



## Pretreatment of coking wastewater by acid out, micro-electrolysis process with in situ electrochemical peroxidation reaction

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### HIGHLIGHTS

- ▶ Acidification brought about precipitation and induced special chemical reactions.
- ▶ The COD removal was 65% in micro-electrolysis with in situ ECP.
- ▶ A synergistic effect between micro-electrolysis and Fenton reaction was revealed.

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### ABSTRACT

The coking wastewater was pretreated by acid out, micro-electrolysis process with in situ electrochemical peroxidation (ECP) (approximately 0.013–0.015 M H<sub>2</sub>O<sub>2</sub>) reaction to reduce the subsequent processing load. The results showed that the acidification process brought about changes not only in organic species of contaminants but also in decrease of COD, NH<sub>3</sub>-N in wastewater through precipitation and some special reactions, resulting in 33% of COD and 9.7% of NH<sub>3</sub>-N removal. Then Fe/C micro-electrolysis (ME) with in situ ECP reaction exhibited a stronger ability to remove the COD and NH<sub>3</sub>-N than that with ex situ Fenton reaction, because at this stage, for the two reaction models, the total COD and NH<sub>3</sub>-N removal were 65%, 26% and 43%, 25% in sequence, but in view of the contribution of only Fenton reaction to the whole COD and NH<sub>3</sub>-N removal, they were 26%, 4.2% (the former was about six times as strong as the latter) and 9.3%, 8.1%, respectively. So it was reasonable to deduce that there was a prominent synergistic effect on COD removal between the dynamic Fe/C micro-electrolysis and the Fenton reaction; furthermore, the Fenton reaction in in situ ECP process was not only high-efficient but also low-cost. These advantages might mainly be attributed to the technique of dynamic Fe/C ME with in situ ECP reaction, as it was presumed that the technique might promote some favorable reactions involved, but inhibit those unfavorable ones. The major degradation mechanism of organic contaminants in effluent had been proposed.

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### 1. Introduction

With the rapid development of world economy, a lot of coke plants of different scales have appeared, which discharge a great deal of coking wastewater every year. The wastewater quality changes with the components of raw coal and coking processes. Actually, coking wastewater from coal coking, coal gas purification and refining processes of chemical products in the coke plant comprises complex, highly concentrated, recalcitrant and toxic organic pollutants including aromatic compounds such as phenolics, polynuclear or heterocyclic aromatic hydrocarbons, and cyanogen, nitrogen-, oxygen-, and sulfur-containing heterocyclic compounds

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[1,2]. So, before discharging them into the surroundings, the removal of these toxic and refractory organic pollutants in the wastewater has been of great importance to prevent living beings and their environment from contamination by these hazardous substances. The treatment processes used for coking wastewater remediation usually include not only physical-chemical methods but also biochemical ones. For instance, the former involves coagulation-flocculation, membrane filtration technology, advanced oxidation process (AOP) and micro-electrolysis (ME) [3–10], and the latter are related to general sequence batch reactors (SBRs) activated sludge process and biological denitrogenation process [11,12]. However, any single method mentioned above often has some limitations, such as high cost, long time, and low load. In recent years, a trend of combining various methods referred to above has been adopted to achieve a better quality of treatment [13–17].

Sometimes, the combined processes were extraordinarily robust and exhibited specific performance, relatively low cost and little maintenance.

Nowadays, micro-electrolysis process and AOP technology (e.g. Fenton reaction) have gradually become a promising research focus in the wastewater-treatment field at home and abroad [18–29]. Micro-electrolysis has been successfully applied in the pretreatment of many wastewaters because it can offer some particular advantages such as simple process, easy operation, low cost and high efficiency. In the condition of micro-electrolysis, iron (Fe) chips and activated carbon (C) are commonly used as the basic materials, that is, when these materials are mixed together at a certain Fe/C mass ratio and then put in contact with the wastewater (electrolyte solution) with a certain initial pH value, numerous macroscopic galvanic cells are formed spontaneously. Thereupon, organic pollutants in the wastewater are reduced by [H] (i.e. atomic hydrogen with a significant reducing power), electrons or removed by adsorption, coprecipitation by ferric and ferrous hydroxides, or oxidized by some oxidative species. The effects of carbon/iron micro-electrolysis pretreatment on various wastewater treatments have been investigated and relative mechanisms on chemical oxygen demand (COD) and contaminants removal have been proposed or analyzed by many researchers. In general, the COD removal of wastewater under internal Fe/C micro-electrolysis process was attributed to a combination of chemical and physical processes, and their results implied that contaminants might be removed not only by redox reaction and flocculation-adsorption by co-precipitation with, and enmeshment in ferrous and ferric hydroxides resulted from  $\text{Fe}^{2+}$  released during anode oxidation but also by electrophoresis under electric fields created by electron flow. More importantly, it was considered that the pH value of wastewater might affect directly or indirectly the chemical states of contaminants, the Fe (II)/Fe (III) molar ratio and the redox potential, and thus influence the effects of electrophoresis, flocculation and redox action on the contaminant and COD removal [21].

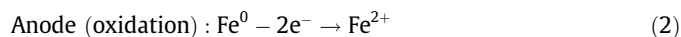
The hydroxyl radical  $\cdot\text{OH}$  has such an extremely great redox potential ( $E^0 = 2.80 \text{ V vs SHE}$ ) that it can react almost non-selectively with organic pollutants at near-ambient temperature and pressure [4,5,7]. The Fenton reaction has been widely applied in wastewater treatment, for it could produce in situ hydroxyl radical  $\cdot\text{OH}$  effectively. The main advantages of Fenton reaction are as follows: simple and flexible operation; easy-to-handle chemicals and no need for energy input. Usually during the course of Fenton process, ferrous iron ( $\text{Fe}^{2+}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) are used to generate hydroxyl radical under the acidic condition (pH 2.0–4.0) in the reaction below [26]:



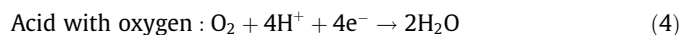
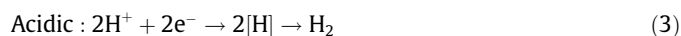
On the other hand, it is deemed that, besides those advantages referred to above such as simple process, and easy operation, the Fenton reaction is also green and friendly to our environment. But the traditional Fenton reaction process has some disadvantages, such as the risks related to the storage and transportation of  $\text{H}_2\text{O}_2$ , the relatively low utilization of  $\text{H}_2\text{O}_2$ , which result in a relatively high treatment cost and conversely restricted its practical extension and application to a great scale. Just because of this, the combination of traditional Fenton reaction and other wastewater treatment techniques has come into being naturally.

In this study, a reasonable and appropriate combination of micro-electrolysis process and Fenton reaction has been applied in order to achieve an expected effect of pretreatment of coking wastewater. It was worth pointing out that, though the initial pH of the raw coking wastewater was on a range of 9.1–9.4 with a high strength of COD and a heavy color, the wastewater firstly underwent a disposal of acid out, that is, 98% sulfuric acid was

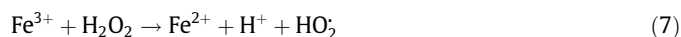
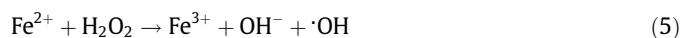
introduced into the wastewater sample to adjust the effluent pH to the desired level (between 2.0 and 4.0), which could not only provide an acidic environment for internal Fe/C micro-electrolysis but also bring about a remarkable decrease of COD and chromaticity through precipitation, i.e. acid out. Then the substrates (i.e. a mixture of iron chips (zero-valent iron) and activated carbon with a certain mass ratio) of Fenton reaction were mixed uniformly and contacted the acidified-filtered coking wastewater; with that, micro-electrolysis took place leading to the formation of ferrous iron ( $\text{Fe}^{2+}$ ); if  $\text{Fe}^{2+}$  encountered hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) introduced almost at the same time, Fenton reaction (Eq. (1)) occurred simultaneously generating hydroxyl radicals and  $\text{Fe}^{3+}$ . It was obvious that the combined process replaced ferrous iron ( $\text{Fe}^{2+}$ ) by solid iron ( $\text{Fe}^0$ ) through micro-electrolysis reaction [27]; in other words, it entailed the displacement of homogeneous Fenton reaction by the heterogeneous type. The proposed main reaction mechanism related to the combined process was shown as follows (Eqs. (2)–(11) [20,25,26,29–31]).



Cathode (reduction):



Fenton and mediated reactions:



Eq. (2) produced ferrous iron ( $\text{Fe}^{2+}$ ), and then, by adding hydrogen peroxide, the Fenton reactions were initiated by the formation of hydroxyl radical in accordance with the classical reaction, Eq. (5). From Eq. (6) proposed above, it could be seen that  $\text{Fe}^0$  reduced  $\text{Fe}^{3+}$  back to  $\text{Fe}^{2+}$ , a cycle continued meant to be a cost-saving combined process due to the substitution of  $\text{Fe}^0$  for  $\text{Fe}^{2+}$  and recycling utilization of  $\text{Fe}^{3+}$ . Interestingly, under micro-electrolysis conditions, Eq. (6) was very important for the regeneration of  $\text{Fe}^{2+}$ ; although Eqs. (7) and (8) could also regenerate  $\text{Fe}^{2+}$  through the reduction of  $\text{H}_2\text{O}_2$  or  $\text{HO}_2$  [25], they might cause some unfavorable influence on Fenton reaction because of the consumption of  $\text{H}_2\text{O}_2$  and hydroperoxyl radical ( $\text{HO}_2$ ).

## 2. Materials and methods

### 2.1. Materials

The raw coking wastewater employed in this work was obtained from a coke plant in southern China. The main characteristics of the wastewater were as follows: the initial pH of the raw coking wastewater was on a range of 9.1–9.4 with a high strength of COD ( $7200\text{--}8000 \text{ mg L}^{-1}$ ),  $\text{NH}_3\text{--N}$  ( $800\text{--}1100 \text{ mg L}^{-1}$ ), as well as a heavy brownish-black color and a bad odor. In addition, from the results obtained by GC–MS analysis, the major organic pollutants

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