



Article Decomplexation of Ni-EDTA by Three-Dimensional Electro-Fenton

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Abstract: Ni-ethylenediaminetetraacetic acid (Ni-EDTA) poses serious threats to the ecological environment and human health, due to its acute toxicity and low biodegradability. The decomplexation efficiency of Ni-EDTA through the conventional Fenton process has been constrained to pH; thus, other appropriate approaches are required to destroy the stable chelate structure at a neutral pH. In this study, the effect of operating parameters such as the pH, Fe²⁺ concentration, particle electrode dosage, current density, and coexisting ions was studied. The results revealed that the 3D-EF system owned advantages for the removal of Ni-EDTA in the broadening of the pH application window. The Ni-EDTA removal efficiency in the 3D-EF system reached 84.89% after 120 min at a pH of 7. In addition, the presence of coexisting ions slightly affected the decomplexation efficiency of Ni-EDTA.

Keywords: Ni-EDTA; three-dimensional electro-Fenton; neutral pH; decomplexation

1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is widely used as a stabilizer of some metal ions in the process of plating and metallurgy, as it can react with Ni, Cu, and Fe to form stable chelates with different structures [1,2]. Ni as a typical plating metal is easy with EDTA to form a stable complex Ni-ethylenediaminetetraacetic acid (Ni-EDTA), and its high stability and acute toxicity to environment can be detrimental to life. Ni-EDTA usually has high stability and low biodegradability, resulting in lower removal efficiency of Ni-EDTA in conventional treatments [3]. Therefore, how to effectively remove metal–EDTA complexes remains a challenge, and numerous studies have been conducted to explore the treatment methods of metal–EDTA complexes from wastewater. Some promising treatments, such as non-thermal plasma oxidation/alkaline [4,5], microwave-assisted Fenton reaction [6], zero-valent iron [7], and ozone-based oxidation process [8], have been demonstrated to be effective in removing metal–EDTA at acidic conditions, and the high capital costs of these methods limits their widespread application.

Electrochemical advanced oxidation processes (EAOPs) are considered to be the most promising processes for the treatment of the metal–EDTA complex, with benefits including high versatility, mild conditions, and environmental compatibility [9,10]. Previous studies have shown that the hydroxyl radical (·OH) generated based on the electro-Fenton (EF) systems has the characteristics of strong oxidation, high reactivity, and harmless, and it has exhibited satisfactory efficiency in decomposing [11,12]. Basturk et al. (2021) studied the removal efficiency of antibiotics in the EF process and found that the removal efficiency



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of antibiotics exceeded 98% at a pH of 2.99 [13]. The Stupar team reported that the mineralization efficiency of acid blue 111 in the EF system achieved up to 76% at a pH of 2.5 [14]. Interestingly, outstanding results were achieved in the EF process with a $Ti/Ru_{0.3}Ti_{0.7}O_2$ as a cathode in the study of Gamarra-Güere et al. (2019), who completed methylparaben degradation in both synthetic and real water at a pH of 3 [15]. However, the EF system can achieve a high removal efficiency only in a lower pH range. The problem of strong dependence on pH restricts its practical application. To overcome this drawback, a three-dimensional electro-Fenton (3D-EF) system based on an EF system filled with some particle electrodes has received extensive attention.

Particles are polarized to form a tiny electrolyzer in the 3D-EF system that not only can provide a shorter mass transfer distance but also improve the processing efficiency and enlarge the pH application window [16]. Lu et al. (2022) found a synergistic effect of the 3D-EF system in the presence of CuO-doped red mud particle electrodes and found that the system exhibited a higher degradation efficiency of ciprofloxacin at an initial pH of 7.0 [17]. It has also been reported that used Fe_3O_4/N -doped reduced graphene oxide as particle electrodes by Zhang et al. (2020) for bisphenol A (BPA) removal in a 3D-EF system. As a result, BPA exhibited excellent degradation efficiency within 90 min [18]. It can be noted that Mohammadi et al. (2018) demonstrated highly efficient degradation of ibuprofen and naproxen at near-neutral pH in a 3D-EF system with Fe-coated nickel foam particle electrodes [19].

The particle electrodes and polar plates play an important role in the efficiency of electrochemical treatment in the 3D-EF system. Granular activated carbon (GAC) is recognized as one of the most outstanding particle electrode materials due to its abundance and relatively low cost [20]. Graphite is a perfect electrode material, as it has excellent electrical conductivity and nontoxicity [21]. Previous studies have suggested that graphite cathode [22,23], graphite anode [24], and graphite bipolar plates [25] are promising polar plate materials for removing organic contaminants.

In this study, a 3D-EF system was constructed with cheap and easily available graphite as polar plates and GAC introduced as particle electrodes. The widening effect of the pH application window in the 3D-EF system was evaluated by the decomplexation performance of Ni-EDTA. The effect of process parameters (including Fe²⁺, particle electrode, current density, and coexisting ions) on the 3D-EF system was further studied. In addition, the reaction kinetics of each factor in the 3D-EF system were also fitted. This study provides a view of practical applications for the decomplexation of Ni-EDTA in different pH water environments.

2. Materials and Methods

2.1. Materials

Analytical purity ethylenediaminetetraacetic acid disodium salt (Na₂EDTA·2H₂O) was bought from Macklin Biochemical Co., Ltd. (Shanghai, China). The reagents of nickel sulfate (NiSO₄·6H₂O), sodium chloride (NaCl), sodium nitrate (Na₂NO₃), disodium hydrogen phosphate (Na₂HPO₄·12H₂O), and sodium sulfate (Na₂SO₄) were of analytical grade and obtained from Damao Chemical Reagent in China Factory (Tianjin, China). Sulfuric acid (H₂SO₄) was bought from Kaixin Chemical Reagent Co., Ltd. (Hengyang, China). Ferrous sulfate (FeSO₄·7H₂O) and sodium hydroxide (NaOH) were from Xilong Scientific Co., Ltd. (Shantou, China). GAC (particle size, 0.6–2 mm) was received as a particle from Aladdin Reagents Co., Ltd. (Shanghai, China). The Ni-EDTA (1000 mg/L) stock solution was prepared by dissolving NiSO₄ and Na₂EDTA·2H₂O in the molar ratio of 1:1 with ultrapure water with stewing for 24 h.

2.2. Experimental Setup

A glass reactor device (0.5 L) was used for Ni-EDTA decomplexation. Graphite bipolar plates (10 cm \times 5 cm, 7 cm plate spacing) were used as the cathode and anode in the reactor devices, respectively. The 3D-EF system was realized by filling a certain dose of GAC

(0.6–2 mm) particle electrodes in the reactor. Desired 50 mg/L Ni-EDTA reserve solution was added to the reactor, and then the solution pH was adjusted by 0.2 mol/L NaOH and H₂SO₄ immediately. Reactions were initiated when 0.047 mol/L Na₂SO₄ was added to the solution. Aliquots were sampled at predetermined time intervals, and samples' pH was adjusted to 11 by NaOH and H₂SO₄ to form hydroxide precipitates, which were then removed.

2.3. Experimental Procedure

2.3.1. Degradation of Ni-EDTA by 3D-EF

An initial pH of 3, Fe^{2+} dosage of 1 mmol/L, GAC of 2 g/L, and current density of 4 mA/cm² were used to study the superiority of the 3D-EF system. The EF system was performed by using the same reactor devices without GAC. GAC was used as an absorbent to remove Ni-EDTA in the GAC system.

2.3.2. The pH Window Was Widened in 3D-EF System

The widening of the pH application window of the 3D-EF system was evaluated at different initial pH values of 3–9, Fe^{2+} dosage of 1 mmol/L, GAC of 2 g/L, and current density of 4 mA/cm².

2.3.3. Parameter Optimization of Ni-EDTA Degradation by 3D-EF

Fe²⁺ dosage, GAC dosage, and current density were used to evaluate the parameters of Ni-EDTA degradation in 3D-EF system. Under the optimal pH condition, an Fe²⁺ dosage of 0.5–2.0 mmol/L, GAC of 1–6 g/L, and current density of 2–12 mA/cm² were discussed in the decomplexation of Ni-EDTA in the system.

2.3.4. The Effect of Coexisting Ions in 3D-EF System

The most suitable conditions, namely the pH, Fe^{2+} dosage, particle electrode, and current density, were prepared. The effect of coexisting ions (Cl⁻, NO₃⁻, and HPO₄²⁻) in the 3D-EF system on Ni-EDTA decomplexation was investigated.

2.4. Analytical and Statistical Methods

The pH value of the solution was monitored by a potentiometric titrator meter (PB-10, Sartorius). Experimental samples were taken at a certain time (10, 20, 30, 60, 90, and 120 min) for the determination of Ni²⁺. Samples were diluted 500 times and passed through 0.22 μ m membranes for detection. Each experiment was performed in three replicates to ensure the repeatability of the experiment. Inductively Coupled Plasma–Mass Spectrometry (ICP–MS, NexlON 2000, PerkinElmer, Waltham, MA, USA) was used to analyze the Ni²⁺ level of the filtrate. Origin 2018 software was used to analyze data.

The Ni-EDTA removal efficiency (*R*) was calculated by using Equation (1).

$$R = (1 - C_t / C_0) \times 100\%$$
(1)

The kinetics of Ni-EDTA degradation were characterized by the first-order equation, and the reaction rate constants (K_{obs}) were determined according to Equation (2).

$$\operatorname{Ln}\left(\mathrm{C}_{0}/\mathrm{C}_{\mathrm{t}}\right) = K_{obs} \mathsf{t} \tag{2}$$

where $C_0 (mg/L)$ and $C_t (mg/L)$ are the Ni²⁺ initial concentration and the concentration at time, t, respectively.

3. Results and Discussion

3.1. The Advantages of Ni-EDTA Decomplexation in 3D-EF System

The concentration of Ni-EDTA decreased gradually with the extension of reaction time (Figure 1a). The results showed that the performance of the 3D-EF system was higher than that of the EF and GAC systems, respectively. After 120 min, the residual concentrations of

Ni-EDTA in each system were 44.33, 18.99, and 11.64 mg/L, respectively, and the removal rates were calculated to be 9.17%, 61.08%, and 76.14%. From Figure 1b, we can see that the K_{obs} of 3D-EF system was higher than that of other systems, creating a sharp contrast. This illustration was consistent with Zhang et al. (2020) [18].



Figure 1. Decomplexation of Ni-EDTA in different systems (a) and kinetics fitting lines (b).

The 3D-EF system based on GAC particle electrodes gives an excellent Ni-EDTA decomplexation performance. In the 3D-EF system, GAC particle electrodes become independent electrodes through electrostatic induction, which could not only expand the electrode specific surface area but also increase space utilization [26]. Moreover, the mass transfer effect could be improved due to the shorter distance between the GAC particle electrode in the 3D-EF system. Hence, the 3D-EF system could provide a higher removal efficiency of Ni-EDTA compared with the conventional EF system, thus greatly enhancing the current efficiency, the rate of chemical reaction, and the treatment effect [27,28].

3.2. pH Application Window of 3D-EF for Ni-EDTA Complex Breaking

The pH is related to the generation of H_2O_2 in the cathode and to the present form of iron ions, which further can affect the treatment performance of 3D-EF system. A too-high or too-low pH would result in a change in treatment performance. It could be seen from Figure 2a that the residual concentration of Ni-EDTA at different pH values was 12.25, 6.64, 7.62, and 8.29 mg/L in 3D-EF system, respectively, which can also be effectively removed at a near-neutral pH. The K_{obs} within 120 min was the highest at a pH of 5 (Figure 2b). K_{obs} increased first and then decreased with the increase of the initial pH, which was consistent with the removal trend of Ni-EDTA.



Figure 2. Decomplexation of Ni-EDTA with different pH values (a) and kinetics fitting lines (b).

As shown in Table 1, in many 3D-EF studies, lower pH values tended to have a higher contaminant removal rate. Liu et al. (2019) found that the mineralization efficiency of *m*-cresol at a pH of 2.0 was about average, at 70% [29]. Dargahi et al. (2021) determined that the three-dimensional sono-electro-Fenton achieved 96.2% removal efficiency for 2,4-dichlorophenoxyacetic acid within 60 min, at a pH of 3.0 [30]. In addition, Wan et al. (2021) found that the 3D-EF reactor with AC@Ti-Cu-Ni-Zn-Sb-Mn particles serving as

particle electrodes could achieve the degradation of p-aminophenol at a pH of 7.0 [31]. Compared with other research reports, this study used GAC particle electrodes without additional preparation; inexpensive and easily available graphite was used as the polar plate to construct a 3D-EF system which can achieve higher Ni-EDTA removal efficiency and break through the application window of pH.

In this study, the 3D-EF system with the GAC particle electrode could break through the limitation of pH in the traditional EF process and broaden the application window of pH; thus, better removal efficiency of Ni-EDTA was achieved at a near-neutral pH. The 3D-EF system could produce a hydrogen evolution reaction at a lower pH, which reduced the generation of H_2O_2 and \cdot OH. The 3D-EF system inhibited the formation of \cdot OH at a higher pH, produced Fe(OH)₃ precipitation, and significantly reduced the decomposition of H_2O_2 into H_2O and O_2 [32]. However, the EF system needs to be carried out under acidic conditions. Fe(OH)⁺ would be generated at a lower pH, and it could compete with Fe²⁺ to react with H_2O_2 . The reaction rate of Fe(OH)⁺ with H_2O_2 was slower, resulting in the lower generation of \cdot OH. On the other hand, Fe(OH)₃ precipitation was easy to form and cover the particle electrodes at a higher pH, which resulted in current loss and increased the processing costs [33]. The 3D-EF system has excellent removal of Ni-EDTA in the near-neutral pH range, and the pH was not an adjusted pH (pH = 5) in the following experiments.

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Anode	Cathode	Particle Electrode	Process Parameters	Efficiency	Reference
Ti/RuO ₂	Ti/RuO ₂	Activated carbon fiber loaded with MnO _x	pH = 2	Total organic carbon: 70%	[29]
SS316/β-PbO ₂	Stainless-steel plate	Powder activated carbon/Fe ₃ O ₄	pH = 3	2,4-dichlorophenoxyacetic acid: 96.2% COD: 92.3% Total organic carbon: 86.5%	[30]
RuO ₂ -IrO ₂ -Ti	Activated carbon fiber	Cu-Fe/Sodium alginate Carbon	pH = 5.4	Fulvic acid: 81.1%	[34]
Ti/RuO ₂	Ti/RuO ₂	GAC	pH = 5.56	Amoxicillin: 98.98% Total organic carbon: 47.6%	[35]
Ti/RuO ₂ -IrO ₂ -Ta ₂ O ₅	Stainless-steel plate	AC@Ti-Cu-Ni-Zn-Sb-Mn	pH = 7	P-aminophenol: 99.87%	[31]

3.3. Influence Factors on Decomplexation of Ni-EDTA

3.3.1. Effect of Fe²⁺ Dosage

Figure 3a illustrated that the effect of Fe²⁺ dosage on the Ni-EDTA. With the increase of Fe²⁺ dosage, the removal efficiency of Ni-EDTA in the 3D-EF system first increased and then decreased. At an Fe²⁺ dosage of 1 mmol/L, the removal efficiency of Ni-EDTA in the 3D-EF system was the highest. Figure 3b showed that K_{obs} reached a maximum at an Fe²⁺ dosage of 1 mmol/L. An Fe²⁺ dosage was a key factor in the 3D-EF system. In the absence of Fe²⁺, the decomplexation of Ni-EDTA mainly depends on the oxidation of plates and particle electrodes.



Figure 3. Decomplexation of Ni-EDTA in different Fe²⁺ dosages (a) and kinetics fitting lines (b).

The activity of micro-electrolysis was weak when the Fe²⁺ dosage was smaller, but the Ni-EDTA removal efficiency also increased gradually with the increasing Fe²⁺ dosage to generate more \cdot OH [36]. When the dosage of Fe²⁺ was too high, the contact probability between Fe²⁺ and H₂O₂ increased, and the amount of \cdot OH produced increased. However, excessive Fe²⁺ would react with \cdot OH to generate Fe³⁺, and a large amount of \cdot OH was consumed, further reducing the oxidation capacity and Ni-EDTA removal efficiency in the 3D-EF system [18,37].

3.3.2. Effect of Particle Electrode Dosage

It could be observed from Figure 4a that the residual concentration of Ni-EDTA decreases first and then increases with the increase of particle electrode dosage. When the particle electrode dosage was 4 g/L, the removal efficiency of Ni-EDTA was the highest, and the concentration of Ni-EDTA decreased from 47.89 to 6.96 mg/L. As shown in Figure 4b, the K_{obs} reached the maximum when the particle electrode dosage was 4 g/L, which has a faster reaction rate than other particle electrode doses.



Figure 4. Decomplexation of Ni-EDTA in different particle electrode dosages (**a**) and kinetics fitting lines (**b**).

The particle electrode was evenly distributed in the electrolyzer, resulting in the increase of electrode specific surface area and shortened electrode distance. Thus, it was a crucial factor affecting the treatment efficiency of the 3D-EF system and greatly improved the treatment efficiency for Ni-EDTA. The appropriate particle electrode could increase the electrode surface area and current efficiency, and the Ni-EDTA removal efficiency was further improved [38]. When the particle electrodes continued to be added, the current efficiency and mass transfer efficiency would not continue to improve after the polarized particle electrodes reached saturation in a limited reaction space. The short-circuit current formed between the mutually bonded particle electrodes further restricts the removal of pollutants, resulting in the decline of the decomplexation performance of Ni-EDTA [27].

3.3.3. Effect of Current Density

The effect of different current density on the decomplexation of Ni-EDTA was studied. The results are shown in Figure 5a; when the current density was 2 mA/cm², the residual concentration of Ni-EDTA was the highest after 120 min, and the Ni-EDTA concentration was removed from 47.19 to 21.63 mg/L. At a current density of 10 mA/cm², the residual concentration of Ni-EDTA was 8.36 mg/L after 120 min, and it achieved the best removal efficiency of Ni-EDTA, at 82.28%. It was found that, by continuing to increase the current density, the removal efficiency of Ni-EDTA decreased and was only 79.87% at a current density of 12 mA/cm². In Figure 5b, the *K*_{obs} is much larger than that of the other current density experimental groups at a current density of 10 mA/cm².



Figure 5. Decomplexation of Ni-EDTA in different current density (a) and kinetics fitting lines (b).

The increase of current density further increases the electron density on the electrode, and the H_2O_2 generating ability was also enhanced. Fe²⁺ reacted with H_2O_2 by Equation (3) to generate \cdot OH, and the amount of \cdot OH increased accordingly. Moreover, the increasing current density would also increase the electron transfer between electrodes, accelerate its direct oxidation reaction at the electrode surface, and increase the Ni-EDTA removal efficiency [39,40]. A high current density will accelerate the decomposition of H_2O_2 and increase the probability of competitive side reactions of hydrogen evolution (Equation (4)) and oxygen evolution (Equation (5)). Further \cdot OH was scavenged, and the removal efficiency of Ni-EDTA was reduced [18,41].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH$$
(3)

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \to \mathrm{H}_{2} \tag{4}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (5)

3.4. Effect of Coexisting Ions on Ni-EDTA Removal

Actual wastewater contains specific pollutants and a variety of ions. Coexisting ions would have competitive adsorption with H₂O₂, which would have negatively affected the treatment effect of the 3D-EF system. Figure 6a displayed the effect of Cl⁻, NO₃⁻, and HPO₄²⁻ on the removal efficiency of Ni-EDTA. In the control group, the concentration of Ni-EDTA reached 81.04% after 120 min. The removal efficiency of Ni-EDTA reached 87.47% in the presence of Cl⁻; it can be seen that Cl⁻ promotes the removal of Ni-EDTA. After adding NO₃⁻ and HPO₄²⁻, the removal effect of Ni-EDTA was reduced: 78.87% and 73.79%, respectively. Therefore, NO₃⁻ and HPO₄²⁻ could inhibit the removal effect of Ni-EDTA, and the inhibition effect followed as HPO₄²⁻ > NO₃⁻. Figure 6b reflected that the K_{obs} of Cl⁻ was higher than that of other groups, indicating that Cl⁻ accelerated the decomplexation of Ni-EDTA.



Figure 6. Decomplexation of Ni-EDTA in coexisting ions (a) and kinetics fitting lines (b).

Cl⁻ could accelerate the decomplexation of Ni-EDTA in the 3D-EF system. This could be explained by the fact that Cl⁻ generated Cl₂ through hydrogen evolution at anode, which further hydrolyzed to form strongly oxidized ClO⁻ and then promoted the removal of Ni-EDTA (Equations (6)–(8)) [42,43]. However, NO₃⁻ and HPO₄²⁻ inhibited the removal effect of Ni-EDTA, because the standard electrode potential of NO₃⁻ /NO₂⁻ (0.01 V) was higher than that of Fe²⁺/Fe (-0.44 V). When the NO₃⁻ existed within the 3D-EF system, NO₃⁻ would compete with Ni-EDTA for electrons. Meanwhile, NO₃⁻ could scavenge with ·OH to further generate NO₃· with a lower reaction activity, which led to a decrease in the Ni-EDTA removal effect (Equation (9)) [44,45]. In the 3D-EF system, HPO₄²⁻ could quench a certain amount of ·OH to form less reactive H₂PO₄· (Equation (10)), resulting in a lower removal efficiency of Ni-EDTA [46].

$$2\mathrm{Cl}^- \to \mathrm{Cl}_2 + 2\mathrm{e}^- \tag{6}$$

$$Cl_2 + H_2O \leftrightarrow HOCl + Cl^- + H^+$$
 (7)

$$HOCl \leftrightarrow H^+ + OCl^-$$
 (8)

$$NO_3^- + \cdot OH \to NO_3 \cdot + OH^- \tag{9}$$

$$HPO_4^{2-} + \cdot OH \to OH^- + H_2PO_4 \cdot$$
(10)

4. Conclusions

In summary, the 3D-EF system is a novel and effective method for the decomplexation of Ni-EDTA. The decomplexation performance of Ni-EDTA in the 3D-EF system was superior to its performance in the GAC and EF system. The removal efficiency of Ni-EDTA reached 84.89% at a near-neutral pH in the 3D-EF system. The 3D-EF system with GAC particle electrode could break through the limitation of pH and broaden the application window of pH. Influencing factors analysis by selecting Ni-EDTA as a target contaminant suggested that Fe²⁺ of 1 mmol/L, GAC of 4 g/L, and current density of 10 mA/cm² accelerated the Ni-EDTA decomplexation. In addition, the presence of coexisting ions can affect the decomplexation of Ni-EDTA.

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