Desalination 341 (2014) 87–93

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

# Comparative study of different electrochemical methods for petroleum refinery wastewater treatment

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## HIGHLIGHTS

- Different electrochemical methods were used to treat petroleum refinery wastewater.
- Fe and air were introduced separately or simultaneously into a traditional reactor.
- The generated $H_2O_2$ and the residual $Cl^-$ was measured after the wastewater treatment.
- UV spectrum and GC–MS were used to analyze the water quality.
- The possible mechanism was GDEs, three-dimensional electrodes and Fenton reaction.

## ARTICLE INFO

*Article history:*
Received 29 November 2013
Received in revised form 25 February 2014
Accepted 27 February 2014
Available online 18 March 2014

*Keywords:*
Electrochemical process
Fe particle
Air
Refinery wastewater
COD removal

## ABSTRACT

In this study, petroleum refinery wastewater was treated by different electrochemical processes when Fe particle and air were introduced separately or simultaneously into a traditional two-dimensional reactor. The effects of Fe particle and air on the electrochemical processes were investigated, and the possible reaction mechanisms of these processes were discussed by comparing the results of COD removal and instantaneous current efficiency. The experimental results showed that the effluent with a satisfactory COD removal efficiency (89.91%) and $NH_3$-N removal efficiency (99.47%) was obtained when the initial pH was 3, and fine Fe particle and air were introduced simultaneously. This result can also be supported by the analysis of UV spectrum and GC–MS. All of these results suggested that the electrochemical system with Fe particle, air and pH = 3 was an effective approach for petroleum refinery wastewater treatment due to the cooperative action of efficient GDEs, three-dimensional electrodes and the normal Fenton reaction.



## 1. Introduction

A large amount of water is used in refinery processes, especially during distillation, hydro-treating, desalination and system water cooling, which means that wastewater from a petroleum refinery is typically characteristic of heavy pollution subsequently running into rivers [1]. It is generally regarded that a light fraction of aliphatic, aromatic petroleum hydrocarbons, ammonia and halogenated organic substances, which are the most important contaminants contribute to high chemical oxygen demand (COD) and ammonia nitrogen ($NH_3$-N) value [2]. The traditional treatments of refinery wastewater are based on mechanical and physico-chemical methods such as oil–water separation and coagulation followed by biological treatment. Several solutions have been proposed in this regard, including the use of chemical coagulation [3,4], biodegradation [5,6], wet oxidation [7], ozone treatment [8], membrane bioreactor [9] and ceramic membrane filtration [10]. However, these techniques were not suitable to treat heavily contaminated water with chemical oxygen demand (COD) concentration over 4000 mg $L^{-1}$. So there is an urgent need to develop advanced techniques to remove nonbiodegradable organic substances from petroleum refinery wastewater.

Electrochemical technology has been attracting great attention for treatment of wastewater, as reported in several books and reviews [11–15]. It offers many distinctive advantages such as versatility, high energy efficiency, safety, amenability of automation, and cost effectiveness because the main reagent is the electron [16]. However, traditional electrochemical methods such as electrocoagulation, electroflotation, electroflocculation, electrochemical reduction and electrochlorination can only partially remove persistent organic pollutants (POPs) and/or produce undesirable and harmful byproducts [16]. Furthermore, the Fenton method is the most popular chemical advanced oxidation process (AOPs) and has also been successfully used to degrade organic molecules from wastewater over the past decade [16]. In a conventional

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http://dx.doi.org/10.1016/j.desal.2014.02.037
0011-9164/

Fenton process, a combination of $Fe^{2+}$ and $H_2O_2$ (Fenton's reagent) under acidic milieu can generate very highly reactive hydroxyl radicals (•OH), the second strongest oxidizing agent after fluorine, which then react with target organic contaminants leading to the mineralization of some organic compounds through conversion into $CO_2$, $H_2O$ and inorganic ions. The electro-Fenton (EF) process is an indirect electrochemical process based on Fenton's reaction chemistry while Fenton's reagent is partially or completely generated from electrode reactions. Generally, $H_2O_2$ is generated at the cathode with $O_2$ or air feeding, and $Fe^{2+}$ is generated when an iron elementary substance exists in acidic solution. Nevertheless, introducing iron particles and air simultaneously into the electrochemical process has never been reported apart from our group [17].

In this work, in order to verify the effect of Fe particles and air on removing pollutants from refinery wastewater through the electrochemical process, iron particles and air were introduced separately or simultaneously into a traditional two-dimensional reactor to constitute different electrochemical systems for petroleum refinery wastewater remediation, and different electrochemical methods were compared, the possible reaction mechanism in treatment process was also proposed based on the analysis of COD, instantaneous current efficiency (ICE), UV spectrum, GC–MS, and the concentration of $NH_3$-N, the residual $Cl^-$ and the generated $H_2O_2$ after the wastewater treatment.

## 2. Materials and methods

### 2.1. Characteristics of refinery wastewater

The refinery wastewater was provided by the Yulin refinery plant located in Shaanxi province of China. The characteristics of wastewater as determined by the supplier are listed in Table 1. Here, the high conductivity resulting from many inorganic salts in the wastewater would promote the electrochemical process.

### 2.2. Experimental procedure and set-up

The wastewater was treated by different electrochemical methods, and the scheme of the electrochemical apparatus is shown in Fig. 1. All experimental studies were accomplished at ambient temperature with 300 mL of wastewater, porous graphite plates (60 mm × 110 mm × 2 mm) were employed as anode and cathode, which were positioned vertically and parallel to each other. The direct-current voltage was supplied by a DC power source (Type 3240.2, Statron, Germany), and sodium sulfate ($Na_2SO_4$) had been selected as electrolyte, Fe particles or/and air were also introduced into the direct electrochemical process (EC), respectively. The different electrochemical methods and conditions are shown in Table 2, and concentrated $H_2SO_4$ solution was used to adjust the pH of wastewater to about 3 in the last electrochemical process, which is the optimum pH of the Fenton process according to the literature [16,18]. During the experiment, aliquots of the processed solution were periodically extracted from the reaction system by airtight syringes, filtered and analyzed in time since the current occurred. All of the chemical reagents used in this work were of analytical grade without further purification. Fe particles and $H_2SO_4$ were obtained from Xi'an Reagent Co., China, and all the other reagents were purchased from Tianjin Reagent Co., China.

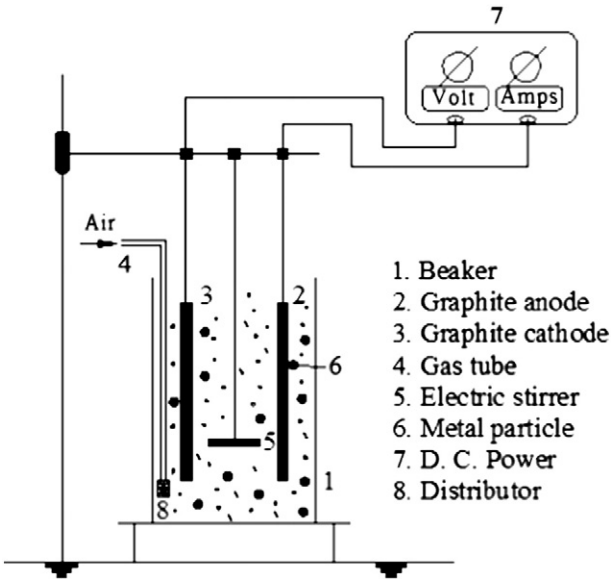


**Fig. 1.** The scheme of experimental setup.

### 2.3. Analytical methods

The COD and $NH_3$-N of the samples were chosen as index to evaluate the effect of electrochemical treatment, with data reported as the average of three trials. The COD value was measured with 5B-3(c) COD tester (Lianhua, China), and the concentration of $NH_3$-N was measured by the colorimetric method with Nessler's reagent. The initial pH (pH meter-290, Thermo-Orion, USA), UV–vis spectrum (UV-160, SHIMADZU, Japan) and the gas chromatography–mass spectrometry (GC/MS-QP2010, SHIMADZU, Japan) of the samples were also detected. The instantaneous current efficiency (ICE) can be used to calculate the apparent Faradic efficiency of COD removal by using the following formula [19–21].

$$\mathrm{ICE} = \frac{\left[(\mathrm{COD})_t - (\mathrm{COD})_{t+\Delta t}\right] FV}{8I\Delta t}. \quad (1)$$

This is an average value calculated from the values of the COD, where $(COD)_t$ and $(COD)_{t+\Delta t}$ are the COD values ($gO_2 \cdot dm^{-3}$) at $t$ and $t + \Delta t$ (s), respectively, $I$ is the current intensity (A), $F$ is the Faraday constant (96487C $mol^{-1}$), $V$ is the electrolyte solution volume (L), the constant 8 is the oxygen equivalent mass (g $eq.^{-1}$).

The residual $Cl^-$ and the generated $H_2O_2$ after the wastewater treatment was also measured by silver nitrate titration and iodimetry, respectively [22,23]. The determination of $H_2O_2$ was completed in blank solution to avoid affecting the result because $H_2O_2$ could be consumed and generated simultaneously in the wastewater treatment process.

**Table 1**
Characteristics of the refinery wastewater.

| Constituent | Value | Constituent | Value |
|---|---|---|---|
| COD | 4753 mg $L^{-1}$ | $NH_3$-N | 3308.7 mg $L^{-1}$ |
| Conductivity | 24.96 mS $cm^{-1}$ | Volatile phenol | 146 mg $L^{-1}$ |
| $Fe^{2+/3+}$ | 6.7 mg $L^{-1}$ | $Mg^{2+}$ | 213 mg $L^{-1}$ |
| $Ca^{2+}$ | 2136 mg $L^{-1}$ | $Cl^-$ | 4633 mg $L^{-1}$ |
| $S^{2-}$ | 63 mg $L^{-1}$ | $SO_4^{2-}$ | 418 mg $L^{-1}$ |
| pH | 8.85 | | |