCUSSION

Removal of Cu²⁺ and Ni²⁺

The dependence of the removal efficiencies of Cu²⁺ and Ni²⁺ by MF-HP on time is shown in Figure 1. At 0 min, the removal efficiency of Cu²⁺ in the Cu–EDTA wastewater was significantly higher than in the Cu–Ni–EDTA wastewater (P < 0.05), which were 70.7% and 56.6%, respectively. However, after 2.5 min, the removal efficiency of Cu²⁺ in the Cu–Ni–EDTA wastewater was significantly higher than in the Cu–EDTA wastewater (P < 0.05), and the significant difference (P < 0.05) remained to the end of the experiment. After 7.5 min, the removal efficiency of Cu²⁺ in the Cu–Ni–EDTA wastewater system remained constant above 97.0% (residual Cu²⁺ concentration was 2.1–4.8 mg/L). In contrast, the removal efficiency of Cu²⁺ in the Cu–EDTA wastewater system reached a maximum of only 94.4% at 15 min (residual Cu²⁺ concentration was 17.8 mg/L).

During the whole reaction process, the removal efficiency of Ni²⁺ in the Cu–Ni–EDTA wastewater was significantly higher than in the Ni–EDTA wastewater (P < 0.05). The removal efficiency of Ni²⁺ in the initial stage in the Cu–Ni–EDTA wastewater system was higher than that in the Ni–EDTA system (i.e., 70.0% in Cu–Ni–EDTA and 49.5% in Ni–EDTA). The removal efficiency of Ni²⁺ in the Cu–Ni–EDTA wastewater system rapidly increased. After 7.5 min, the removal efficiency of Ni²⁺ remained constant at 94.5% (residual Ni²⁺ concentration was 5.0–8.0 mg/L). The removal efficiency of Ni²⁺ in the Ni–EDTA wastewater system slowly increased. Even after completion of the reaction, the removal efficiency only reached a maximum of 67.5% (residual Ni²⁺ concentration was 95.3 mg/L). Therefore, the removal rate and efficiency of Ni²⁺ in the Cu–Ni–EDTA wastewater system was much higher than that in the Ni–EDTA system.

Figure 1 | Comparisons of metal removal efficiencies for three metal(II)-EDTA complexes by MF-HP (1:1 ratio of metal(II)/EDTA, 5 mM EDTA, 0.5 mM Fe²⁺, 185 mM H₂O₂, initial pH of 2.5, temperature 80 °C by microwave control).
the ligand exchange equilibrium is driven to the right, releasing Ni$^{2+}$ from its EDTA complex. Therefore, in the Cu–Ni–EDTA system, Ni$^{2+}$ can be released via two steps including major oxidation by hydroxyl radicals and minor ligand exchange of Ni–EDTA/Cu$^{2+}$, as shown in the following equations:

\[
\text{Ni(II)} - \text{EDTA} + \cdot \text{OH} \rightarrow \text{Ni}^{2+} + \text{EDTA}_{\text{ox,prod}} \tag{2}
\]

\[
\text{Cu(II)} - \text{EDTA} + \cdot \text{OH} \rightarrow \text{Cu}^{2+} + \text{EDTA}_{\text{ox,prod}} \tag{3}
\]

\[
\text{Cu}^{2+} + \text{Ni(II)} \rightarrow \text{Cu(II)} - \text{EDTA} + \text{Ni}^{2+} \tag{4}
\]

Therefore, in the initial stage, the Cu–Ni–EDTA system exhibited a higher Ni(II) removal efficiency than the Ni–EDTA system and a lower Cu(II) removal rate than the Cu–EDTA system.

Owing to the ease of conversion between Cu$^{+}$ and Cu$^{2+}$ and difficulty in changing the valence of Ni$^{2+}$, Cu was employed to catalyze H$_2$O$_2$ to form a Fenton-like reaction, which resulted in a strong ability to form hydroxyl groups (Cu$^{2+}$ + H$_2$O$_2$ → Cu$^{+}$ + HO$_2$ + H$^+$, Cu$^{+}$ + H$_2$O$_2$ → Cu$^{2+}$ + HO + OH$^-$). Therefore, the removal efficiency of Cu in the Cu–EDTA system was higher than that of Ni in the Ni–EDTA system. In addition, the Ni$^{2+}$ released from the Cu–Ni–EDTA system possessed a strong microwave energy absorption ability, which helped to increase the reaction temperature. Therefore, the microwave thermal effect and the Fenton-like reaction created by Cu catalyzed H$_2$O$_2$ exhibited a synergetic effect, which resulted in a higher removal efficiency of Cu compared to the Cu–EDTA system. After 15 min, the removal efficiency of Cu$^{2+}$ and Ni$^{2+}$ remained constant, which was primarily due to the formation of multiple ligands between EDTA degradation products, such as NH$_4^+$ and Cu$^{2+}$ or Ni$^{2+}$, and the multiple ligands inhibited the removal of Cu$^{2+}$ and Ni$^{2+}$ by chemical precipitation.

**Removal of EDTA and reduction of COD**

Figure 2 shows the dependence of the removal efficiencies of EDTA and the reduction efficiencies of COD by MF-HP on time. When the temperature reached 80 °C, the removal efficiencies of EDTA in the three wastewater systems were higher than 84%, which indicated that the EDTA degradation rate with MF was much faster than that with UV/H$_2$O$_2$ (Ku et al. 1998; Jiraroj et al. 2006), Fenton and photo-Fenton (Gislain et al. 2004). Compared to the Cu–EDTA system, the EDTA in the Ni–EDTA wastewater system degraded faster, and an equilibrium state was observed at 80 °C. This was because Ni$^{2+}$ possessed a strong microwave energy absorption ability, thus a synergetic effect between the microwave thermal effect and the Fenton reaction accelerated the EDTA degradation. When EDTA reached the equilibrium value, the EDTA removal efficiencies of the Cu–EDTA, Ni–EDTA and Cu–Ni–EDTA systems were 99.8%, 99.6% and 98.5%, respectively. The removal efficiency of EDTA in the Cu–Ni–EDTA system was low, due to the synergistic effect between the microwave thermal effect in the Cu–Ni–EDTA system and the Fenton-like reaction created by the Cu catalyzed H$_2$O$_2$. The interaction altered the EDTA degradation pathway and increased the pH of the Cu–Ni–EDTA wastewater system (after the reaction, the pH of Cu–Ni–EDTA, Cu–EDTA and Ni–EDTA were 7.6, 7.1 and 6.6, respectively) inhibiting residual EDTA degradation. Compared to EDTA, the reductions of COD in the three systems were typically low (<90%) but all of the efficiencies increased slowly. During the EDTA degradation process, EDTA did not completely mineralize, but primarily underwent an organic partial degradation under the microwave radiation.

**Comparison of microwave-enhanced Fenton and water-bath Fenton**

The reduction efficiencies of COD by MF and water-bath Fenton (WF) are shown in Table 2. These results suggest that the reduction efficiencies of COD were closely dependent on time and temperature, and the change trend of MF showed good consistency with that of WF. It can be
seen that the COD reduction of MF was lower than that of WF from 0 to 1 min. It was because the time to the set temperature for microwave heating was shorter than that for water bath heating. After 3 min, the COD reduction of MF was higher than that of WF, suggesting there was a synergistic effect between MW and Fenton. It could be inferred that the microwave not only generated thermal degradation, but also enhanced the oxidation ability of Fenton.

**Degradation mechanism of metal(s) – EDTA**

Because the byproducts of EDTA oxidation typically exhibit a reduced capacity for binding metals, the oxidation of EDTA in a metal–EDTA system is a prerequisite for the removal of metals from an aqueous solution (Madden et al. 1997; Park et al. 2006). To explore the degradation mechanism of EDTA, the most effective system – Cu–Ni–EDTA wastewater – was chosen to be treated with the microwave-Fenton reaction method. And the reaction times at 0, 5 and 20 min represent the earlier, middle and stable period. Aliquots were withdrawn at 5 and 20 min, and the pH was adjusted to 9.0. The filtrate was analyzed for EDTA and its intermediate products, which were withdrawn and filtered through a 0.45 μm Millipore membrane. The detection results are shown in Table 3.

As shown in Table 3, intermediates including formic acid, acetic acid, oxalic acid, amino acetic acid and formaldehyde were identified. The concentration of oxalic acid increased with the reaction time, and acetic acid appeared at 20 min. Owing to the refractory nature of the Fenton reagent (Rivas et al. 2001), some by-products (e.g., oxalic acid) formed in this process may have accumulated in the reaction media. Ammonium and acetaldehyde were also qualitatively detected but not quantified. No ethylenediamine was observed at 5 and 20 min, which was different from the results of decomplexation of Cu–EDTA in a photoelectrocatalytic system (Zhao et al. 2013; Babay et al. 2001). This result was most likely due to the synergetic effect between the thermal effect of the microwave and the Fenton-like reaction created by Cu catalyzed H2O2 in the Cu–Ni–EDTA system. In addition, the competition of Cu2+ and Ni2+ for the oxidation sites under the microwave-enhanced Fenton reaction may have altered the degradation pathway of EDTA.

Based on these results, a degradation pathway for the metal–EDTA complexes has been proposed and is shown in Scheme 1. Under the action of Fe2+, H2O2 and heavy metal ions, the reaction system generated a large number of free radicals and active ions, such as ·OH, ·O2 and H+ during the early period of the reaction. Therefore, the bonds between the EDTA and the metal ions were broken by the microwave radiation and strong oxidation system. Second, the C–N bond on the main chain of EDTA started cracking and dehydrogenating to form ethylene and iminodiacetic acid, which were both unstable. Third, ethylene was oxidized to formaldehyde and further transformed to formic acid. Iminodiacetic acid was decomposed to glycine and glyoxylic acid. Fourth, the C–N bond of glycine started cracking, and was further decomposed to ammonia and acetic acid. Glyoxylic acid was oxidized to oxalic acid. In the early stage of the reaction, reactive oxygen species, such as H2O2, ·OH and ·O2, were abundant, and the cracking of the C–C and C–N bonds as well as the oxidation of

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**Table 2 | Reduction efficiency of COD in MF and WF (%)**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Temperature (MF) (°C)</th>
<th>Temperature (WF) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>0</td>
<td>29.67 ± 0.64</td>
<td>36.75 ± 0.89</td>
</tr>
<tr>
<td>1</td>
<td>34.25 ± 0.68</td>
<td>41.23 ± 1.23</td>
</tr>
<tr>
<td>3</td>
<td>38.75 ± 1.03</td>
<td>44.94 ± 2.12</td>
</tr>
<tr>
<td>5</td>
<td>41.21 ± 1.45</td>
<td>46.23 ± 1.65</td>
</tr>
<tr>
<td>7</td>
<td>42.45 ± 1.79</td>
<td>47.79 ± 1.89</td>
</tr>
<tr>
<td>9</td>
<td>42.53 ± 2.25</td>
<td>48.96 ± 2.23</td>
</tr>
</tbody>
</table>
compounds occurred at a fast rate. Therefore, none of the ethylene, Schiff base or acetic acid was detected during the 5-min test. In the later stages of the reaction, the oxidizing agent and free radicals were gradually consumed, and oxidation became far less effective. Therefore, a small amount of amino acetic acid, oxalic acid, acetic acid, formaldehyde and formic acid remained in the system. Among these compounds, organics, such as amino acetic acid and oxalic acid, and ammonia could form stable complexes with metal ions, which resulted in the incomplete removal of the metal ions by hydroxide precipitation.

**CONCLUSIONS**

Microwave-enhanced Fenton oxidation followed by hydroxide precipitation was successfully employed to treat metal-EDTA complexes. Compared to the Ni-EDTA and Cu-EDTA systems, the removal efficiencies of both Cu$^{2+}$ and Ni$^{2+}$ in Cu–Ni–EDTA wastewaters were higher. The Ni$^{2+}$ released from the Cu–Ni–EDTA system exhibited a strong microwave absorption, which increased the reaction temperature. Therefore, the microwave thermal effect and the Fenton-like reaction created by Cu catalyzed H$_2$O$_2$ exhibited a synergetic effect, which resulted in a higher degradation rate of complexes and altered the EDTA degradation pathway. Therefore, for treating Ni–EDTA wastewater, the use of microwave-enhanced Fenton oxidation with an appropriate amount of Cu$^{2+}$ may be employed as a potential engineering application.

**ACKNOWLEDGEMENTS**

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