



Oxalic acid mineralization by electrochemical oxidation processes

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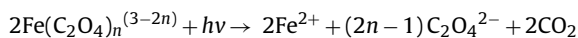
ABSTRACT

In this study, two electrochemical oxidation processes were utilized to mineralize oxalic acid which was a major intermediate compound in the oxidation of phenols and other aromatic compounds. The anode rod and cathode net were made of a titanium coated with RuO₂/IrO₂ (Ti-DSA) and stainless steel (S.S. net, SUS304), respectively. First, the Fered-Fenton process, which used H₂O₂ and Fe²⁺ as additive reagents, achieved 85% of TOC removal. It proceeded with ligand-to-metal charge-transfer (LMCT), which was evidenced by the accumulation of metallic foil on the selected cathode. However, in the absence of H₂O₂/Fe²⁺, it showed a higher TOC removal efficiency while using Cl⁻ only as an additive reagent due to the formation of hypochlorite on the anode. It was also found that the mineralization of oxalic acid by electrolysis generated hypochlorite better than the dosage of commercial hypochlorite without electricity. Also, pH value was a major factor that affected the mineralization efficiency of the oxalic acid due to the chlorine chemistry. 99% TOC removal could be obtained by Cl⁻ electrolysis in an acidic environment.

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1. Introduction

Oxalate is the major intermediate in advanced oxidation processes (AOPs) used to treat organic contaminated waters [1–7]. Various AOPs were used to degrade citric acid wastewater in our previous study [8]. The derivation of oxalate in the COD residue reached 50–70%. Normally, oxalate exists in natural water due to incomplete combustion, oxidation decomposition of ozone, and photo-oxidation of hydrocarbon, and can be decomposed by UV rays in sunshine as the ferric ions precipitate. Therefore, the degradation of ferric-oxalate complexes formed from Fenton reactions through photo-treatment have been usually executed as follows [9–13]:



The oxalic acid contents of the discharged water decrease oxygen dissolution and become a secondary pollutant after AOP treatment. Photocatalytic, ultrasonic, and biochemical methods for destroying oxalic acid have all been studied [14–16]. However, the reagent cost, energy consumption, and treating periods all limit the efficiency of degradation [17].

In previous studies, an efficient electro-Fenton reactor was designed for treating benzene sulfonic acid (BSA) [18]. This novel Fenton process, called the Fered-Fenton method, was then used to mineralize oxalic acid. The effects of cathode material on TOC

and COD removal have been investigated [19]. The results showed that 95% TOC could be successfully mineralized through an electrochemical oxidation process using FeCl₃ as a ferric source. However, the drawback of this process is that it produces a significant amount of ferric hydroxide sludge that needs further separation and disposal.

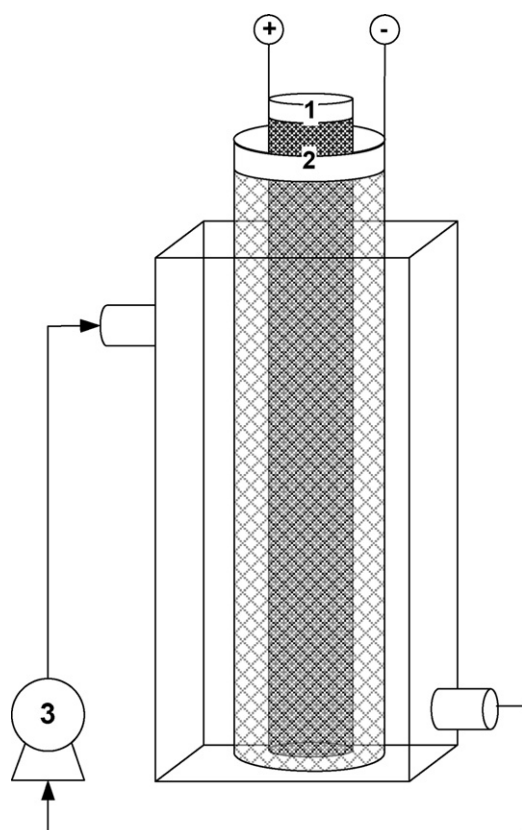
In this study, we applied RuO₂/IrO₂ (Ti-DSA) and stainless steel (S.S. net, SUS304) as electrodes, and tried to elucidate the mechanism of the Fered-Fenton process by observing the Fe²⁺ reduction on the anode. Furthermore, in order to reduce the chemical sludge and high operation cost of the Fered-Fenton process, several chemical reagents, such as Fe₂(SO₄)₃, NaCl, and Na₂SO₄, were added to the electrolysis system instead of H₂O₂ and Fe²⁺. We also attempted to clarify the solution variables that affected the oxalic acid mineralization, including chloride concentration, applied current and initial pH.

2. Materials and methods

The source of the raw oxalic acid solution was artificially prepared in distilled water. Chemical agents used in this study, such as Fe₂(SO₄)₃·xH₂O, FeCl₃·6H₂O, FeCl₂·4H₂O, NaCl, HClO, and Na₂SO₄, were all analytical grade.

Batch electrolysis was carried out in a rectangular reactor (12 cm-L × 12 cm-W × 30 cm-H) which was adjusted at a constant current mode. The schematic apparatus is shown in Fig. 1. The cylindrical anode and cathode nets were made of titanium coated with RuO₂/IrO₂ (Ti-DSA, 1.3 cm-φ, 30 cm-H) and stainless steel (S.S. net, SUS304, 5 cm-φ, 30 cm-H), respectively. The solution in the elec-

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1. Cathode: SUS304 stainless steel net
2. Anode: Ti-DSA net
3. Centrifugal pump

Fig. 1. Schematic apparatus of the electrochemical reactor.

trolytic cell was mixed by cycling 9 L/min. The given concentration of oxalic acid, ferric ions, and NaCl, were added to the reactor, in which the total solution volume was 3.5 L, and then the pH was adjusted to the desired value. As the power was turned on, the pH, ORP, temperature, and conductivity were conditioned. Solution was sampled for each specific period, and measured for Total Organic Carbon (TOC) and Ion Chromatography (IC). The sample was pretreated with phosphoric acid to remove inorganic carbon. TOC removal (%) was defined as follows:

$$\text{TOC}_r = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100\%$$

where 0 and t indicate the sampled solution initially and at time t , respectively. Concentration of oxalic acid was measured by an ion-chromatography system consisting of an automatic sample injector (100 μL injection volume).

3. Results and discussions

3.1. Comparison of traditional Fenton and Fered-Fenton processes

In the first 60 min, the traditional Fenton process was carried out to treat 10 mM of oxalic acid where the pH was conditioned to the appropriate value. Then Fered-Fenton processes followed for the rest of 60 min. The theoretical dosage of H_2O_2 was 340 mg/L, and FeCl_2 as the ferrous source was 5 mM during the Fenton stage. The current applied during the electrolysis stage was set at 20 A. During the two stages, as shown in Fig. 2, only 20% of the TOC was removed by the traditional Fenton process. However, electrolysis

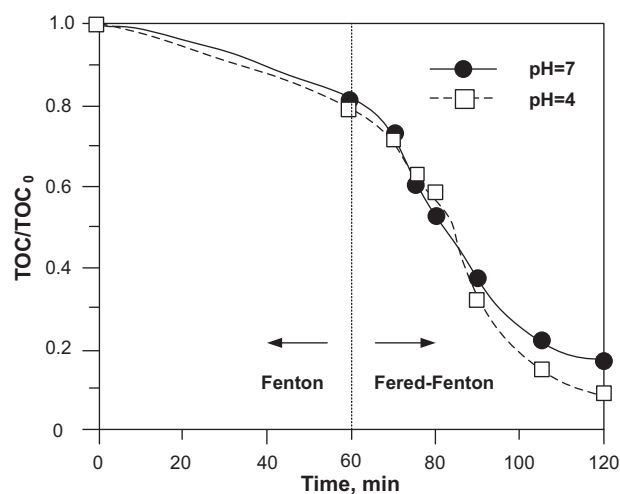


Fig. 2. Comparison between the traditional Fenton and Fered-Fenton processes [oxalic acid]: 10 mM; $[\text{FeCl}_2]$: 5 mM; $[\text{H}_2\text{O}_2]$: 340 mg/L; anode: Ti-DSA net; cathode: S.S. net; volume: 3.5 L; fixed current: 20 A.

process removed about 85% of the TOC, when the initial pH value was either 4 or 7.

3.2. Ligand-to-metal charge-transfer (LMCT) on the cathode

After the electrolysis stage, the cathode would be coated with a silver gray metallic foil, as shown in Fig. 3. Balmer and Sulzberger proposed an iron cycling mechanism with oxalate through the photo-Fenton system [20]. Fe (III)-oxalate complexes would be excited into a charge-transfer state by ligand-to-metal charge-transfer (LMCT). Fe (II) and C_2O_4^- were then generated. Finally the C_2O_4^- reacted with the oxygen to create 2CO_2 and O_2^- . In the present study, the exciting energy of the Fe (III)-oxalate complexes was supposed come from electricity. The LMCT was also believed to work on the cathode.

The oxalic acid, which formed complexes with ferric ions, $\text{Fe}(\text{C}_2\text{O}_4)^+$, were adsorbed on the cathode. The applied electric current then transferred the electron from $\text{C}_2\text{O}_4^{2-}$ and caused the reduction of Fe^{3+} to Fe^{2+} . $\text{C}_2\text{O}_4^{2-}$ ions, therefore, decomposed into CO_2 and CO_2^- . The latter is a strong reductive radical [21], which attacks Fe^{2+} . The electron generated from the cathode simultaneously reduces Fe^{2+} . Therefore, Fe^0 metallic foil accumulated on the cathode, as the two CO_2 molecules were released.

To rationalize this hypothesis, the amounts of ferrous ions and iron were monitored during the electrolysis process. As shown in

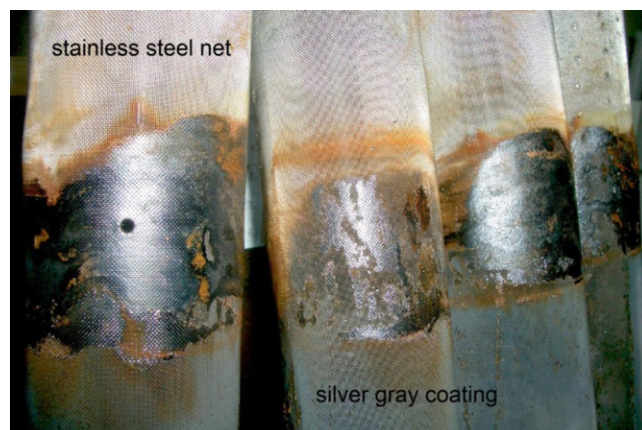


Fig. 3. Metallic foil coated on the stainless steel net after the electrolysis stage.

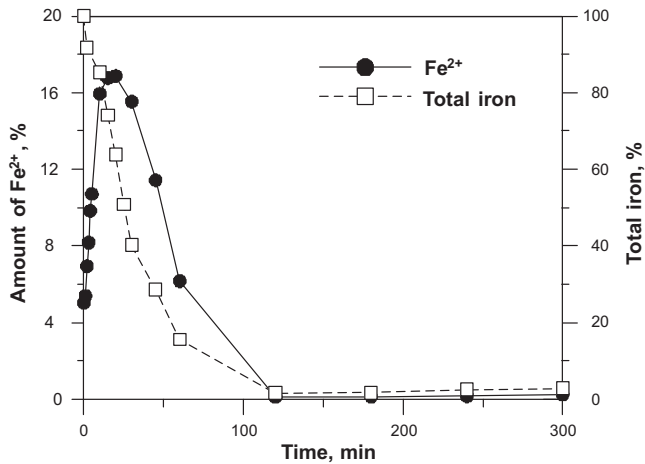


Fig. 4. The amounts of ferrous ions and iron as a function of the reaction period of the electrolysis process. [Fe³⁺]: FeCl₃ 30 mM; [Ox]: 20 mM; anode: Ti-DSA; cathode: stainless steel net; volume: 3.5 L; fixed current: 20 A; pH=3.

Fig. 4, initially, Fe³⁺ reduction using electricity led to an increase in the amount of ferrous ions, while the total amount of iron (the summation of Fe²⁺ and Fe³⁺) decreased. After reaching the maximum value, the ferrous ions decreased and almost disappeared over 120 min. Meanwhile the total amount of iron showed a similar tendency, and coincidentally also disappeared during the 120 min. It is logical to conclude, therefore, that the reduction of Fe³⁺ to the Fe⁰ coating on the cathode material indeed occurred during the electrolysis of the oxalic acid.

3.3. Effects of additive species in electrolysis process

Oxalic acid is a major byproduct of using AOPs to treat organic pollutants. Bossmann et al. found that oxalic acid was mainly produced from the degradation of 2,4-dimethylaniline (2,4-xylydine) using the H₂O₂/UV method, and its further oxidation was not observed [11]. In our previous studies, we thought the derivation of oxalic acid occurred due to an over dosage of H₂O₂ when using Fered-Fenton technology to treat azo dye reactive-Black B (RBB, COD = 4800 mg/L) [19]. Therefore, the TOC removal of oxalic acid in the presence of various species was used to examine whether the electrolysis oxidized process worked in the absence of H₂O₂.

Since the ferrous source used in the Fered-Fenton process in previous section was FeCl₂, three compounds, Fe₂(SO₄)₃, NaCl, and Na₂SO₄, were added separately to the reaction solution. As shown in Fig. 5, the presence Na₂SO₄ and of Fe₂(SO₄)₃, as well as a blank test (direct electrolysis), did not reduce TOC significantly during the reaction periods, while the presence of NaCl only led to about 95% of oxalic acid mineralization during the electrolysis process.

Subramanyan et al. proposed a mechanism to explain the oxidation of As (III) to As (V) using in situ generated hypochlorite [22]. The derivation of oxidant, ClO⁻, follows the equations listed below:

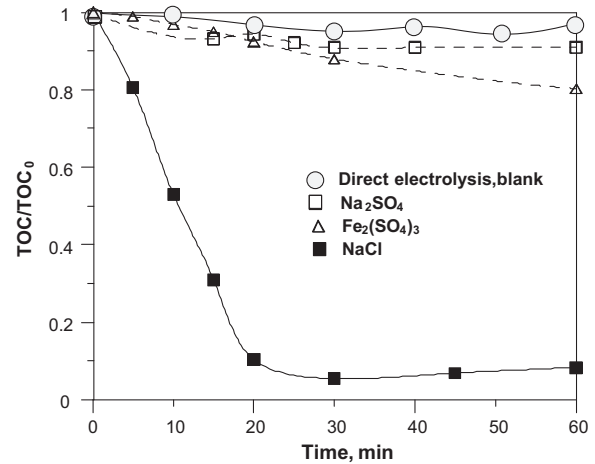
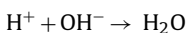
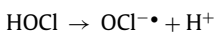
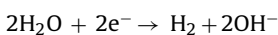
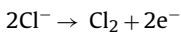


Fig. 5. Effect of additive species in the electrolysis oxidized process on TOC removal of oxalic acid. [Ox]: 10 mM; [Fe₂(SO₄)₃]: 2.5 mM; [NaCl]: 15 mM; [Na₂SO₄]: 0.1 M; anode: Ti-DSA net; cathode: stainless steel net; volume: 3.5 L; fixed current: 20 A; pH=3.

The chloride ions were converted to chlorine on the anodic surface, while the water was ionized on the cathode to create hydroxyl ions and hydrogen. In the bulk solution, the liberated chlorine reacts with the water to produce hypochlorous acid. The generated hypochlorous acid was further dissociated to create hypochlorite and hydrogen ions. The hydroxyl ions reacted with the hydrogen ions to form water molecules. Depending on the pH, chlorine forms various chlorine species (Cl₂, HOCl and ClO⁻) in the reactor [23,24]. Therefore, such an efficient electrolysis reaction in the presence of Cl⁻ only can be re-defined as the simple oxidation of oxalic acid by in situ generated hypochlorite or chlorine.

3.4. Effects of chloride ion concentrations and applied current

Conventionally, the oxalic acid was degraded via bio-treatment. However, the efficiency of the bacterium significantly decreased when treating trace amounts of oxalic acid, even to attain the standard content in drinking water. In this study, Fig. 6, curve (a) shows that 95% of the 20 mM oxalic acid was successfully mineralized in one hour with 90 mM NaCl by electrolysis oxidation in the absence of iron and H₂O₂. As shown in Fig. 6 curve (b), the removal of 2 mM oxalic acid also reached 94% in 30 min using 10 mM NaCl.

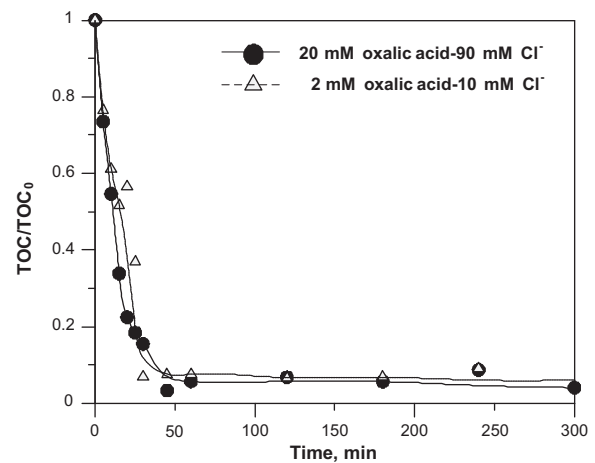


Fig. 6. The mineralization of oxalic acid in the presence of NaCl. (a) [Ox]: 20 mM; [NaCl]: 90 mM and (b) [Ox]: 2 mM; [NaCl]: 10 mM; anode: stainless steel net; volume: 3.5 L; fixed current: 20 A; pH=3.

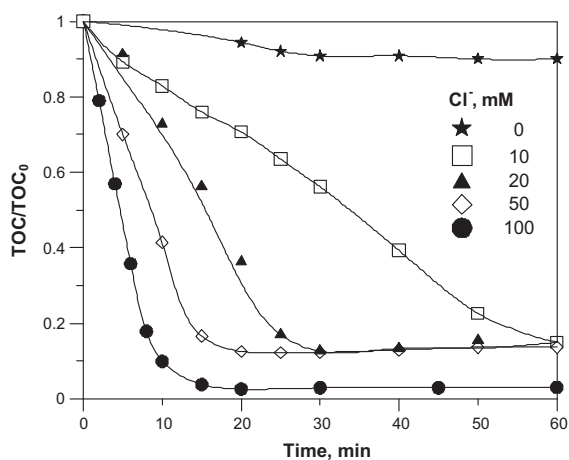


Fig. 7. Effect of the concentration of Cl^- on TOC removal. [Ox]: 2 mM; [NaCl]: 0–100 mM; anode: Ti-DSA net; cathode: stainless steel net; volume: 3.5 L; fixed current: 20 A; pH = 3.

The effects of the Cl^- concentration and current applied to the mineralization of oxalic acid were discussed in Figs. 7 and 8. Obviously, the TOC removal would depend on both the Cl^- concentration and strength of the current applied. TOC removal could have about a 95% maximum value if 100 mM Cl^- and a 20 A current were adopted. However, for industrial use, the optimum conditions for oxalic acid treatment should consider cost and energy consumption. The observed rate constants were calculated as shown in Fig. 9, in which the k_{obs} presents a linear relation with both parameters. The k_{obs} is used to criticize the parameter efficiency, therefore, the suggested the Cl^- dosage and energy applied in this study could validly attain maximum oxalic acid removal.

3.5. The effect of initial pH values

According to chlorine's chemistry, the various species Cl^- of chlorine (HOCl , ClO^- , Cl_2 , etc.) formed in the solution is pH dependent [25]. The effect of the initial pH value was used to clarify the electrolysis efficiency of Cl^- in acidic and basic environments, as shown in Fig. 10. Lower pH values lead to the higher TOC removal. Typically, in the pH range 6–9, hypochlorous acid and hypochlorite were the main chlorine species. Cl_2 and other chlorine intermediates (including Cl_3^- , Cl_2O) dominate at pH levels below 4. Therefore, the electrolysis generated hypochlorite might

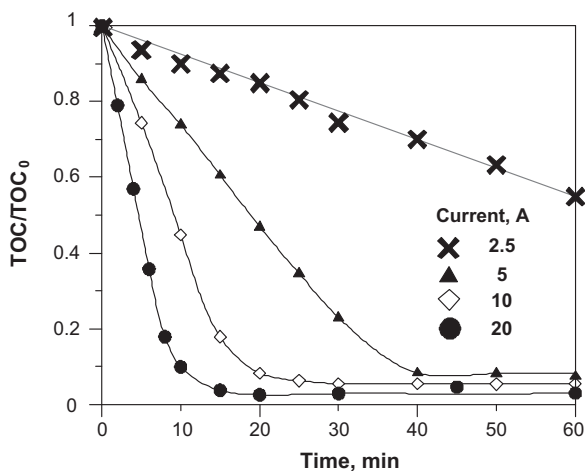


Fig. 8. Effect of current intensity on TOC removal. [Ox]: 2 mM; [NaCl]: 0.1 M; anode: Ti-DSA net; cathode: stainless steel net; volume: 3.5 L; fixed current: 0–20 A; pH = 3.

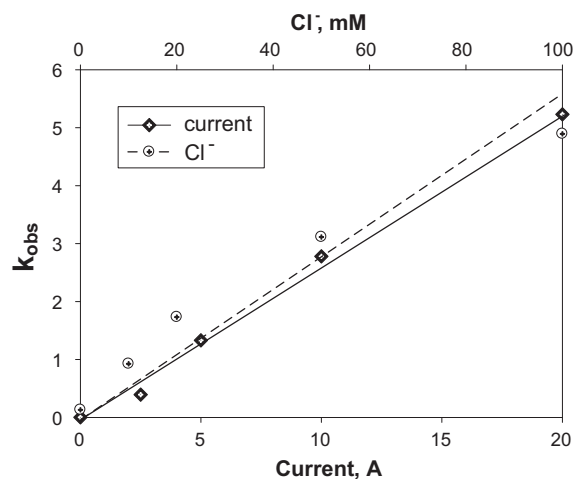


Fig. 9. Calculated k_{obs} of various Cl^- concentrations and current intensities.

be transformed to Cl_2 , which has a greater oxidation ability, to further enhance the mineralization of oxalic acid in an acidic environment. Almost 99% of the TOC was removed when the initial pH was adjusted to 1.

3.6. The effects of the commercial and the electro-generated hypochlorite

The theoretical quantity of HClO produced from Cl^- electrolysis in 40 min was 17.7 mM. Fig. 11 compares the abilities of commercial and electro-generated hypochlorite for TOC and IC removal, and both initial concentrations were adjusted to a given value. In the (a) curve, about 60% of oxalic acid dosed with 10 mM was degraded by commercial HClO in 40 min without electricity, while the degradation in the (b) curve reached 98% in one hour utilizing electro-generated hypochlorite. The ability of Cl^- electrolysis to oxidize oxalic acid is greater than that of HClO without electricity. Normally, the oxalic acid mineralized by ClO^- would proceed with a metastable reaction stage to CO_2 . The excellent oxidation power of the non-soluble Ti-DSA anode net provided not only electricity, but also attacked these metastable compounds.

Furthermore, in these curves, tendencies as functions of reaction time of TOC and IC removal were almost identical. This reveals that the mineralization of oxalic acid by hypochlorite decom-

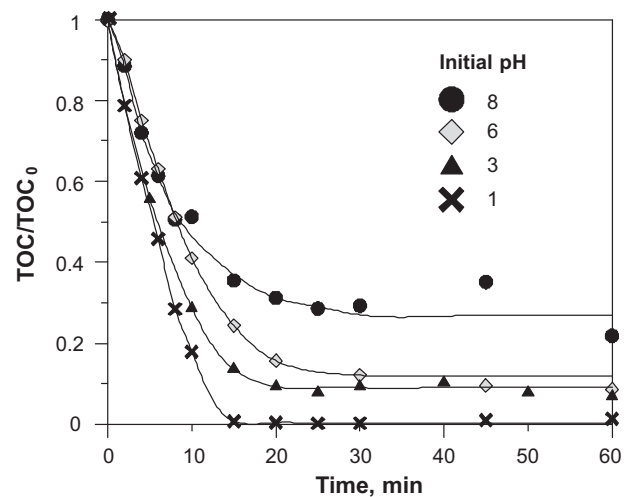


Fig. 10. Effect of initial pH value on TOC removal. [Ox]: 10 mM; [NaCl]: 0.1 M; anode: Ti-DSA net; cathode: S.S. net; volume: 3.5 L; pH = 3.

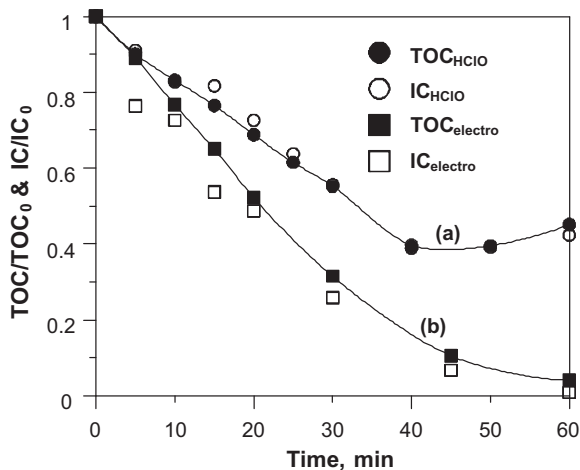


Fig. 11. TOC and IC analysis of oxalic acid in the presence of NaCl and commercial hypochlorite. (a) [Ox]: 10 mM; [HClO]: 17.7 mM; without electricity; pH = 1.5; volume: 3.5 L and (b) [Ox]: 10 mM; [NaCl]: 0.1 M; with electricity; pH = 3; volume: 3.5 L; fixed current: 5 A; pH = 3.

posed to CO₂ directly and did not leave the stable intermediates in solution.

4. Conclusions

In this study, oxalic acid efficiently mineralized in the Fered-Fenton H₂O₂/Fe²⁺ process was attributed to the ligand-to-metal charge-transfer (LMCT) mechanism. This was evidenced by the metallic Fe foil forming on the cathode after the Fered-Fenton process. However, the additives, Fe₂(SO₄)₃, NaCl, and Na₂SO₄, were then used to examine whether the mineralization occurred in the absence of H₂O₂/Fe²⁺. It was found that the electrolysis only generated HClO in the presence of Cl⁻ and could mineralize the oxalic acid directly. Moreover, the acidic environment enhanced the TOC removal due to the chlorine chemistry. The observed rate constant of the given range of Cl⁻ concentrations and applied currents showed that excellent TOC removal efficiency could be achieved with a Cl⁻ electrolysis system. Finally, the hypochlorite generated by the Cl⁻ electrolysis showed a higher TOC removal rate than that without electricity. This suggested that the oxalic acid was mineralized not only by the hypochlorite but also by the good oxidation power of the selected anode, Ti-DSA net.

The successful oxalic acid mineralization, which could reduce the cost of chemical reagent and byproduct sludge disposal simultaneously, has been evidenced through the use of Cl⁻ electrolysis as a replacement for the Fered-Fenton H₂O₂/Fe²⁺ process. However, for discussing how the mineralization occurred, more precise TOC detection on electrode through a newly designed membrane is being studied. On the other hand, the feasibility of Cl⁻ electrolysis for treating the other 30–50% of COD residue from the AOP process, such as succinic acid, muconic acid, tartaric acid, and malonic acid [26], will be also discussed in the future.

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