



## Electrochemical catalytic treatment of phenol wastewater

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### ABSTRACT

The slurry bed catalytic treatment of contaminated water appears to be a promising alternative for the oxidation of aqueous organic pollutants. In this paper, the electrochemical oxidation of phenol in synthetic wastewater catalyzed by ferric sulfate and potassium permanganate adsorbed onto active bentonite in slurry bed electrolytic reactor with graphite electrode has been investigated. In order to determine the optimum operating condition, the orthogonal experiments were devised and the results revealed that the system of ferric sulfate, potassium permanganate and active bentonite showed a high catalytic efficiency on the process of electrochemical oxidation phenol in initial pH 5. When the initial concentration of phenol was 0.52 g/L (the initial COD 1214 mg/L), up to 99% chemical oxygen demand (COD) removal was obtained in 40 min. According to the experimental results, a possible mechanism of catalytic degradation of phenol was proposed. Environmental estimation was also done and the results showed that the treated wastewater have little impact on plant growth and could totally be applied to irrigation.

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### 1. Introduction

The removal of hazardous organic pollutants from groundwater and wastewater is one of the most critical and urgent topics in environmental research. Phenols and phenolic compounds have been declared to be hazardous pollutants [1]. Many industrial processes, such as oil refineries, plastic plants, paper plants, synthetic chemicals, pesticides, coal conversion have been attributed to the phenolic compounds [2,3]. Due to the resistance to common microorganisms, phenolic wastes cannot be treated by biological action. Moreover, they are toxic even in the presence of low concentration. Therefore, the treatment of phenolic pollutants will be of considerable importance in environmental protection [4].

Many technologies and processes have been conventionally attempted for phenolic wastewater, such as extraction [5], biological treatment [6,7], chemical oxidation [8], wet oxidation [9], ozone oxidation [10], photo-catalytic oxidation [11], oxidation in supercritical water [12]. But there are few suitable processes to deal with this high toxicity effluent [13].

Electrochemical method offers the prospect of relatively simple equipment, environmental friendliness, and the possibility of high-energy efficiency. So, electrochemical oxidation method for removal of phenolic compounds has attracted a great deal of attention [14]. The oxidation of wastewater is principally depended on

the hydroxyl radical generated on the surface of the electrodes. Therefore, the processes are called advanced electrochemical oxidation processes (AEOPs) [13]. Nowadays a single process alone may not be adequate for the treatment of high concentration organic compounds. In order to improve the efficiency of oxidation and accelerated the reaction rate, lots of heterogeneous catalysts have been investigated in the AEOPs processes.

Potassium permanganate (KMnO<sub>4</sub>) has strong oxidation capability that has been used to control taste and odor, remove color, control biological growth in treatment plants and remove iron and manganese. In addition, potassium permanganate may be useful in enhancing coagulation and filtration processes [15]. Potassium permanganate may oxidize organic compounds through several reaction pathways including electron exchange, hydrogen abstraction or direct donation of oxygen [16,17].

Potassium permanganate and ferric sulfate adsorbed on active bentonite as the catalyst used in the electrochemical system is a new and effective approach in our present study. On account of high surface area, structural properties and cation exchange capacity [18], bentonite or active bentonite (mainly montmorillonite) is very preferable clay mineral for barrier applications. But bentonite or active bentonite was rarely reported to catalyze degradation of wastewater in electrochemical systems.

The aim of this work is to study the conjunctive effect when integrating the catalyst (adsorbed onto active bentonite) into the electrochemical system and find out the optimal operating parameters in treating phenol making wastewater and life span were described, and possible mechanism of decomposition of phenol was also proposed.

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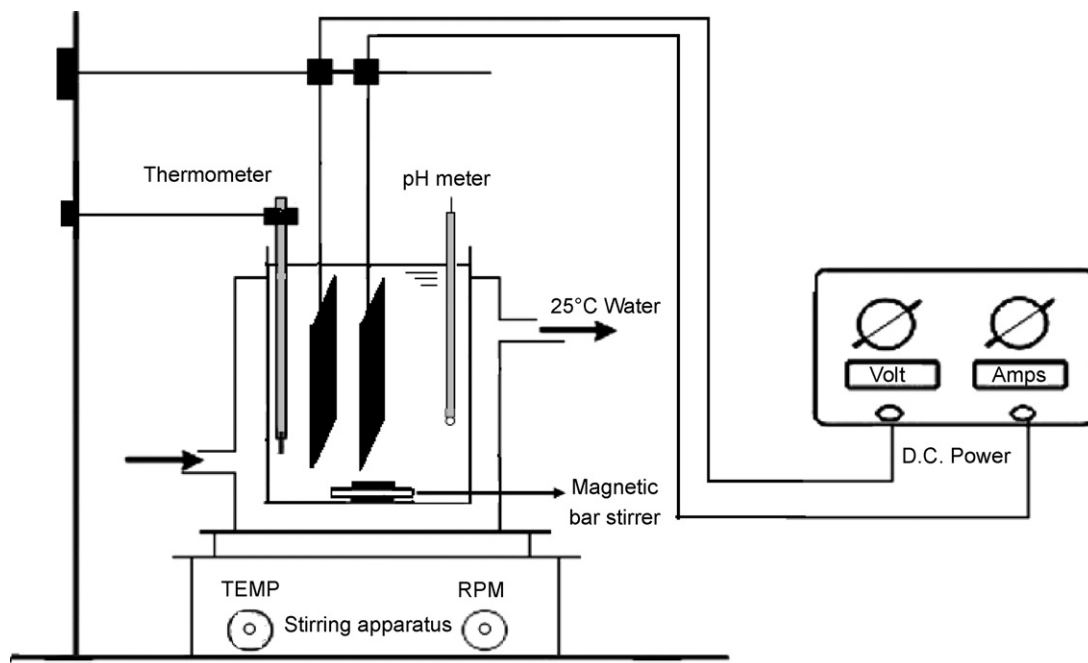


Fig. 1. Sketch of the electrochemical cell for the oxidation of phenol water.

## 2. Experimental

### 2.1. Materials and general measurements

The chemical reagents used were of analytical grade and employed without further purification. Active bentonite was purchased from Guang Da active clay plant in Xin Yang, Henan province. The solution for treatment was prepared by dissolving phenol to 520 mg/L in distilled water, its conductivity was raised by adding  $\text{Na}_2\text{SO}_4$  (4 g/L), and its pH was adjusted by adding either dilute sodium hydroxide or dilute sulfuric acid.

### 2.2. Electrochemical cell

Fig. 1 shows the schematic diagram of the experimental apparatus. The experiments were conducted by batch process using undivided cell of 300 mL capacity under constant temperature conditions (298 K). Electrodes were served by sheet porous graphite. The anode and cathode were positioned vertically and parallel to each other with an inner gap of 0.5 cm. The superficial surface of the working electrode was approximately 24 cm<sup>2</sup>. The relevant proportions of catalyst were added into the system to form an oxidizing electrochemical reactor. The solution was constantly stirred at 200 rpm with a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. The electric power was supplied with regulated dc power supply, WYK302b, Xi'an, China. The current and voltage were adjustable between 0 and 2.5 A and between 0 and 35 V.

### 2.3. Analytical method

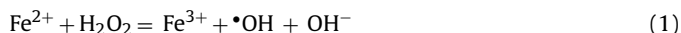
All the experiments were carried out in duplicate and analysis of each parameter was done in triplicate for each run. The initial pH of the solution was measured using an Orion 290 pH meter. Chemical oxygen demand (COD) was chosen as a parameter in order to evaluate the oxidation process and was determined according to standard methods [19,20]. And the concentration of  $\text{H}_2\text{O}_2$  accu-

mulated in the system in the absence of  $\text{KMnO}_4$  was obtained by titration with  $\text{KMnO}_4$ .

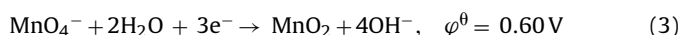
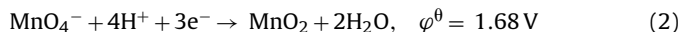
## 3. Results and discussion

### 3.1. Effect of pH on COD removal

In previous studies [21–24], it can be seen that the initial pH strongly affected COD removal efficiency of wastewater containing phenol: the initial pH was ascertained in acidic pH(5) attribute to the following reasons: (1) an effective iron cycle can be taken place at low pH values. Almost constant  $\text{Fe}^{3+}$  concentration and traces of  $\text{Fe}^{2+}$  which will be readily transformed, mainly according to the reaction:



because  $\text{Fe}^{3+}$  ion and  $\cdot\text{OH}$  all displayed as oxidant in the phenol oxidation process; (2) the oxidation ability of  $\cdot\text{OH}$  was fairly stronger in acidic conditions. So in acidic solution, free radical can be formed and organics was oxidized easily [23]; (3) when pH was in the range 3.5–12, potassium permanganate usually undergoes a three-electron exchange according to Eq. (2) for acidic pH conditions or Eq. (3) for alkaline conditions [24], indicating that the oxidation ability of permanganate ion is stronger in acidic pH conditions than that of in alkaline conditions.



Since the solution pH was not buffered, the pH may changes with the time elapsed, pH elevated and the end pH was about 8.5 after 40 min treatment, maybe due to that  $\text{H}_2$  produced resulted in pH value shifted to the alkaline region. Moreover, with pH elevated, the degradation rate obviously slowed down, which is consistent with our previous studies [21,22], so the optimal pH was selected as 5.

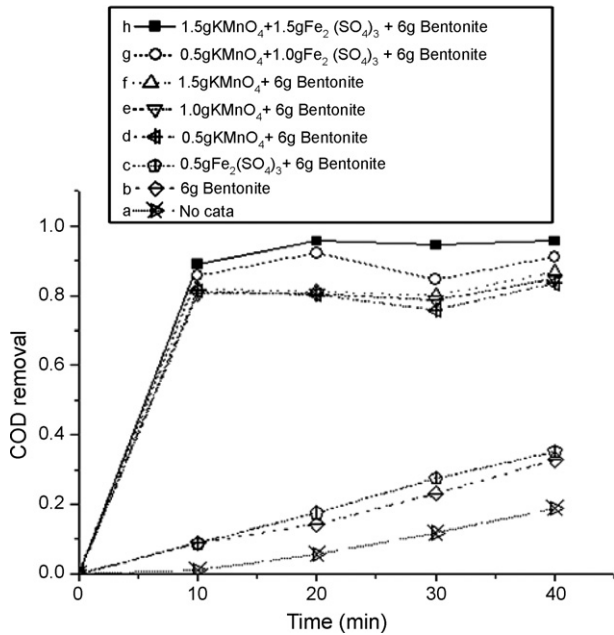


Fig. 2. COD removal for various systems (COD<sub>0</sub>: 1214 mg dm<sup>-3</sup>; current: 2.0 A; pH 5; 220 mL).

### 3.2. Effect of bentonite on COD removal

The effect of active bentonite on COD removal in pH 5 with graphite electrodes electrolysis was investigated (curves (a) and (b) in Fig. 2). 32.9% COD removal was obtained within 40 min and the decomposition efficiency of this system is higher than that of only electrolysis without active bentonite (18.8%) in the same pH value. In the meanwhile, only about 20% COD removal was obtained with active bentonite alone without electrolysis. It can be interpreted as follows: (1) adsorption process. Owing to its high surface area, a great lot of organics can be adsorbed by the active bentonite; (2) electrochemical oxidation process. Organics, adsorbed on active bentonite, can be directly or indirectly oxidized through electrochemical process. During this process, some strong oxidants, such as hydroxyl radicals, have an extremely short life due to their high oxidation potential, and decompose rapidly to other oxidants (O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>). These oxidants (O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>) that are produced from the destruction of radicals have quite a long life, they are diffused and then adsorbed on the surface of active bentonite away from the electrodes. The organic pollutants were destroyed through oxidation reaction by these generated active hydroxyl radicals (•OH) and the oxidants (O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>). Due to the oxidation capability of oxidants (O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>) is weaker than that of the radicals such as hydroxyl radicals, so it will mainly affect the whole reaction system electrolysis efficiency [22].

### 3.3. Effect of ferric sulfate on COD removal

The effect of ferric sulfate on the COD removal in pH 5 in the presence of graphite electrodes electrolysis with active bentonite was also studied (curves (b) and (c) in Fig. 2). 35.2% COD removal was obtained in pH 5 within 40 min. Comparing with the COD removal of electrolysis with active bentonite in the same pH, the improvement of COD removal of active bentonite containing ferric sulfate forming slurry bed was not obvious, but some difference was observed in the UV-vis spectra of the reaction system (Fig. 3). With the time prolong, the absorption at 211 nm was disappeared, the band at 270 nm was weakened with Einstein shift, and the absorption at 238 nm

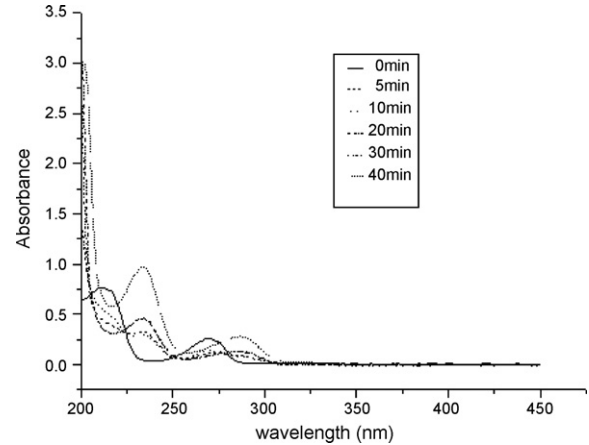
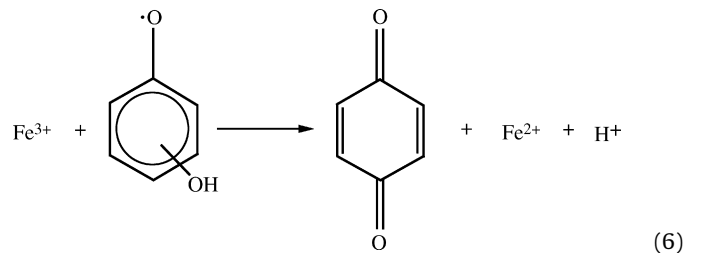
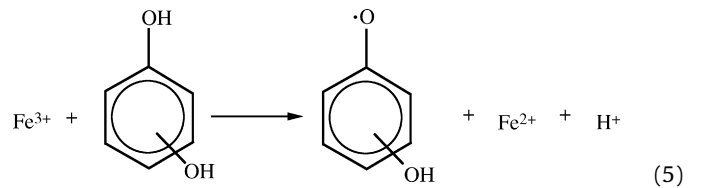
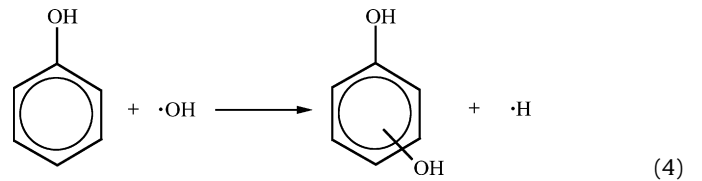


Fig. 3. UV-vis spectra of the wastewater with electrolysis in pH 5 (0.5 g Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 6.0 g Bentonite).

attributed to the characteristic absorption of quinone species was appeared in the first 5 min, this maybe due to that the benzene ring was oxidized to some intermediates, such as hydroquinone, benzoquinone. In the last 20 min, the absorptions at 238 nm and Einstein shift swell rapidly, indicated that the lots of intermediates (quinone species) came into being, which is consistent with the reference reported [25]. The role of ferric in the degradation of phenol maybe undergo two processes: (1) the first process contains two aspects: one was the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>, which underwent the normal Fenton reaction [21]; the other was that Fe<sup>3+</sup> may oxidized directly the intermediates of phenol decomposition, i.e. hydroxylated phenols, 1,4-benzoquinone [23]:



(2) Electro-coagulation process takes place [26,27]: the OH<sup>-</sup> produced from cathode react with iron ion and formed a number of iron species, such as: Fe(OH)<sup>2+</sup>, Fe(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>, Fe(H<sub>2</sub>O)<sub>5</sub>OH<sup>2+</sup>, Fe(H<sub>2</sub>O)<sub>4</sub>(OH)<sub>2</sub>, Fe(H<sub>2</sub>O)<sub>8</sub>(OH)<sub>2</sub><sup>4+</sup>, [Fe<sub>2</sub>(H<sub>2</sub>O)<sub>7</sub>(OH)<sub>3</sub>]<sup>3+</sup>, [Fe<sub>2</sub>(H<sub>2</sub>O)<sub>7</sub>(OH)<sub>4</sub>]<sup>5+</sup>, Fe(OH)<sub>2</sub> and Fe(OH)<sub>3</sub>, depending on the pH of the mixture during electrochemical degradation. Flocculation occurring in the low pH ranges can be explained by precipitation mechanism, while at higher pH ranges by adsorption

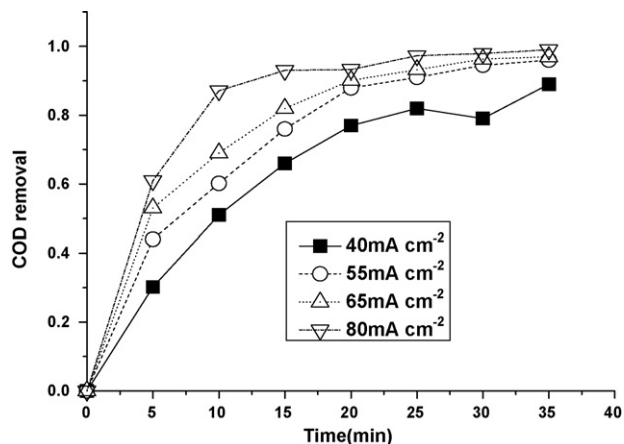
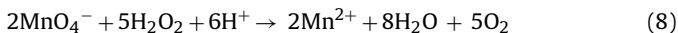


Fig. 4. Effect of current density on COD removal in pH 5 (1.5 g  $\text{KMnO}_4$  + 3.0 g  $\text{Fe}_2(\text{SO}_4)_3$  + 6.0 g Bentonite).

mechanism. At high pH values, the flocs had large surface area that is beneficial for rapid adsorption of soluble organic compounds and trapping of colloidal particles. Because the final pH was 8.5 with sampling process, the final electro-coagulation process should be adsorption process in this experiment. From the above discussion, it may come to the conclusion that electrolysis with active bentonite containing ferric sulfate forming slurry bed can oxidize phenol relatively more effective than that of only electrolysis and electrolysis with active bentonite, but its ability of broken benzene ring is limited within 40 min in the same reaction condition.

#### 3.4. Effect of potassium permanganate on COD removal

The effect of potassium permanganate on the COD removal in pH 5 in the presence of graphite electrodes electrolysis with active bentonite was shown in Fig. 2 (curves (d and e)). In the electrolysis process with active bentonite in initial pH 5 within 40 min, and the dosage of potassium permanganate from 0.5 to 1.5 g did not markedly impact the COD removal at the same reaction condition. When 0.5 g potassium permanganate was added, a significant COD removal (81.3%) can be obtained within 10 min; while 1.0 g potassium permanganate was applied, also a significant COD removal (80.5%) can be obtained within 10 min. In these two processes, a unanimous characteristic that a significant COD removal progress was observed within 10 min, whereafter COD value kept on dropping slowly with time prolong. When the dosage of potassium permanganate was increased to 1.5 g, 86.8% COD removal was ultimately obtained within 40 min in the same electrolysis condition, indicating that soluble organic compounds cannot be decomposed completely and its final COD values (200 mg/L, 183 mg/L, 160 mg/L for 0.5 g, 1.0 g, 1.5 g potassium permanganate respectively) were still high on a certain extent as a result of the formation of the new intermediates within 40 min. The possible reason that influence the COD removal efficiency show as follows:



In Eq. (8), permanganate may be reduced by  $\text{H}_2\text{O}_2$  that was circularly generated by  $\text{O}_2$  electrolysis on the cathode in Eq. (12); In Eq. (9), permanganate can be reduced once again by bivalent manganese ion that was generated by Eq. (8). The results were that not only permanganate were wasted but also electrolysis efficiency was debased, and it also reflect that because of the weak oxidation capability, the electro-generated  $\text{H}_2\text{O}_2$  affected the whole reaction system catalysis and oxidation efficiency, so the COD removal was

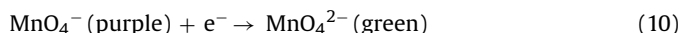
not remarkably increased by increasing dosage (from 0.5 to 1.5 g) of potassium permanganate within 40 min in the same electrolysis condition and in initial pH 5.

#### 3.5. Effect of electrolysis time on COD removal

Fig. 2 showed the effect of time on the COD removal in various systems in pH 5. As can be seen that the COD removal was increased with the time prolong: For the systems without potassium permanganate (curves (a–c)), the COD removal was increased from 0 to 40 min, indicating that phenol removal was directly proportional with time; while for those systems with potassium permanganate (curves (d–g)), in the first 10 min, the COD removal was increased quickly (no less than 80%), then it was proceeded slowly, indicating that most of organics were oxidized and destroyed in the first 10 min, also indicating that  $\text{KMnO}_4$  played a key role in the removal of phenol, which is consistent with the reference reported [22,28,29].

#### 3.6. Effect of combination of potassium permanganate with ferric sulfate on COD removal

Comparing with the COD removal efficiency of different systems, it can be seen that the COD removal (from 83.8% to 91.2%) in the presence of potassium permanganate within 40 min was evidently improved by the addition of ferric sulfate. While the dosage of potassium permanganate and ferric sulfate were all 1.5 g, the COD removal can be reached up to 95.6% in 20 min (curve (g) in Fig. 2), obviously higher than that of only 1.5 g potassium permanganate participated in the same reaction condition (86.8% COD removal). The sludge in the solution present green color at the beginning of the experiment and was disappeared near 10 min and the same phenomena did not take place when 0.5 g potassium permanganate was used. The occurrence of green color on the sludge confirmed the formation of  $\text{MnO}_4^{2-}$  [30] this can be expressed as the following equation:



According to the reference report [31],  $\text{MnO}_4^-$  would be reduced to  $\text{MnO}_4^{2-}$  at higher pH conditions. Although the initial pH value was 5, it was varied with the reaction proceed (the final pH was about 8.5). The imaginable reason maybe also interpreted as follows: the Fenton reaction that was led by a comparative quantity of ferric sulfate can entrap a mass of hydrogen peroxide and restrain the reaction in Eqs. (8) and (9), and so permanganate ion can catalytic oxidize organic compound more adequately by its potential stepwise pathways involving electron transfer [32] and by hydroxyl radical's participation coming from the Fenton reaction. In summary, the present data show that the synergetic effect of ferric sulfate and potassium permanganate was obviously: it can not only improve electrolysis efficiency, but also make use of potential (catalysis and oxidation) of permanganate ion more versatile.

#### 3.7. Effect of current density on COD removal

Current density is the most important parameter for controlling the reaction rate in all electrolysis processes. The effect of current density on COD removal with time during oxidation of the wastewater catalyzed by active bentonite loaded with 1.5 g  $\text{KMnO}_4$ -3.0 g  $\text{Fe}_2(\text{SO}_4)_3$  at pH 5 was investigated (Fig. 4). The COD removal at current density 40, 55, 65 and 80  $\text{mA cm}^{-2}$  at 35 min were 89%, 96%, 97% and 99%, respectively, showing that a higher current density caused a faster COD removal. It was further noted that there were minor differences in COD removal at the relatively higher different current densities. Furthermore, higher current density causes high

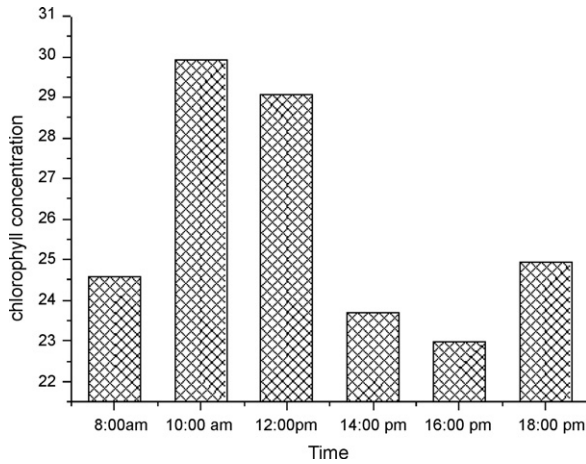


Fig. 5. Changes of chlorophyll concentration of Impatiens as the function of time.

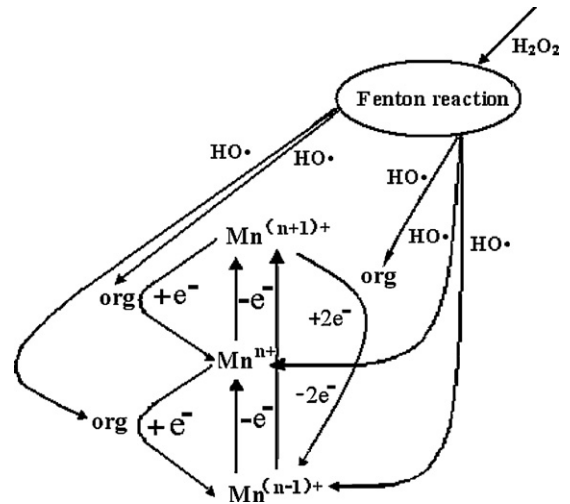
electrical energy consumption and operating cost. Therefore that current density at 55–65 mAcm<sup>-2</sup> can be chosen for this experiment.

### 3.8. Environmental estimate

Many papers have studied environmental effect of the discharged pollutants from the pulp and paper industry, such as water, air and land [33,34]. Less information was available today concerning the effect of irrigation of secondary treated phenol water on ecologies. In the present study, the effect of irrigation of treated wastewater (pH 7) on the amount of chlorophyll changes of Impatiens holstii was investigated. It can be seen from Fig. 5 that the treated wastewater has little effect on the content of chlorophyll, the overall chlorophyll content gradually increased when the treated wastewater was irrigated into the soil, and then the chlorophyll content reduced rapidly from 10:00 a.m. to 16:00 p.m. However, it was interesting to find that its content gradually recovered to normal level (the chlorophyll content at 8:00 a.m. was pre-irrigation) at 18:00 p.m., which indicated that the treated wastewater could be totally applied to irrigate.

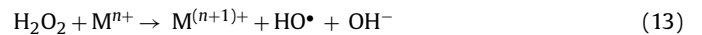
### 3.9. Theoretical approach [27,32]

In this paper, the combined electro catalytic oxidation of phenol wastewater in the presence of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>-KMnO<sub>4</sub> adsorbed onto active bentonite was investigated. Three processes are involved in the whole degradation process: adsorption process, synergetic oxidation process and flocculation-coagulation process: (1) By adsorption process, pollutants can be immediately adsorbed on the catalyst due to its high surface area. (2) By combined electro-chemical oxidation process, manganese ion can destruct organic pollutants and convert them into CO<sub>2</sub> and H<sub>2</sub>O assisted with electro-generated strong oxidants. According to the above experimental results, a possible catalytic cycle mechanism (Scheme 1) of the catalyst was proposed. But few points need to explain as follows: ① owing to manganese ion having multiple valency, the whole valent evolution pathways were possibly very complex, so the three kinds of manganese ion that have ordinal valency are list in Scheme 1. ② Near porous graphite anode, the evolution of O<sub>2</sub> with high yields can immediately reduced on the porous graphite cathode to form H<sub>2</sub>O<sub>2</sub>:



Scheme 1. Catalytic cycle of catalyst (KMnO<sub>4</sub> + Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + active bentonite) in degradation of phenol.

In the presence of transition metal adsorbed on active bentonite, oxidant formation is as follows (M<sup>n+</sup>: Fe<sup>2+</sup>):

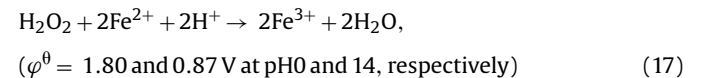
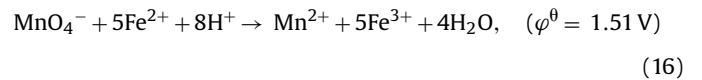
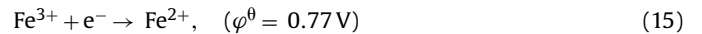


In this process, owing to decomposition of electro-generated H<sub>2</sub>O<sub>2</sub> and production of powerful oxidizing agent (HO•), Fenton reaction inhibited that electro-generated H<sub>2</sub>O<sub>2</sub> can diffuse onto the anode forming O<sub>2</sub> in Eq. (14) and improve the electrolysis efficiency:



③

From the above equations, there may occur competitive reactions among MnO<sub>4</sub><sup>-</sup>, H<sub>2</sub>O<sub>2</sub> and Fe<sup>3+</sup>:

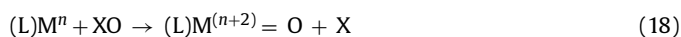


The competitive reaction between MnO<sub>4</sub><sup>-</sup>/Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> is affected by several factors, such as pH, redox potential, and concentrations of MnO<sub>4</sub><sup>-</sup>, H<sub>2</sub>O<sub>2</sub> and iron ion. pH and redox potential value in normal environmental conditions is usually varied, but the concentration factor can be easily controlled. When the dosage of MnO<sub>4</sub><sup>-</sup> and iron ion is certain, with current density enhanced, electro-generated H<sub>2</sub>O<sub>2</sub> will be more preponderant to contest Fe<sup>2+</sup> than MnO<sub>4</sub><sup>-</sup>. As a result, hydroxyl radical's participation coming from H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> reaction and reaction between MnO<sub>4</sub><sup>-</sup> and organic compounds will be accelerated, at the same time, MnO<sub>4</sub><sup>-</sup>/Fe<sup>2+</sup> reaction will also be inhibited because of the decreasing of MnO<sub>4</sub><sup>-</sup> concentrations. The optimal dosage of potassium permanganate and ferric sulfate is correlated with the current density, organic compounds concentrations and initial pH nearly and need to be further studied.

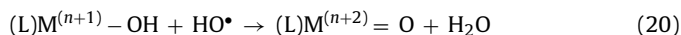
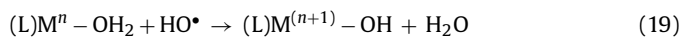
④ Because a mass of iron ion, manganese ion and organic compounds are adsorbed onto active bentonite, hydroxyl radical from Fenton reaction can take part in oxidation reaction before decomposed due to its short life.

⑤ Besieged by large numbers of hydroxyl radical (powerful oxidizing agent) from Fenton reaction, (L)M<sup>n</sup> (manganese-oxo species)

are usually prepared by oxygen-atom transfer from an oxygen donor XO (hydroxyl radical) to a metal precursor.



They can also be formed via loss of electrons and protons from an aqua species, by hydroxyl radical participation.



© Owing to having strong oxidation capability, hydroxyl radical can inhibit the possible self-redox reaction between manganese-oxo species with different valency, which can also improve the catalytic properties and oxidation potential of manganese ion.

(3) By flocculation-coagulation process, phenol and intermediates that have been adsorbed by ferric hydroxide will create a floc deposition and then be decomposed.

#### 4. Conclusion

Based on the above discussions, it can be concluded that the active bentonite containing  $Fe_2(SO_4)_3$ - $KMnO_4$  can act as a good catalyst in the process of electrochemical oxidation degradation of phenol in initial pH 5. When the initial concentration of phenol was 0.52 g/L (the initial COD 1214 mg/L), up to 99% chemical oxygen demand removal was obtained in 40 min. Environmental estimate indicated that the treated wastewater have little influence on plant growth and could totally be applied to irrigation. The possible mechanism was also discussed on theoretical approach.

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