

Degradation of Phenol-containing Wastewater Using an Improved Electro-Fenton Process

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Received: 16 March 2012 / Accepted: 7 April 2012 / Published: 1 May 2012

An improved Electro-Fenton (EF-Fere) method using H₂O₂ amendments and electrogenerated ferrous ions is investigated to treat phenol-containing wastewater. The regeneration of ferrous ions on a porous steel cathode is evaluated, and variables including initial ferric concentration and electrical current are assessed. When the initial ferric ions concentration was 800mg/L and current density was 0.75A, the generation rate and equilibrium concentration of ferrous ions are highest. For the phenol degradation experiments conducted in the EF-Fere electrolytic system, the maximum COD removal efficiency of phenol-containing wastewater is achieved at the condition of 800mg/L initial ferric ions concentration, 1.0A electric current and 1.2Q_T H₂O₂ with continuous H₂O₂ addition mode. Furthermore, SnO₂ film anode and UV irradiation in the EF-Fere system are beneficial to COD removal efficiency.

Keywords: phenol; Fe²⁺ generation; EF-Fere; COD removal

1. INTRODUCTION

Phenolic compounds constitute a family of pollutants particularly toxic to the aquatic fauna, flora and man [1]. These compounds are released to the environment by a considerable number of industries, such as pharmaceutical plants, oil refineries and coke plants [2,3], posing great risk to environmental ecology and public health. Most phenols are recalcitrant to the conventional physicochemical and biological treatments. Advanced oxidation processes (AOPs) have been thought as effective routes for treatment of wastewater containing phenols. Some AOPs like ozonation [4], heterogeneous photocatalysis [5], UV-H₂O₂ [6] and wet oxidation [7] have been studied as treating method for phenol wastewater.

Fenton reaction is another option for phenol degradation. The classical Fenton reagent, consisting of the reactions between homogeneous $\text{Fe}^{2+}/\text{Fe}^{3+}$ catalysts and hydrogen peroxide (H_2O_2), is highly efficient for the destruction of phenols due to the hydroxyl radicals generated by the Fenton reactions. However, the classic Fenton processes require a strong acid condition ($\text{pH} < 3$) to avoid the hydrolysis of ferrous and ferric ions, and to achieve optimal removal rate of pollutants. Additionally, non-recyclable soluble iron salts yield large amount of iron oxide sludge, which needs further separation from the treated water [8]. Therefore, some AOPs processes based on classic Fenton processes are developed to treat aqueous phenols. Fenton process using zero valence iron [9], Fenton-like reactions [10,11], photo-Fenton [12,13], and electro-Fenton (EF) [14-17] have been proven effective for the degradation of phenols. For an electro-Fenton process, either H_2O_2 or ferrous ion is continuously generated or regenerated on the electrode and their accumulative concentrations in aqueous solution depend on a competition between their generation rate and consumption rate [18]. Usually the electro-Fenton processes can be classified into two categories, EF process involving H_2O_2 generation and EF process involving ferrous regeneration, which can be named as EF-Fere. The efficiencies of both processes can be comparable with the conventional chemical dosing methods [19-21]. More importantly, they can decrease the risk of handling H_2O_2 reagents, or decrease the production of ferric hydroxide sludge.

In this study, we propose an improved EF-Fere process for the treatment of concentrated phenol-containing wastewater. A porous cathode, instead of a plate cathode, is adopted in the electrolytic process. The porous cathode is capable of reducing the ferric species (ferric sulfate or ferric hydroxide sludge) to ferrous species more efficiently. Factors that affected Fe^{2+} generation and chemical oxygen demand (COD) removal efficiency of phenol-containing wastewater were evaluated in this work. In addition, the UV irradiation is introduced to the electrolytic system to further enhance the efficiency of phenol degradation.

2. EXPERIMENTAL

2.1 Chemicals and Materials

All chemicals are analytical grade and purchased from Sinopharm Chemical Reagent Company. Phenol was purified by distillation and dissolved into distilled water as stock solution. Phenol concentration in the simulated wastewater was 1.0g/L. Before the EF-Fere experiment, ferric salts were added and dissolved in the phenol-containing solution. The pH of solution was adjusted with sulfuric acid and NaOH solution. The H_2O_2 solution (30 wt%) was used as amendments without dilution. All the solutions were prepared using double distilled water. Several kinds of materials were used as electrodes. Stainless steel fiber felt ($\text{Cr}_{17}\text{Ni}_{14}\text{Mo}_2$) (10cm×10cm), used as cathode, was provided by Baosteel Group Corporation. RuO_2 electrode (5cm×8cm) was purchased from Northwest Institute of Non-ferrous Metal. SnO_2 and PbO_2 electrodes (5cm×8cm working area, on titanium mesh substrate) were prepared in our laboratory and the details can be found in the literature [22].

2.2 EF-Fere system

The degradation process of phenol was carried out in an EF-Fere system, which was composed of a power source, a cylindrical electrolytic cell (35cm height and 10cm diameter) and a H_2O_2 dosing system, as shown in Fig.1. The electrolysis was controlled by an electrochemical working station (PARSTAT 2273). Electrolyte was recirculated by a magnetic pump with 3L/min flow rate. The cathode materials were stainless steel fiber felt and the anode materials included RuO_2 , SnO_2 and PbO_2 film electrodes. Except for the trials specially referred, PbO_2 film electrode was used as anode in experiments. As the trials under UV (254nm, 250W) or solar radiation (sunlight, average temperature 25°C), a quartz glass tube was connected with the electrolytic system, and electrolyte can be irradiated by the light source. The distance between UV lamp and quartz glass tube was 20cm. A peristaltic pump was adopted in the H_2O_2 dosing system, and dosing rate can be changed by adjusting the speed of pump.

For each experiment, the ferric sulfate stock solution was added to the phenol solution and the pH of the mixed solution was adjusted to 3. Then the electrolysis was started and water samples were collected from the electrolytic cell for COD determination (10mL for each sampling event). The dosage of H_2O_2 were 0.6, 0.8, 1.0 and 1.2 times of the theory dosage (Q_T , g H_2O_2) of the simulated wastewater. The oxygen gas generated from the Q_T amount of H_2O_2 is equal to the theoretical chemical oxygen demand (g, O_2) of the wastewater. For the phenol solution, the theoretical chemical oxygen demand (g, O_2) is twice of the mass of phenol (g) in this study.

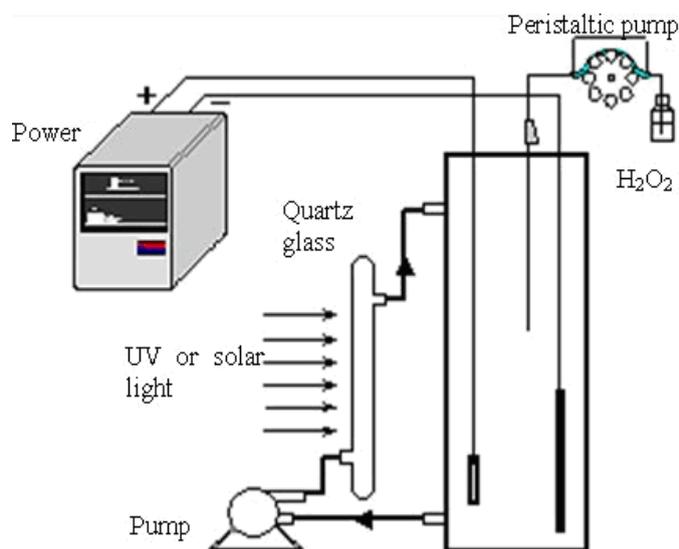


Figure 1. Schema of the experimental apparatus

2.3 Analytical methods

The ferrous ions concentration was analyzed by permanganate titration method [23]. The degradation of phenol solution was characterized by chemical oxygen demand (COD) of water sample. The COD was measured by potassium dichromate titrimetric method as described in Standard Methods

(2000). For each determination, the samples were pretreated with NaOH (pH=7-9), heated at 40°C to remove residual H₂O₂ [24]. The COD concentration of simulated wastewater was measured at 0h, 1h, 2h, 3h and 4h.

3. RESULTS AND DISCUSSION

3.1 Performance of Fe²⁺ generation

In the electrolytic system, the Fenton reaction induced by the hydroperoxide and ferrous ions is the target reaction. However, the ferrous ions and ferric ions concentration are affected by both anodic and cathodic reactions.

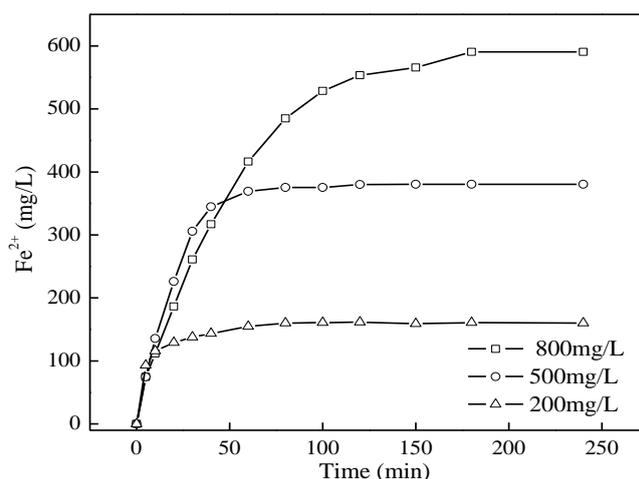
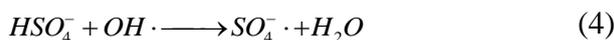
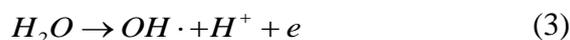
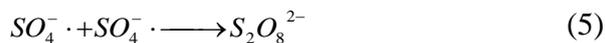


Figure 2. Effect of initial Fe³⁺ concentration ($C_{Fe^{3+}}^i$) on ferrous ions generation, electrical current (i) is 0.5A.

The main reaction on inert anode is believed to be the oxygen evolution (Eq.1) and ferrous ions oxidation (Eq.2). At the same time, hydroxyl radicals generation (Eq.3), peroxy radicals generation and reactions involving the persulfate (Eq.4 to Eq.6) can occur. As a result, the ferrous ions can be oxidized by these oxidizing substances, causing fast decay of ferrous ions and low ferrous ions utilization.





In the case of cathodic reactions, the hydrogen evolution (Eq.7) is the main reaction and the ferric ions can be directly reduced the cathode (Eq.8).



The ferrous ions generation profiles under different initial ferric ions concentration are shown in Fig.2. As we can see, the initial ferric dosage has great impact on the generation rate and equilibrium concentration of Fe^{2+} . When concentration of Fe^{3+} changes from 200mg/L to 800mg/L, at the initial stage of electrolysis, the accumulations of ferrous ions occur for all three concentration conditions. However, at lower concentration of 200 mg/L, the ferrous ions reach equilibrium concentration 15 minutes after the electrolysis. For the 500 mg/L and 800 mg/L condition, the times when the ferrous ions reach equilibrium concentration are 50 minutes and 175 minutes, respectively. After 240 minutes electrolysis, the equilibrium concentration of ferrous ions in solution reach 160mg/L, 380.5mg/L and 590.5mg/L respectively, being proportional to the initial ferric ions concentrations.

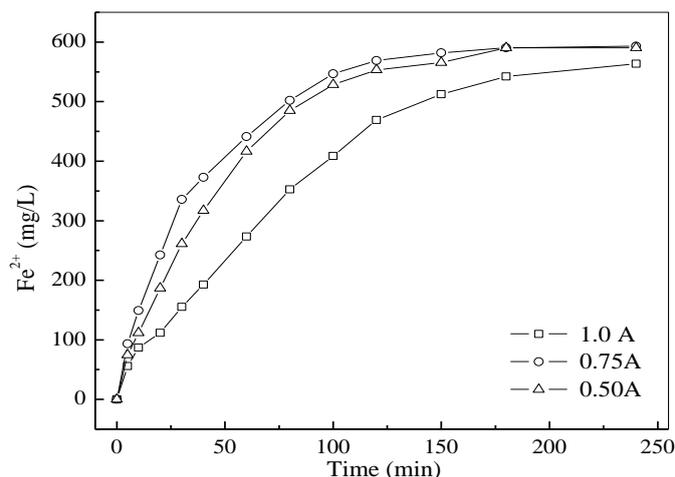


Figure 3. Effect of electrical current on Fe^{2+} generation, $C_{Fe^{3+}}^i = 800\text{mg/L}$

Effect of electrical current on the ferrous ions generation is shown in Fig.3. As the current intensity increases from 0.5A to 0.75A, the generation rate of Fe^{2+} is accelerated, however, when the electrical current further increases to 1.0A, the regeneration rate of Fe^{2+} clearly slows down compared

with that of 0.75A. This phenomenon indicates that increasing current facilitates the regeneration of Fe^{2+} , however, when the current exceeded a certain value, the effect on Fe^{2+} generation acceleration is very limited. This observation may be due to the competitive process proceeding on the electrodes. At higher current intensity, the reactions such as the evolution of hydrogen at the cathode (Eq.7) and the oxidation of ferrous ions on anode can be also enhanced via Eq.2. Generally, from the ferrous ions generation experiment, it is concluded that the suitable electrolytic conditions for the regeneration of ferrous ions are highest initial ferric ions concentration and electrical current in the range of 0.50A to 0.75A.

3.2 Treatment of phenol-containing wastewater by EF-Fere method

3.2.1 Effect of initial ferric ions concentration

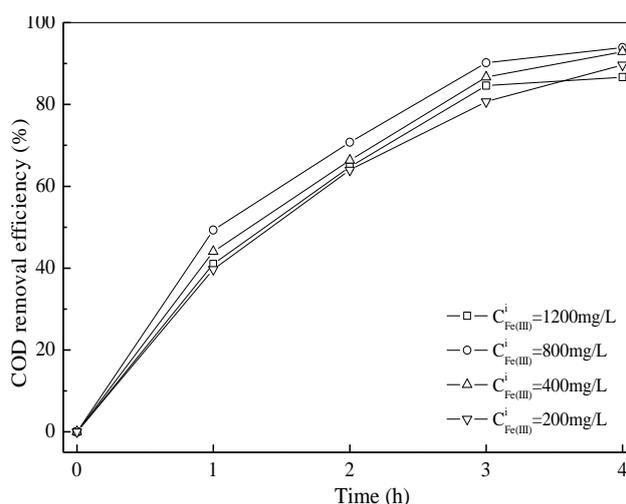
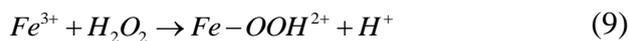


Figure 4. Effect of initial Fe^{3+} concentration ($C_{\text{Fe}^{3+}}^i$) on COD removal efficiency, $Q_{\text{H}_2\text{O}_2}$ (H_2O_2 dosage) = $1.2Q_T$, $i = 0.5\text{A}$

Fig.4 shows the effect of initial ferric ions concentration on the COD removal efficiency of phenol-containing wastewater. As can be observed, when the dose of ferric ions increased from 200mg/L to 800mg/L, the COD removal efficiency after 4 hours electrolysis increases from 89.7% to 92%. The increase of initial ferric ions concentration was beneficial for the Fe^{3+} - H_2O_2 complexes formation (Eq.9 and Eq.10), which would be enhanced and consequently accelerated the formation of Fe^{2+} and $\text{OH}\cdot$. Thus, phenol degradation in the wastewater is enhanced. However, when initial ferric ions concentration further increased to 1200mg/L, COD removal efficiency instead declined to 86.7%. This observation probably can be explained by the negative effects of the presence of large amount of ferric ions: 1) H_2O_2 consumption by the Fenton-like reactions is also enhanced, resulting in lower utilization of H_2O_2 ; 2) higher ferric ions concentration causes the presence of more ferrous ions, which may quench hydroxyl radicals (Eq.11), leading the COD removal efficiency of phenol because of less available hydroxyl radicals.



3.2.2 Effect of electrical current

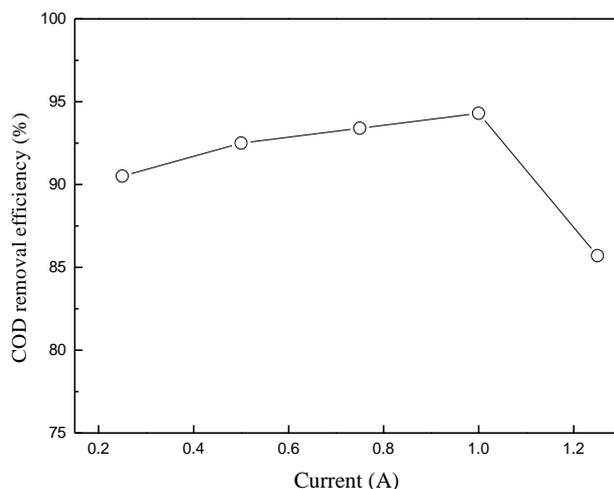


Figure 5. Effect of electrical current (i) on COD removal efficiency, $Q_{H_2O_2} = 1.2Q_T$, $C_{Fe^{3+}}^i = 800\text{mg/L}$

Effect of electrical current on COD removal efficiency is shown in Fig.5. Apparently, the COD removal efficiency goes up when applied current increases from 0.25A to 1.0A, indicating an enhancement on the degradation capacity. At higher current, the electro-regeneration of Fe^{2+} is enhanced with the increasing of current, as a result, the efficiency of Fenton reactions and degradations of phenol are improved. However, further increase of the electrical current to higher than 1.0A, causes lower COD removal efficiency, as we can see from Fig.5. When the current exceeds a certain value, it can be inferred that the competitive reactions on electrodes such as the evolution hydrogen at the cathode via reaction (Eq.7) and the discharge of oxygen at the anode (Eq.1) would become pronounced [25]. Consequently, the phenol degradation is inhibited at higher current intensity.

3.2.3 Effect of anode materials

Three different anodes including SnO_2 , PbO_2 and RuO_2 film electrodes were tested at the anode of EF-Fere system. The COD removal efficiencies are shown in Fig.6. The results show that 4 hours COD removal efficiency is 31% when the electrochemical oxidation on SnO_2 anode works individually for the degradation of phenol without applying H_2O_2 . In contrast, if the EF-Fere system is adopted, the COD removal efficiency is improved to more than 78% for all anode conditions. Furthermore, it can be observed that different anode materials exhibit different electro-catalytic

activities on COD removal efficiency. In this EF-Fere system, the SnO₂ film electrode has the highest COD removal efficiency of 85.73%, followed by PbO₂ and RuO₂ film electrode. This observation suggests that the SnO₂ electrode, as an effective electrocatalytic anode for organic mineralization, really takes effect in this electrolytic system. During the electrochemical degradation process, hydroxyl radicals ($\cdot\text{OH}$) can be detected on SnO₂ and PbO₂ film electrode [26-28]. More hydroxyl radicals are produced on the SnO₂ film electrode, promoting the removal of COD. However, there is no $\cdot\text{OH}$ being detected on the RuO₂ electrode. Thus, different degrading performances on phenols were observed in the experiments.

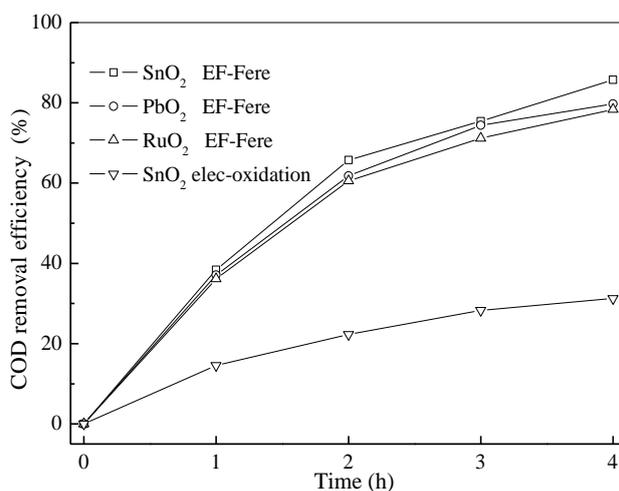


Figure 6. Effect of anode materials on COD removal efficiency, $Q_{\text{H}_2\text{O}_2} = 0.8Q_{\text{T}}$, $C_{\text{Fe}^{3+}}^i = 800\text{mg/L}$, $i = 0.5\text{A}$

3.2.4 Effect of H₂O₂ feeding way and dosage

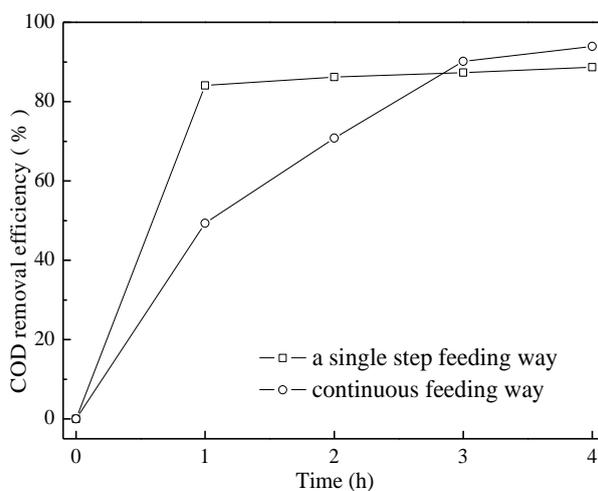


Figure 7. Effect of H₂O₂ feeding way on COD removal efficiency, $Q_{\text{H}_2\text{O}_2} = 1.2Q_{\text{T}}$, $C_{\text{Fe}^{3+}}^i = 800\text{mg/L}$, $i = 0.5\text{A}$

The effect of H_2O_2 feeding way on COD removal efficiency is shown in Fig.7. If H_2O_2 is added into the reactor by a single step at the beginning of electrolysis, COD removal efficiency of 60 minutes after the starting of the electrolysis reached 84.1%, being much higher than that of continuous H_2O_2 feeding mode. However, the COD removal efficiency does not increase further in the duration of experiment. On the contrary, continuous addition of H_2O_2 keeps an increasing COD removal efficiency, and the 4-hours removal efficiency finally exceeds that of the single step feeding way. For one step feeding of H_2O_2 , instant high concentration of H_2O_2 in solution is formed, which may cause the faster consumption of H_2O_2 . The hydroperoxyl radicals generated by the decomposition of H_2O_2 (Eq.12) [29] are a species with much weaker oxidizing power compared with the hydroxyl radical. Thus, worse degradation efficiency is observed in the one single step feeding way. Compared with a single step feeding way, the continuous mode appears more reasonable.



Effect of total H_2O_2 dosage on phenol degradation and COD removal efficiency was investigated, shown in Fig.8. As the H_2O_2 dosage increases from $0.6Q_T$ to $1.2Q_T$, the COD removal efficiency of phenol-containing wastewater is consequently enhanced. After 4 hours treatment, the highest COD removal efficiency is 93.9% at $1.2 Q_T$, followed by 89.1%, 77.7% and 75.0% at other dosages. The improvement on the COD removal efficiency is apparently due to the increasing amount of hydroperoxide. However, a further increase in H_2O_2 dosage for the organics degradation is no more cost-effective if the specific utilization of H_2O_2 is considered. For example, $0.6 Q_T$ of H_2O_2 can achieve more than 75% COD removal efficiency, while twice amount of H_2O_2 ($1.2 Q_T$) only increase the COD removal efficiency by less than 20% with respect to that of $0.6 Q_T$. Additionally, H_2O_2 over dosage is reportedly to pose a detrimental effect on phenol degradation and toxic intermediates could be observed in the solution [25].

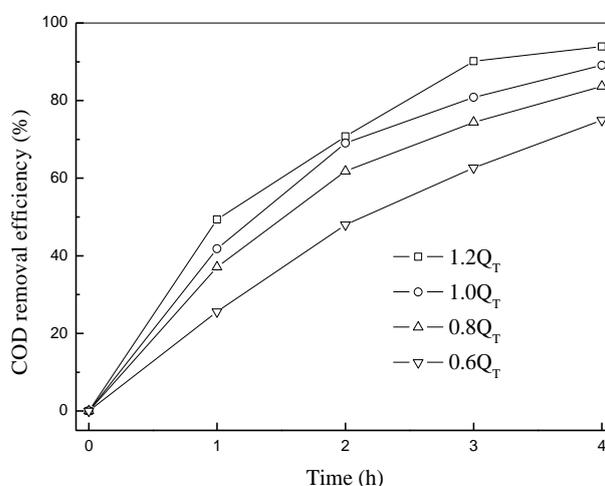
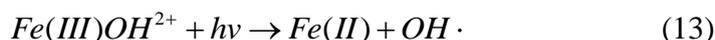


Figure 8. Effect of H_2O_2 dosage on COD removal efficiency, $C_{Fe^{3+}}^i = 800\text{mg/L}$, $i = 0.5\text{A}$

3.2.6 Effect of irradiation conditions

The optimal operation conditions of EF-Fere system were adopted for the comparison of EF-Fere, solar/EF-Fere and UV/EF-Fere process. Fig.9 presents the degradation of phenol by these processes as a function of time. The 4 hours COD removal efficiencies with UV light, solar light and without light irradiation are 95.5%, 84.6% and 79.7%, respectively. Irradiation of UV and natural sunlight on EF-Fere process may have two aspects of effects. One is the direct destruction of phenol due to the photolysis of phenol molecules under UV and visible light, and another effect is the enhancement of $\text{OH}\cdot$ by the following reactions (Eq.13).



Under the irradiation of solar light and UV light (254nm), ferric species can be reduced and hydroxyl radicals are produced for the phenol oxidation process [24,30]. In other words, in addition to the reactions proceeding in the EF-Fere process, the light irradiation can further catalyze the production of hydroxyl radicals and degrade the phenol.

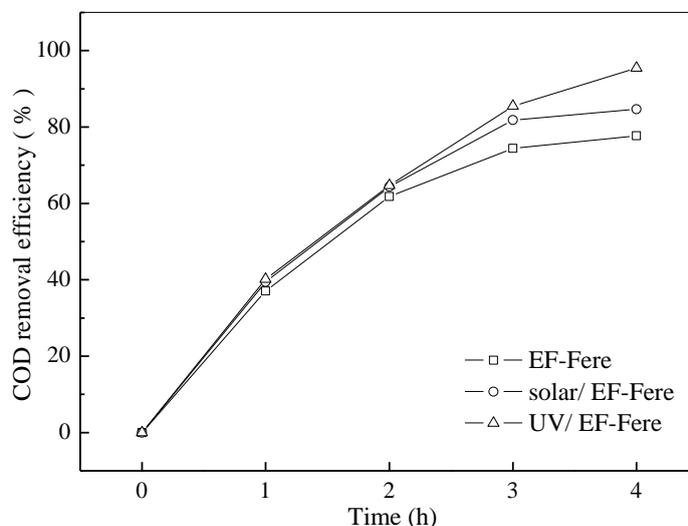


Figure 9. Effect of irradiation conditions on COD removal efficiency, $Q_{\text{H}_2\text{O}_2} = 0.8Q_T$, $C_{\text{Fe}^{3+}}^i = 800\text{mg/L}$, $i = 0.5\text{A}$

4. CONCLUSIONS

Phenol-containing wastewater treated by EF-Fere method is studied in this paper. The results show that stainless steel fiber felt can be used as a cathode for EF-Fere process. Operations with middle level current (0.75A) and high initial ferric ion concentration (800mg/L) lead to higher ferrous ions generation efficiency in the electrolytic system. The operation variables that affect the COD removal efficiency of EF-Fere process are evaluated. Higher COD removal efficiency is obtained at

the following conditions: 800mg/L initial ferric ions concentration, 1.0A current and 1.2Q_T H₂O₂. Furthermore, continuous addition of H₂O₂ is more effective than the addition of H₂O₂ in a single step. In the EF-Fere system, SnO₂ film anode and UV irradiation are beneficial for the degradation of phenol.

ACKNOWLEDGEMENT

This research was supported by funds from the National Science Foundation of China (No. 51108353) and Education Commission of Zhejiang Province of China (No. Y201122332)

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