



Enhanced electrochemical oxidation of phenol by introducing ferric ions and UV radiation

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Abstract

The mineralization of phenol in aerated electrochemical oxidation has been investigated. The results show that a cathodic Fenton process can occur when the Ti-0.3Mo-0.8Ni alloy material is used as cathode in solution containing ferric or ferrous ions; moreover, the reinforcement of cathodic Fenton process on the total organic carbon (TOC) removal rate of phenol is quite distinct. Among the metallic ions investigated, the ferric ion is the best catalyst for the electrochemical mineralization of phenol at initial pH 2.0, and the optimal concentration range is from 50 to 200 mg/L. The favorable pH range and supporting electrolyte (Na_2SO_4) concentration for mineralization of phenol in solution containing ferrous ions are 1.8–2.3 and below 0.10 mol/L, respectively. UV radiation can improve the TOC removal rate of phenol, but the enhanced effect varies in different solutions. In the solution containing ferric ions, an equal sum or synergetic effect can be observed. The optimal effect of electrolysis system under UV radiation is achieved in the solution containing 50 mg/L Fe^{3+} with a final removal percentage of 81.3%.

Key words: mineralization; phenol; electrochemical oxidation; cathodic Fenton process; UV radiation

Introduction

Among many technologies available for the treatment of toxic and biorefractory organic pollutants, the electrochemical advanced oxidation process (EAOP), also called electrochemical incineration, attracts much attention, in which organic pollutants are destroyed by electro-produced hydroxyl radical ($\text{OH}\cdot$). EAOP has the advantages of amenability to automation, cost-effectiveness, and versatility, but at present, it is still difficult to popularize EAOP in environmental engineering because its unit water treatment consumption is not ideal yet. As it's known, electrochemical processes are of a heterogeneous nature and their performance may suffer from limitations of mass transfer, as a result, valuable electricity is cost in vain (Juttner *et al.*, 2000; Walsh, 2001).

To improve the efficiency of EAOP, the use of cathodic process and combination with other physicochemical process are both of interest (Do and Yeh, 1998; Fockedey and Van Lierde, 2002; Saracco *et al.*, 2001; Rajkumar *et al.*, 2005). As for the use of cathodic process, it is achieved mostly by electrogeneration of H_2O_2 from the two-electron reduction of O_2 gas, and then a Fenton effect induced by H_2O_2 can occur in the aqueous solution containing ferrous ions.

From the published works, the cathodes that yield high H_2O_2 production rate are mainly gas diffusion elec-

trode and reticulated vitreous carbon electrode (Brillas *et al.*, 1998, Brillas and Casado, 2002; Alvarez-Gallegos and Pletcher, 1999). Especially, the current efficiency on carbon-polytetrafluoroethylene O_2 -fed cathode can reach 50%–80%. However, the fabrication of large oxygen diffusion electrode for engineering application is still difficult, and the antifouling ability of this porous electrode in practical use is also dubious. At the same time, the reticulated vitreous carbon electrode material is believed to be efficient for electrochemical production of H_2O_2 in aqueous solutions, but it is expensive and fragile, which makes it not suitable for practice at present. In comparison with these carbonaceous materials, anticorrosive metal and alloy materials are more stable in aggressive medium, and their good mechanical workability makes the design and fabrication of electrodes easy to implement. But it is still uncertain whether the electro-Fenton effect can be realized, when metallic materials served as cathodes.

In this study, a kind of titanium alloy material, Ti-0.3Mo-0.8Ni, was chosen as cathode in aerated solution. By introducing ferric ions into the aqueous solution, an enhanced effect for mineralization of phenol caused by cathodic oxidation process was observed. Imposing UV irradiation on the electrolysis system also improves the total organic carbon (TOC) removal rate of phenol, additionally, an equal sum or synergetic effect of irradiation and electrolysis could be observed. The results showed that introducing ferric ion and UV radiation were good ways to

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improve the total efficiency of electrochemical oxidation system when suitable titanium alloy electrode was used.

1 Experimental

All chemicals were analytical grade obtained from Shanghai Chemical Regent Ltd., Shanghai, China. In this study, the concentration of phenol is 200 mg/L, which was prepared by diluting a concentrated phenol solution. Anhydrous sodium sulfate was used as supporting electrolyte. Except the trials for investigation of the influence of supporting electrolyte concentration, the concentration of SO_4^{2-} in solution was always 0.1 mol/L. Heptahydrated ferrous sulfate, ferric sulfate, cobalt sulfate, and manganese sulfate were used as catalyst. All the solutions were prepared using ultra-pure water obtained by a double distilled system. In each run, 400 ml solution containing phenol was used. The pH of the solution was adjusted with sulfuric acid, and then, it was electrolyzed at current of 1 A with a Parstat 2273 potentiostat-galvanostat (AMETEK, USA). During the process, aqueous samples were taken from the solution and their TOC concentrations were determined on 2100 TOC analyzer (Jena, Germany). All experiments were performed under ambient temperature (i.e., 25–30°C).

The degradation process of phenol with or without UV radiation was carried out in the composite reactor, which is shown in Fig.1. In this setup, a cuboid cell (4 mm × 5 cm × 22 cm) served as the reactor. The anode was PbO_2 film electrode electrode posited on Ti meshes with a working size of 5 cm × 7 cm. The cathode was a rod (3 mm i.d., 26 cm in length) made of Ti-0.3Mo-0.8Ni alloy, and the immersion depth of electrode was 15 cm. The gap between anode and cathode was fixed at 4 cm. During the electrolysis, the solution was aerated by a minitype air pump continually. Before the start of a new trial, the PbO_2 electrode was electrolyzed in 0.1 mol/L Na_2SO_4 solution at 1.0 A for 0.5 h aiming at cleaning the surface of the electrode. The cathode was polished with sand paper to keep the same surface condition in each run. In the trials under UV radiation, an 8-W UV quartz lamp (20

cm long) with a peak at max 253.7 nm was located in the centre of the cuboid reactor, 12 cm of the lamp was dipped into solution and a quartz tube was set up to separate the solution and lamp. Except the trials specially referred, the experiments were conducted without UV radiation.

To evaluate the performance of an electrochemical reactor, the apparent current efficiency (ACE) at a given time is calculated from the following:

$$\text{ACE} = \Delta(\text{TOC})_{\text{exp}}/\Delta(\text{TOC})_{\text{theo}} \times 100\% \quad (1)$$

where, $\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC decay ($C_{\text{TOC}}^0 - C_{\text{TOC}}^t$) and $\Delta(\text{TOC})_{\text{theo}}$ is the theoretically calculated TOC decay assuming that the applied electrical charge is completely used for organic degradation.

2 Results and discussion

2.1 Influence of metal ion catalyst on the mineralization of phenol

Some metallic ions, such as $\text{Mn}^{2+}/\text{Mn}^{3+}$, $\text{Co}^{2+}/\text{Co}^{3+}$, and $\text{Fe}^{2+}/\text{Fe}^{3+}$, can be used as catalyst in electrochemical oxidation system. On one hand, they have indirect oxidation effect to some easily oxidated organics; on the other hand, Fe^{2+} and Co^{2+} also can react as Fenton catalyst. Fig.2 gives the results of the catalysis of several metallic ions for the mineralization of phenol. As can be seen, the percentages of TOC removal after 4 h of electrolysis for Co^{2+} , Fe^{2+} , Fe^{3+} , and Mn^{2+} were 51.2%, 66.3%, 68.5%, and 55.6%, respectively. The results show that the ferric ion is the best catalyst in the given condition. The enhanced effect of ferric ion for the mineralization of phenol during the whole electrolysis process also can be seen from the ACE data depicted in Fig.3. When the solution contained 50 mg/L ferric ions, the oxidation process initially presents a high efficiency (38.8% after 0.5 h of electrolysis), although it rapidly decreases with time. While for the solution without ferric ion, much smaller efficiencies continue during 4 h electrolysis.

The results also indicate that the Ti-0.3Mo-0.8Ni alloy electrode is a suitable cathode to excite the cathodic oxidation process by producing H_2O_2 . In fact, this phe-

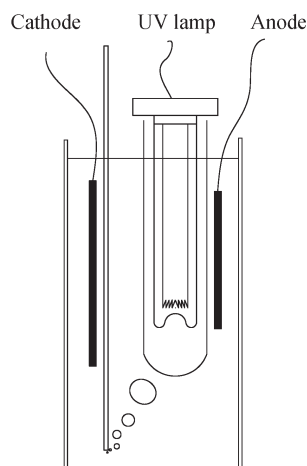


Fig. 1 Schematic electrochemical setup.

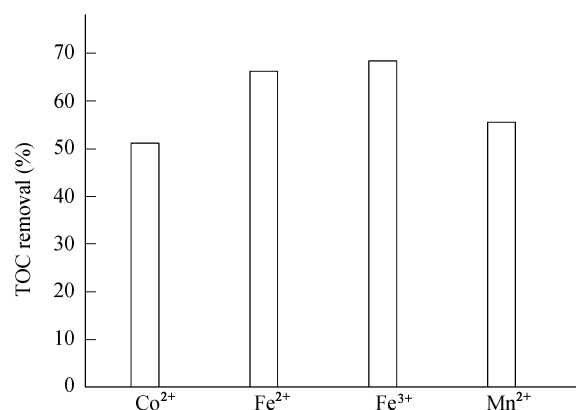


Fig. 2 Mineralization of phenol in the presence of different metal ions as catalyst. Conditions: initial pH 2; concentration of all kinds of metallic ion 3.57 mmol/L.

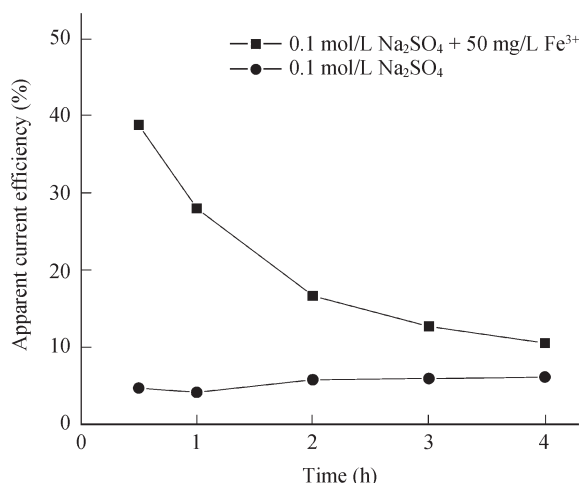


Fig. 3 Enhanced effect of ferric ions for the mineralization of phenol. Condition: initial pH 2.

nomenon cannot be observed in the electrolysis system using a 17CrNi stainless steel electrode as cathode in our previous study, namely only some titanium alloy materials are adoptable for the cathodic Fenton process. This is most likely due to the electrocatalytic activities of Ti electrode. Generally, for Ti or titanium alloy materials, there is a thin oxide film consisting of Ti(IV), Ti(III), and Ti(II) oxides on the surface. During the electrolysis, the redox system of Ti(IV)/Ti(III) or Ti(III)/Ti(II) in the film may catalyze the electroreduction of O₂ as a medium (Bard and Larry, 1980). In addition, the alloy element of Ni may promote the reduction of O₂. Because of the disturbance of oxidative substances (e.g., S₂O₈²⁻) produced on anode, the actual concentration of H₂O₂ produced by cathodic reaction cannot be measured accurately. We determined the total oxidative substances in organic free solution (0.1 mol/L Na₂SO₄, aerated, pH 3, without Fe³⁺ or Fe²⁺) by spectrophotometrical method (Ge and Qu, 2004). The result showed that the equilibrium concentration of the total oxidants produced was about 0.6 mmol/L H₂O₂ (assumed that all the oxidants in solution were expressed by H₂O₂).

Figure 4 presents the effect of ferric ion concentration on the mineralization of phenol. In the range of 0–200 mg/L, the percentage of TOC removal increases with the increase in ferric ion concentration. Beyond 200 mg/L, the percentage of TOC removal decreases and reaches a minimum value of 26.8% at 8,400 mg/L, which indicates that the reduction and oxidation of Fe³⁺/Fe²⁺ have become the main reactions, and thus, the oxidation of organics and yield of H₂O₂ are both suppressed.

2.2 Influence of initial pH on the mineralization of phenol

The condign medium condition for phenol degradation is acid (Rajeshwar and Ibanez, 1997; Sharifian and Kirk, 1986). In acid solution, the phenol exists in molecular form, which is prone to diffuse to the surface of electrode. In addition, higher acid concentration promotes breakdown of the benzoquinone ring (Sharifian and Kirk, 1986). On the contrary, the basic condition can suppress the production of hydroxide radical (Petrier and Micolle, 1992; Zhao *et al.*,

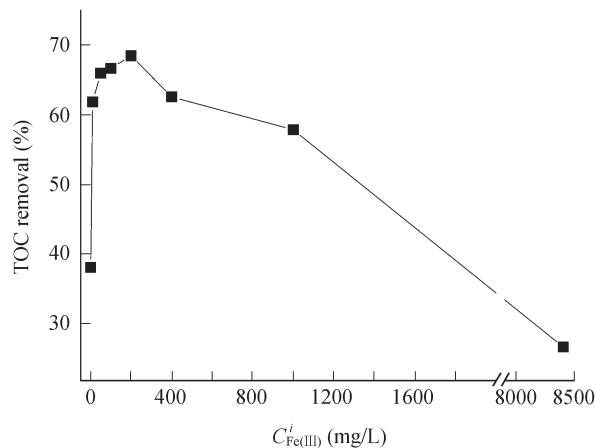


Fig. 4 Effect of ferric ion concentration on the mineralization of phenol. Conditions: initial pH 2.

2004). Hence, electrolyzes at pH range from 1 to 3 were investigated because ferric ion precipitates in the condition of pH above 3. From Fig. 5, it is evident that the reasonable range of pH for phenol mineralization is from 1.66 to 3. Moreover, the condign pH ranges for Fe²⁺ and Fe³⁺ are little different: the suitable pH range for Fe²⁺ is 2.3–3, while for Fe³⁺ the pH range from 1.5 to 2.3 is better. The reason for this difference is that the speciation of Fe³⁺ or Fe²⁺ is pH dependent, i.e., higher pH is not beneficial for the existence of ferric ion.

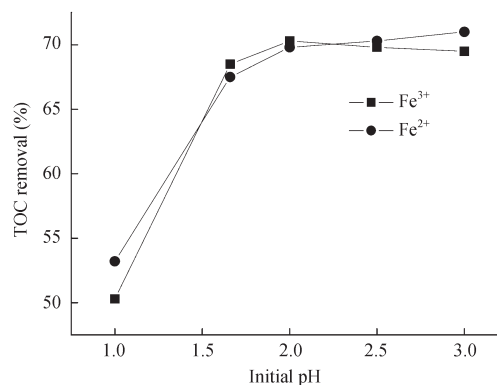
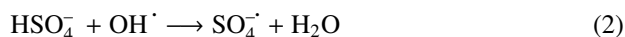


Fig. 5 Effect of initial pH on the mineralization of phenol. Condition: initial ion concentration for both Fe³⁺ and Fe²⁺ is 200 mg/L.

2.3 Influence of concentration of supporting electrolyte on the mineralization of phenol

In general, higher concentration of Na₂SO₄ accelerates the mineralization of organics by the indirect oxidation as shown in the following reactions (Gandini *et al.*, 2000; Polcaro *et al.*, 2003; Mao *et al.*, 2006):

Oxidation of SO₄²⁻:



Oxidation of organics (A is some other products):



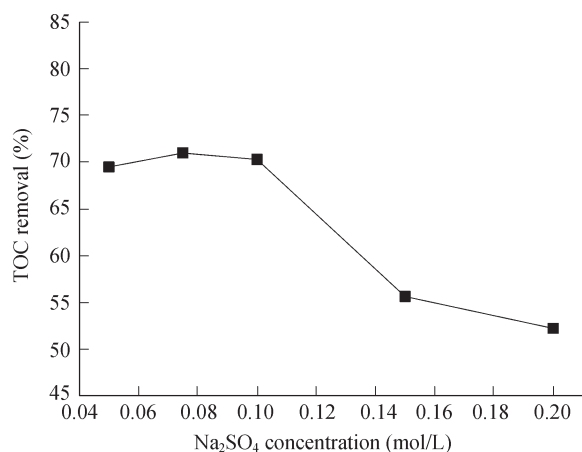


Fig. 6 Effect of concentration of Na₂SO₄ on the mineralization of phenol. Conditions: initial ferric ion concentration 200 mg/L; initial pH 2.

However, in the solution containing ferric or ferrous ion, a different result is obtained as shown in Fig.6. It is very clear that when the concentration of ferric ions is beyond 0.10 mol/L, the TOC removal rate of phenol begins to decrease and reaches a minimum value at 0.20 mol/L. As has been mentioned, the oxidation processes in the solution include anodic oxidation and cathodic Fenton process. Since the increase of the concentration of Na₂SO₄ does not lower the anodic oxidation effect, the decrease of TOC removal percentage is certainly associated with the weakening of cathodic Fenton process. When the concentration of SO₄²⁻ increases to a certain value, the oxidation of SO₄²⁻ will be very remarkable and large amount of persulfate ions are produced. As a result, the ferrous ions produced by cathodic reduction will be oxidized by persulfate ions immediately instead of being the catalyst of Fenton process in bulk solution. Hence, a suitable supporting electrolyte concentration is very important to synchronous utilization of the anodic oxidation and cathodic Fenton oxidation process to attain a maximum total oxidation rate.

2.4 Enhanced effect of UV radiation on electrolysis system

Treimer *et al.* (2001) reported the application of UV radiation in an electrochemical oxidation cell, the results showed that the electrochemical mineralization rate of the organics in solution increased under the extra UV radiation by monitoring the release rate of CO₂. Sires also reported the high degradation power of UV/electro-Fenton method to the destruction of organics in aqueous solutions (Sires *et al.*, 2007). In general, we can conceive three aspects of advantages of imposing UV radiation on electrochemical oxidation process proceeded in solution containing Fe³⁺ or Fe²⁺: the first aspect is a direct decomposition effect on organics by UV, the second aspect is an indirect effect on the degradation of organics by enhancing the Fenton process (Brillas *et al.*, 1998), and the last aspect is the degradation process induced by a photochemical UV/Fe³⁺ system (Abe and Tanaka, 1999; Xu, 2001). In this study, the influence of UV radiation on the electrolysis system,

being composed of anodic oxidation and cathodic Fenton processes, was investigated aiming at better understanding of their relations. In Fig.7, the TOC removal percentages of electrolysis, UV radiation, electrolysis under UV radiation, and sum of electrolysis and UV radiation are shown, respectively. In the solutions without ferric ion, the degradation effect of electrolysis under UV radiation is found to be limited, and its removal percentage value is lower than the sum of electrolysis and UV radiation, indicating that no synergetic or equal effect when UV radiation is applied in the electrolysis system without Fe³⁺. While in the solutions containing 8,400 mg/L Fe³⁺, a synergetic effect can be observed because the percentage of electrolysis under UV radiation is higher than the sum of electrolysis and UV radiation by 7.3%. As for the solutions containing 50 mg/L Fe³⁺, the TOC removal percentage with method of electrolysis under UV radiation after 4 h

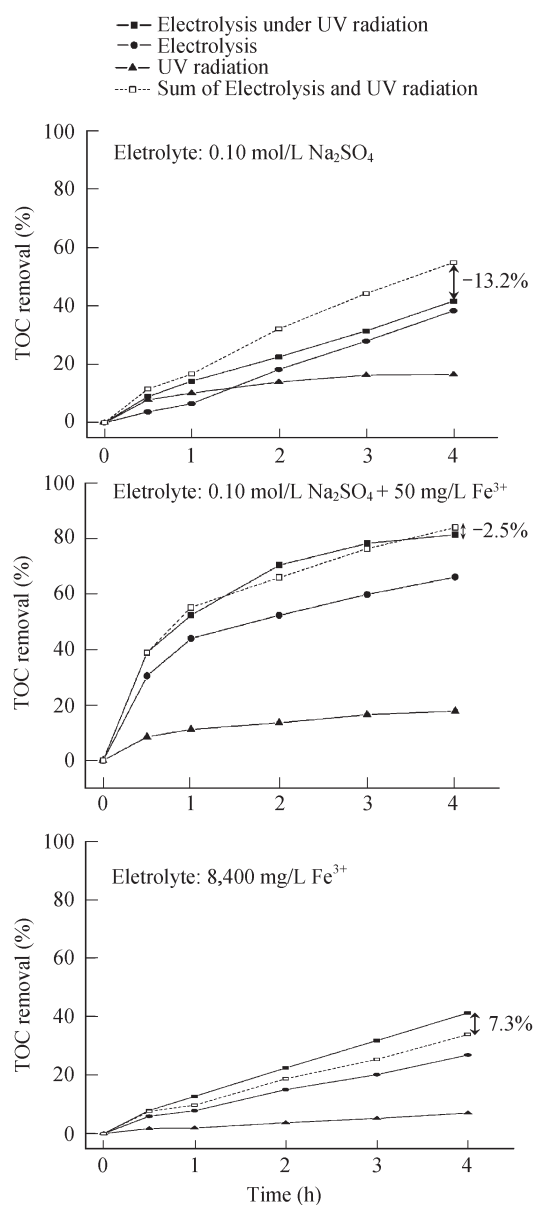


Fig. 7 Effect of UV radiation on the electrochemical mineralization of solution containing phenol under different conditions of initial ferric ion concentration.

is 81.3%, which is almost equal to the sum of electrolysis and UV radiation (the difference is only -2.5%), so we call it equal sum effect. In general, supposing that there is no interaction between these two methods because of concentration restrictive effect, the oxidation efficiency of combining two methods simultaneously should be lower than the sum of using them separately. In this study, an equal sum effect was found in the solution containing 50 mg/L Fe^{3+} , which illuminated that the combination of UV radiation on electro-oxidation system is beneficial because of their interaction. The interaction mechanism may be the fast photolytic decomposition of some intermediates by UV light as reported by Brillas *et al.* (2000).

Although a synergetic effect exists in the solution containing 8,400 mg/L Fe^{3+} , the total TOC removal percentage is not ideal, thus, it is worthless in engineering practice. On the contrary, the application of UV radiation in the solution containing lower concentration of Fe^{3+} (50–200 mg/L) is practical because of its higher efficiency. So, the keypoint is the addition amount of ferric salt.

3 Conclusions

The results show that Fenton oxidation process induced by the cathodic processes (including the reduction of O_2 , Fe^{3+} , and H^+) is an effective way for the mineralization of phenol, which leads to the improvement of total mineralization removal rate of an electrochemical system. The Ti-0.3Mo-0.8Ni alloy is the suitable cathode material for the cathodic Fenton oxidation. The catalysis effect of some metallic ions, such as Co^{2+} , Fe^{2+} , Fe^{3+} , and Mn^{2+} , for the electrochemical mineralization of phenol has been compared. The results show that the ferric ion is the best catalyst at initial pH 2.0. Moreover, its optimal concentration range is 50–200 mg/L.

In this electrochemical oxidation system including anodic oxidation and cathodic Fenton oxidation, the optimal initial pH is an important factor that influences the mineralization of phenol just like the pH to classical Fenton process. But the optimal initial pH range changes with the kind of metal ions, namely pH 1.8–2.3 is suitable for Fe^{3+} and pH 2.5–3 for Fe^{2+} . The suitable concentration range of supporting electrolyte (Na_2SO_4) is not more than 0.10 mol/L.

UV radiation can improve the TOC removal rate of phenol, but the enhanced effect varied in different solution. In the solution containing Fe^{3+} , an equal sum or synergetic effect can be observed. The optimal effect of electrolysis system under UV radiation was achieved in the solution containing 50 mg/L Fe^{3+} with a final removal percentage of 81.3%.

Acknowledgments

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