

## Short communication

## Mineralization of organic acids by the photo-electrochemical process in the presence of chloride ions

Yu-Jen Shih<sup>a</sup>, Kuan-Hsiang Chen<sup>b</sup>, Yao-Hui Huang<sup>a,b,\*</sup><sup>a</sup> Department of Chemical Engineering, National Cheng-Kung University, Tainan 701, Taiwan<sup>b</sup> Sustainable Environment Research Center, National Cheng-Kung University, Tainan 701, Taiwan

## ARTICLE INFO

## Article history:

Received 6 June 2013

Received in revised form 9 September 2013

Accepted 15 September 2013

Available online 18 October 2013

## Keywords:

Ti-DSA

HOCl

Electrolysis

UV-254

Total organic carbon

## ABSTRACT

This investigation demonstrates an indirect chloride photo-electrochemical method for mineralizing the organic acids (5 mM), including acetic, maleic, malonic, citric, oxalic, and succinic acids. The electrolytic reactor (12 cm × 12 cm × 30 cm) held 2.5 L solution, in which both anode and cathode were the titanium-based dimensionally stable anode (Ti-DSA) that was coated with RuO<sub>2</sub>/IrO<sub>2</sub>. Different active chlorine species with various redox potentials, including OCl<sup>-</sup>, HOCl, and Cl<sub>2</sub>, produced in NaCl medium were the major oxidants depending on the pH of the electrolysis. The results revealed that a pH in the range 2.5–7 maximized the removal rate of total organic carbon (TOC) of citric acid solution. The UV-254 nm light was then utilized in the NaCl electrolysis to support a photo-electrochemical reaction. The substantial improvement in the mineralization efficiency for all organic acids was attributed to the hydroxyl radicals (\*OH) and chlorine radicals (Cl\*) from HOCl upon activation by the UV irradiation.

© 2013 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

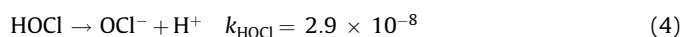
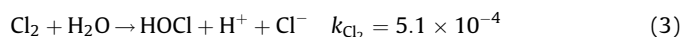
In environmental engineering, advanced oxidation processes (AOPs) are well known to be efficient methods for oxidizing organic recalcitrant pollutants. Hydroxyl radicals, which have a high redox potential ( $E^0 = 2.73$  V) can be formed by catalyzing hydrogen peroxide with ferrous salts in the Fenton reaction, which is an AOP [1–4]. However, the large amount of iron sludge that is produced in this process and the required acidic conditions are shortcomings that affect the use of the Fenton method in the remediation of organic wastewater. The carboxylic acids as a potential residue are the major parts of total organic carbon (TOC) in final solution while Fenton methods do not completely mineralize the aromatic compounds. These byproducts are less reactive toward the hydroxyl radicals and often are more toxic than the original compounds [5–7].

The authors' earlier study found that, in Fenton methods, the concentration of oxalic acid increased with the extent of degradation and the decolorization of the RBB dye [8]. Although the photo- or electrical assistance can extend the life span of hydroxyl radicals, only approximately 50% of oxalic acid was mineralized. To reduce the costs of sludge disposal and reagents, the feasibility of replacing Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> with NaCl in electrochemical

process was investigated. The results showed that almost all of oxalic acid that resisted attacks by the Fenton mechanism could be mineralized [9]. Accordingly, the chlorine chemistry that was induced by the electrolysis was thought to provide a method for selectively treating the carboxylic acids. During electrolysis, chlorine can be produced by anodic chloride oxidation while hydrogen is generated at the cathode [10,11]:



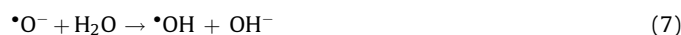
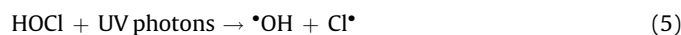
The electrochemical system continuously forms three major chlorine species – chlorine gas (Cl<sub>2</sub>), hypochlorous acid (HOCl) and hypochlorite ion (ClO<sup>-</sup>) – depending on the pH of the solution [12–15]:



HOCl is an efficient oxidant not only for the degradation of organic compounds, such as aliphatic and aromatic compounds, but also for oxidizing inorganic compounds, including metallic ions (Mn<sup>2+</sup>, Fe<sup>2+</sup>, and As<sup>3+</sup>), ammonia, and halide [16,17]. Reduced chloride ions can be oxidized by the anode, and the chloride electrochemical oxidation system is therefore a recycling system. Thus, the chloride ion is important in deconstructing organic contaminants via an indirect electro-oxidation process prior to

\* Corresponding author. Tel.: +886 2757575x62636; fax: +886 6 2344496.  
E-mail address: [yhhuang@mail.ncku.edu.tw](mailto:yhhuang@mail.ncku.edu.tw) (Y.-H. Huang).

direct electrical treatment. However, the photolysis of chlorine at 254 nm generates some active oxidants, such as chloride radicals ( $\text{Cl}^\bullet$ ), hydroxyl radicals ( $\bullet\text{OH}$ ) and oxygen radicals ( $\bullet\text{O}^-$ ) [18–22].



Xiao et al. monitored the ESR signal of DMPO (dimethylpyrrolineoxide)-OH from the photolysis of HOCl, establishing the photo-generation of hydroxyl radicals, which does not occur in the dark [23].

Even though chlorine chemistry has been extensively exploited in disinfecting water [24,25], its potential in treating micropollutants in wastewater has received much great attention only in recent years. Chlorine is a selective oxidant that reacts preferentially with some electron-rich organic moieties (ERMs) [26]. Therefore, chloride photo-electrochemical methods focus on the removal of carboxylic acids that cannot be efficiently removed by AOPs [27,28]. For the treatment of high-salinity wastewater, the indirect oxidation of chlorine was very significant on the titanium-based dimensionally stable anode (Ti-DSA, coated with  $\text{RuO}_2/\text{IrO}_2$ ). Accounting for low energy consumption, the Ti-DSA( $\text{RuO}_2/\text{IrO}_2$ ) was not only cost-effective but also promising in electrochemical oxidation of organic wastewaters [29]. Following our previous works [9,11], in this investigation, a novel chloride electrochemical reactor with UV irradiation was established to mineralize the target organic acids, including acetic, maleic, malonic, citric, oxalic, and succinic acids, using Ti-DSA as the electrodes. The critical behaviors of chlorines associated with the photo-electrochemical process were elucidated by determining the effect of initial pH and UV irradiation on the mineralization of citric acids.

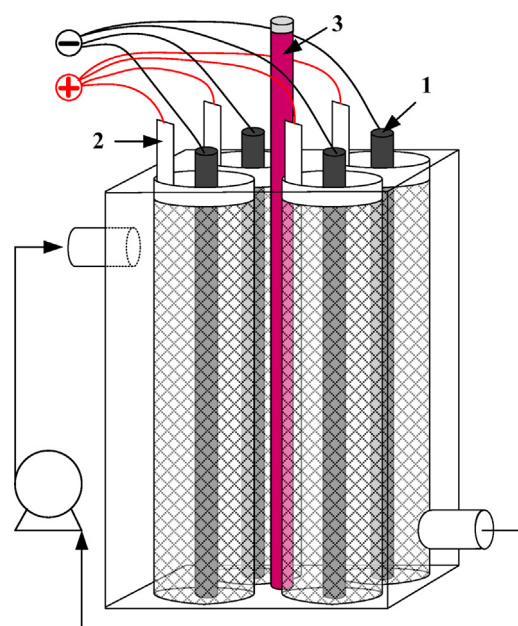
## 2. Materials and methods

### 2.1. Materials

All chemicals were of analytical grade and were used without purification. The target organic acids were citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , J.T. Baker), malonic acid, maleic acid ( $\text{C}_3\text{H}_4\text{O}_4$ ,  $\text{C}_4\text{H}_4\text{O}_4$ , Showa Chemical), acetic acid, succinic acid ( $\text{C}_2\text{H}_4\text{O}_2$ ,  $\text{C}_4\text{H}_6\text{O}_4$ , Fluka), and oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ , Sigma–Aldrich). NaCl, which was utilized as the electrolyte, and NaOH and  $\text{H}_2\text{SO}_4$ , which were used to set the pH, were purchased from Sigma–Aldrich. The reagents were diluted by adding deionized water (resistivity > 18.3  $\text{M}\Omega$ ) that had been purified using a laboratorial grade RO-ultrapure water system.

### 2.2. Experimental apparatus

A batch experiment on the mineralization of the organic acids was carried out in a rectangular photo-electrochemical reactor (12 cm–W  $\times$  12 cm–L  $\times$  30 cm–H) in constant current mode, as presented in Fig. 1. Four pairs of a cathodic rod and an anodic net, made from titanium-based dimensionally stable anode that was coated with  $\text{RuO}_2/\text{IrO}_2$  (Ti-DSA), were mounted in the reactor, while one UV-C lamp (254 nm,  $2.04 \text{ mW cm}^{-2}$ , with a mean light intensity of 3 cm away from the lamp) was inserted between the electrode pairs. The reactor held a total 2.5 L of solution, which was mixed and circulated using a pump (9 L/min). The geometric surface area of the anodic net contacted with the liquid was  $737.5 \text{ cm}^2$ . Before the reaction was begun, the UV lamp was turned on for 10 min to stabilize its irradiation. Once the given concentrations of NaCl and organic acids had been introduced into reactor, the dc-electricity was turned on. At particular



1. cathode, Ti-DSA rod ( $\text{IrO}_2/\text{RuO}_2$ )  
2. anode, Ti-DSA net ( $\text{IrO}_2/\text{RuO}_2$ )  
3. UV lamp (254 nm)

Fig. 1. Photo-electrochemical reactor.

intervals, the extent of organic acid mineralization in extracted samples was determined by measuring TOC (Total Organic Carbon, Siever 900 Innovox).

## 3. Results and discussion

### 3.1. Mineralization of organic acids by chloride electrochemical processes

Our earlier investigation demonstrated chloride electrolysis for mineralizing oxalic acid, which was less reactive with the electro-Fenton system [9]. In this work, the electrolysis of chloride ions using four pairs of electrodes (Ti-DSA) through which flowed 15 A (current density =  $20.3 \times 10^{-3} \text{ A/cm}^2$ ) in 500 mM NaCl was used to treat the selected organic acids (5 mM, acetic, maleic, malonic, citric, oxalic, succinic acids) at pH 2.5. As displayed in Fig. 2, the

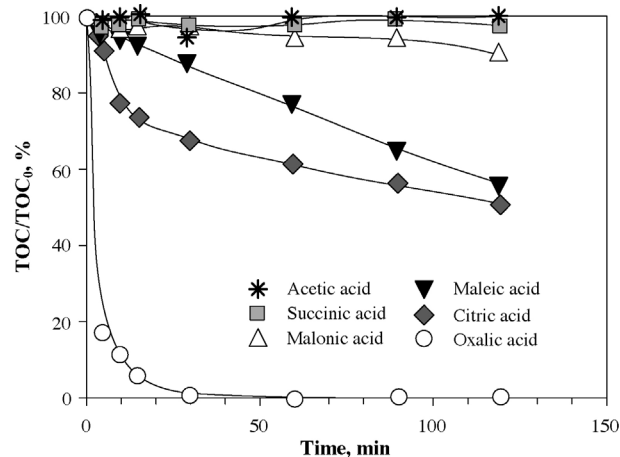


Fig. 2. TOC removal of organic acids by electrochemical oxidation ( $I = 15 \text{ A}$  (current density =  $20.3 \times 10^{-3} \text{ A/cm}^2$ ), [organic acid] = 5 mM, pH = 2.5, [NaCl] = 500 mM).

Download English Version:

<https://daneshyari.com/en/article/691264>

Download Persian Version:

<https://daneshyari.com/article/691264>

[Daneshyari.com](https://daneshyari.com)