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An Optimized Method Using Light Enhanced Fenton to Treat Highly Toxic Phenol Wastewater

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Phenol wastewater is highly toxic and difficult to degrade. Advanced oxidation processes, including Fenton treatment, can oxidize phenol to H_2O and CO_2 and help to solve the phenol pollution problem effectively. The reaction parameters using Fenton treatment to degrade phenol wastewater were optimized in this study. The efficiencies of Fenton treatment and light enhanced Fenton treatment were compared. The feasibility of using Fenton treatment to degrade the phenol wastewater was finally discussed. The results indicated that the removal rate of phenol did not changed significantly under mercury lamp irradiation/Fenton oxidation treatment compared to that of the Fenton oxidation treatment. Otherwise, the UV irradiation can greatly improve the efficiency of degradation of phenol wastewater. The optimal conditions for the removal of phenol at 220 mg/L were: hydrogen peroxide at 4.03 mmol, pH value at 2.8 and ferrous sulfate at 0.1543 mmol. The maximum phenol removal rate reached 98.2 %, which clearly indicated the high efficiency and the great potential of this method.

Key Words: Fenton treatment, Phenol wastewater, UV irradiation.

INTRODUCTION

Phenol wastewater from chemical, pharmaceutical, phenolic resins and other industrial sectors is highly toxic and hardly degradable[1,2]. Phenol wastewater is a big threat to the environment, especially to the aquatic organisms and plants. When the phenol concentration in water is greater than 10 mg/L, it will cause damage on the fish, which might lead the fish to death and even extinction[3,4]. The phenol wastewater also impacts bad influences on the plants and farmland crops. High concentrations of phenol can cause cell degeneration of organism. Treatments of phenolic wastewater mainly depend on physical, biological or chemical methods. Specifically, the wastewater treatment methods popularly used include solvent extraction method[5], adsorption[6], membrane separation[7], biochemical[8] and advanced oxidation processes[9]. All these methods of phenol wastewater have their advantages and disadvantages. Advanced oxidation processes can oxidize phenol into H_2O and CO_2 through different physical and chemical processes, such as photo catalysis[10], ultrasonic catalysis[11], ozone oxidation[12], Fenton oxidation[13] and electrochemical oxidation[14]. Previous studies suggested that the advanced oxidation processes had rapid oxidation rate and high removal efficiency for various organic pollutants, so Fenton oxidation, as an important method of advanced oxidation processes, was employed here tentatively in the study to the phenol wastewater treatment.

Fenton reagent for the decomposition of organic waste has excellent efficiency[15]. Fenton oxidation is proved as an efficient way to deal with aromatic amines, aromatic hydrocarbons, pesticides and reduce nuclear waste and other organic wastewater[16,17]. Light-assisted advanced oxidation technology has gained in great interest in recent studies[18,19]. It is the combined technology of ultraviolet radiation and oxidants or catalysts (such as O_3, H_2O_2, Fenton reagent or semiconductor materials, *etc.*) oxidation. The excitation of light result in more free radical oxidation (such as ˆOH), thus greatly improved the response rate and oxidation effect. This technology can be used to deal with many pollutants effectively which can not completely be degraded by the conventional oxidants. Compared to other advanced oxidation process, Fenton treatment is simple, rapid and easy to flocculation and can be widely applied. Fenton oxidation method for the environmental pollutants treatment is also fast responsive, mild conditions and no secondary pollution. So, in this study, the feasibility of using Fenton treatment to degrade the phenol wastewater was investigated.

EXPERIMENTAL

The phenol wastewater used in the study was attained from a chemical plant in China (Qinhuangdao, Hebei Province). The phenol concentration of wastewater was 220 mg/L determined by the HPLC. The 30 % hydrogen peroxide solution was purchased from Tianjin Chemical Factory (Tianjin, China).

All other chemicals were analytical reagent grade purchased from Beijing Chemical Factory (Beijing, China).

Fenton treatment: The wastewater (200 mL) was firstly mixed with the solution of hydrogen peroxide and ferrous sulfate, the pH of the mixture was adjusted, then the reagents were stirred for a certain time. the concentration of phenol was measured and the removal rate of phenol in the wastewater was calculated. The light enhanced Fenton treatment was also carried out in this paper. Light was placed on the reactor at the distance of 10 cm.

Analysis method: Agilent 1100 HPLC system with UV detector was employed to determine the concentration of phenol. Which was equipped with Agilent ZORBAX Extend-C_{18} (250 mm × 4.6 mm, 5 μm). 65 % Methanol and 35 % water were used as carrier with constant flow at 25 ºC. 20 μL was injected for measurement. The phenol removal rate was also calculated as below, in which phenol and $phenol_0$ was phenol concentration (mg/L) before and after the treatment.

$$\text{Phenol removal rate} = \frac{[\text{phenol}]_0 - [\text{phenol}]}{[\text{phenol}]_0} \times 100\ \%$$

RESULTS AND DISCUSSION

Influence of Fenton parameters on the efficiency: It was reported that pH, reaction temperature, reaction time, H_2O_2 dosage, dosage of catalyst and catalyst species were the main influencing factors on the Fenton oxidation[20,21]. According to the classical mechanism of Fenton oxidation, the oxidation effect of Fenton reagent appeared in acidic circumstance because under neutral and alkaline condition, ˆOH could not generate from H_2O_2. The generation process of ˆOH would be inhibited by the high pH value. Fe^{2+} in the solution would be in the form of hydroxide precipitate and lost the catalytic ability also in the high pH value solution. It was also reported that as the temperature increases, the Fenton reaction would be accelerated. However, Fenton oxidation was such a complex reaction system and with the rising of temperature, not only the main reaction speeded up, but some side reaction was also accelerated. When the temperature was too high, H_2O_2 would also decompose into H_2O and O_2.. So, the ˆOH radicals only could be activated under appropriate temperature. The dosage of catalyst and H_2O_2 in Fenton reagent for treatment of organic wastewater had a great impact on the COD removal efficiency results, because the organic matter was removed by the oxidation effect of hydroxyl radicals and the amount of hydroxyl radicals was related with the dosage of catalyst and H_2O_2. The effect of the reaction time, pH, dosage of ferrous sulfate and H_2O_2 dosage on the removal rate of phenol in wastewater was focused in this paper.

Reaction time: Fenton oxidation treatment is fast reaction at the beginning of the reaction. The removal efficiency of COD always increased with time and after a certain time COD removal efficiency was close to maximum and then remained stable. The essence of Fenton oxidation treatment was the reaction between the organic substance and hydroxyl radicals. So the optimal reaction time was determined by the production rate of hydroxyl radical and the reaction rate of organic substance and hydroxyl radical. At the same time, the production rate of hydroxyl radical was mainly correlated with solution pH, catalyst species and catalyst concentration. So the reaction time of Fenton oxidation treatment on the wastewater was associated with the catalyst species, catalyst concentration, wastewater pH and kinds of organic compounds. 1 mL ferrous sulfate solution (0.2572 mol/L) and 12 mL hydrogen peroxide (0.155 mol/L) were added to the wastewater and the pH of the reaction solution was fixed at 2.8 to investigate the influence of the reaction time. The removal efficiency of phenol changing with the reaction time was shown in Fig. 1. Fig. 1 showed that the removal rate of phenol was increasing with the prolonging of reaction time within 40 min and the time and removal rate maintained a linear relationship. When the reaction lasted for 50 min, the removal rate remained stable. It was deduced that the reaction rate was decreased according to the reaction dynamics and some intermediates had hardly been reduced or oxidized by hydroxyl radical. Further degradation of COD purports to be by changing the reaction conditions or the introduction of new catalysts to achieve.

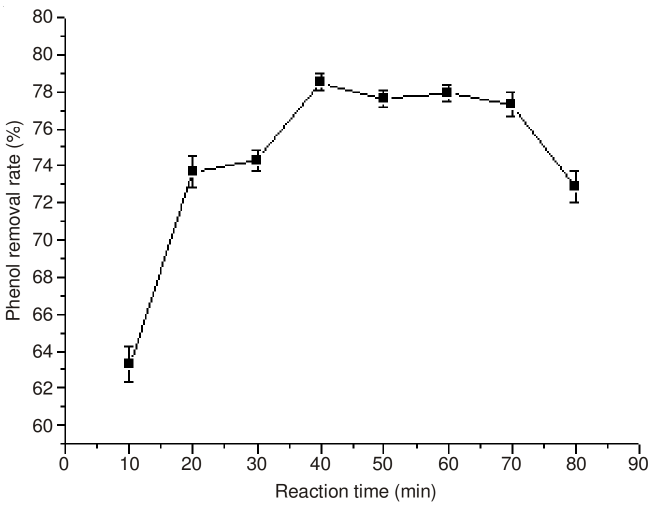

Fig. 1. Variation of removal rate of phenol under different reaction time

Effect of pH on removal rate of phenol: In this part, 1 mL ferrous sulfate solution (0.2572 mol/L) and 12 mL hydrogen peroxide (0.155 mol/L) were added to the wastewater and the reaction time was 40 min. The oxidation effect of Fenton reagent appeared under acidic conditions. In neutral and alkaline solution, the reaction between Fe^{2+} and H_2O_2 could not produce ˆOH, as the form of Fe^{2+} in solution was subject to the pH of the solution. The removal efficiency of phenol changing with the pH of the solution was shown in Fig. 2. The maximum removal rate of phenol was reached at the pH value of 2.8. When the pH value exceeded 3, the removal rate decreased with the increase of pH value. According to the classical theory of Fenton reaction, the higher pH not only inhibits the generation of ˆOH, but also promotes the formation of Fe precipitate and the lost of catalytic ability. When the pH value was below 3, the solution of the H^+ concentration was high, Fe^{3+} could not successfully be reduced to Fe^{2+} and the catalytic reaction was blocked. The pH changes directly affected the complex equilibrium system of Fe^{2+} and Fe^{3+}, thus affected the ability of Fenton reagent oxidation. When pH value was too high, the generation of ˆOH was unfavourable. When the pH value was too low, Fe^{2+} was difficult to be restored and the supply of Fe^{2+} faced shortage and thus the number of ˆOH was reduced. In summary, as shown in Fig. 2, when the pH was 2.8, the removal rate of phenol reached the highest point. when the pH was greater than 5, the solution precipitatation was generated.

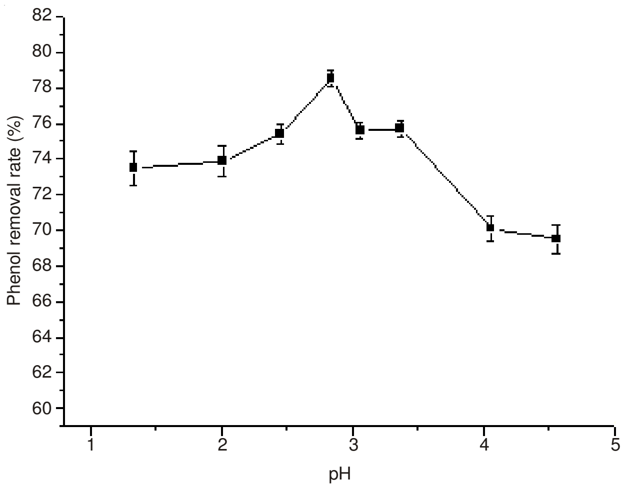

Fig. 2. Variation of removal rate of phenol under different reaction pH

Influence of sulfate concentration: $FeSO_4.7H_2O$ is the most common used catalyst for the catalytic decomposition of hydrogen peroxide to generate hydroxyl radical. Under normal circumstances, with the increase of the amount of Fe^{2+}, the phenol removal rate was increased at first and then declined. In this part, 17 mL hydrogen peroxide (0.155 mol/L) were added to the wastewater and the reaction time was 40 min. The pH of the solution was 2.8. The result was shown in Fig. 3. The probable reason was that when the concentration of Fe^{2+} was low, with the increasing concentration of Fe^{2+}, the number of generating ˆOH was more,and all the generating ˆOH was involved in the reaction. However, when the Fe^{2+} concentration keep higher, some H_2O_2 began to decompose and release O_2.

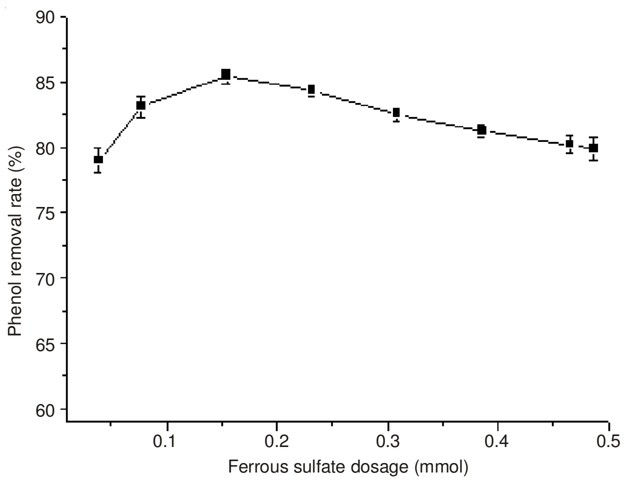

Fig. 3. Variation of removal rate of phenol under different ferrous sulfate dosage

Hydrogen peroxide: The removal efficiency of phenol changing with hydrogen peroxide dosage was shown in Fig. 4. It was showed that the removal rate of phenol was raised with the increasing dosage of hydrogen peroxide. But when the dosage of H_2O_2 was more than 2.79 mmol, the rising rate was decreased. With increased dosage at the same time, the invalid decomposition of hydrogen peroxide was also increased. Thus when the concentration of H_2O_2 was low, the amount of ˆOH was less. But when the concentration of H_2O_2 kept higher, excessive decomposition of H_2O_2 could not generate more free radicals and large amount of Fe^{3+} was soon generated to inhibit the formation of free radicals.

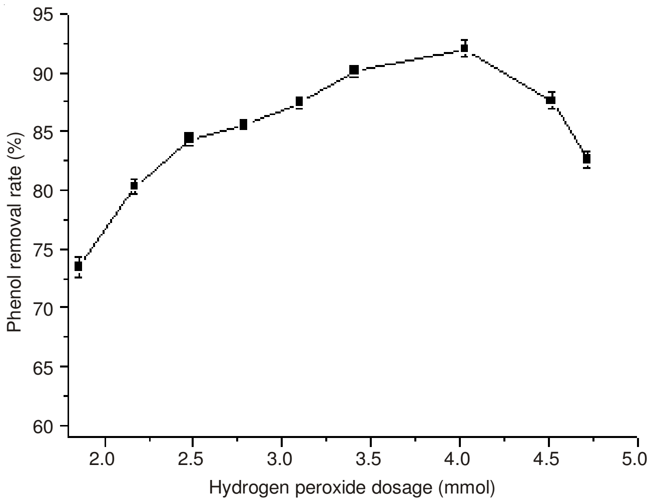

Fig. 4. Variation of removal rate of phenol under different hydrogen peroxide dosage

Orthogonal experiment for Fenton treatment: According to actual conditions the corresponding test indicators need to be resolved. The analyses of the various affecting factors need to be considered excluding those which have little impact on the result or have been better controlled of. The factors which have a greater impact on the experiment were studied. In this experiment, three relevant factors *i.e.*, H_2O_2 dosage, ferrous sulfate dosage and pH were considered. Based on the experiment, the factors were selected for three levels in the orthogonal arrangement with this test. Variable factors and three levels orthogonal experiment was shown in the Table-1 and experiments have been conducted. According to the design of orthogonal experiment list, the experiments were made.

TABLE-1
ORTHOGONAL EXPERIMENT FOR FENTON TREATMENT

Factors	1	2	3	
	Hydrogen peroxide (mmol)	pH	Ferrous sulfate (mmol)	Removal rate (%)
Experiment 1	2.79	2.4	0.1543	0.867
Experiment 2	3.41	2.4	0.2315	0.905
Experiment 3	4.03	2.4	0.3086	0.923
Experiment 4	2.79	2.8	0.2315	0.869
Experiment 5	3.41	2.8	0.3086	0.885
Experiment 6	4.03	2.8	0.1543	0.924
Experiment 7	2.79	3.2	0.3086	0.871
Experiment 8	3.41	3.2	0.1543	0.894
Experiment 9	4.03	3.2	0.2315	0.915
Mean Value 1	0.869	0.898	0.895	
Mean Value 2	0.895	0.892	0.896	
Mean Value 3	0.921	0.893	0.893	
Range	0.052	0.005	0.003	

Table-1 showed that the selected three factors had some impact on the removal of phenol. Among these three factors, the dosage of H_2O_2 has the most important influence on the removal rate of phenol, followed by the pH and the concentration of Fe^{2+}. The amount of hydroxyl radicals was related with the dosage of H_2O_2. Table-1 also showed that the optimal conditions for the removal of phenol was: the amount of hydrogen peroxide of 4.03 mmol, pH value of 2.8, the amount of ferrous sulfate of 0.1543 mmol.

Light enhanced Fenton treatment of phenol wastewater: Fenton method can destroy organic matter in the dark, with equipment investment advantages. But there are two drawbacks for Fenton treatment: Firstly, part of the initial material was transformed into some intermediate product, these intermediates can form complexes with Fe^{3+}, or affect the generation of hydroxyl radical and may cause greater harm to the environment. Secondly, the H_2O_2 utilization was low. So the light-Fenton system was introduced to solve these problems. The light-Fenton system was the combination of two systems (Fe/H_2O_2 and light/H_2O_2). This system has some obvious advantages, for example, it can reduce the amount of Fe and maintain high utilization of H_2O_2. The synergistic effect of light and ferrous ions can help the catalytic decomposition of H_2O_2. The decomposition rate of H_2O_2 is much larger. And some organic compounds can be partially degraded under light. Light/Fenton oxidation method has a strong ability to effectively break down organic matter, but the energy consumption is higher.

Mercury lamp irradiation/Fenton oxidation treatment: The phenol wastewater was treated under the mercury lamp irradiation/Fenton oxidation treatment. The wavelength was 365 nm and the irradiation time was 40 min. The removal rate under mercury lamp irradiation/Fenton oxidation treatment was compared with the removal rate under the common Fenton oxidation treatment. The experiment parameters were selected according to the experimental result from the single factor experiment and orthogonal experiment. The result was shown in Table-2. It can be seen from the comparison test that the removal rate of phenol was not changed greatly. The reason might be that the characteristic wavelength of this light and the absorption wavelength with Fenton reagent were not in the same area.

TABLE-2
COMPARISON BETWEEN MERCURY LAMP IRRADIATION/ FENTON OXIDATION TREATMENT AND ORDINARY FENTON OXIDATION TREATMENT

	Dosage of hydrogen peroxide (mmol)	Dosage of ferrous sulfate (mmol)	pH	Removal rate before irradiation (%)	Removal rate after irradiation (%)
1	1.86	0.2572	2.84	75.5	76.2
2	2.64	0.1543	2.83	86.4	87.0
3	3.41	0.2572	2.84	89.1	90.0
4	4.03	0.1543	2.80	92.4	92.6

UV irradiation/Fenton oxidation treatment: The phenol wastewater was then treated under the UV lamp irradiation/ Fenton oxidation treatment. The wavelength was 253 nm and the irradiation time was 10 min. The removal rate under UV lamp irradiation/Fenton oxidation treatment was compared with the removal rate under the common Fenton oxidation treatment. The experimental parameters were selected according to the experimental result from the single factor experiment and orthogonal experiment. The results were shown in Table-3. The results showed that the UV light irradiation can significantly increase the removal efficiency of phenol, indicating that the UV irradiation can help the oxidation treatment of phenol wastewater with Fenton reagent. But in order to get the optimal condition for the removal of phenol, the orthogonal experiment for light enhanced Fenton treatment was designed and processed.

TABLE-3
COMPARISON BETWEEN UV IRRADIATION/FENTON OXIDATION TREATMENT AND ORDINARY FENTON OXIDATION TREATMENT

	Hydrogen peroxide (mmol)	Ferrous sulfate (mmol)	pH	Without irradiation (%)	With irradiation (%)
1	1.86	0.2572	2.84	75.5	82.3
2	2.64	0.1543	2.83	86.4	93.1
3	3.41	0.2572	2.84	89.1	96.8
4	4.03	0.1543	2.8	92.4	98.2

Orthogonal experiment for light enhanced Fenton treatment: The factors which have a greater impact on the experiment were studied. In this experiment, three relevant factors *i.e.*, H_2O_2 dosage, ferrous sulfate dosage and pH were considered. Based on experiment, the factors were selected for three levels in the orthogonal arrangement with this test. The experiment program is designed with orthogonal experiment method, at the same time the orthogonal experiment list is set up and experiments have been conducted. According to the design of orthogonal experiment list, the experiments were made. Orthogonal experimental results were shown in the following Table-4.

TABLE-4
ORTHOGONAL EXPERIMENT FOR LIGHT ENHANCED FENTON TREATMENT

	1	2	3	
Factors	Dosage of hydrogen peroxide (mmol)	pH	Dosage of ferrous sulfate (mmol)	Removal rate (%)
Experiment 1	2.79	2.4	0.1543	0.925
Experiment 2	3.41	2.4	0.2315	0.955
Experiment 3	4.03	2.4	0.3086	0.969
Experiment 4	2.79	2.8	0.2315	0.928
Experiment 5	3.41	2.8	0.3086	0.944
Experiment 6	4.03	2.8	0.1543	0.982
Experiment 7	2.79	3.2	0.3086	0.935
Experiment 8	3.41	3.2	0.1543	0.952
Experiment 9	4.03	3.2	0.2315	0.975
Mean Value 1	0.929	0.950	0.953	–
Mean Value 2	0.950	0.951	0.953	–
Mean Value 3	0.975	0.954	0.949	–
Range	0.046	0.004	0.004	–

From the orthogonal test results it can be seen that the dosage of H_2O_2 had the most important influence on the removal rate of phenol, followed by the pH and the concentration of

Fe^{2+}. Table-4 also showed that the optimal conditions for the removal of phenol was: the amount of hydrogen peroxide of 4.03 mmol, pH value of 2.8, the amount of ferrous sulfate of 0.1543 mmol. And the maximum phenol removal rate was 98.2 %.

Conclusion

Efficiencies of Fenton treatment and light enhanced Fenton treatment for the phenol wastewater were compared. Influencing factors of Fenton oxidation for the phenol wastewater treatment was considered. The result of orthogonal experiment for Fenton Treatment showed that the optimal conditions for the removal of phenol was: the amount of hydrogen peroxide of 4.03 mmol, pH value of 2.8, the amount of ferrous sulfate of 0.1543 mmol. The removal rate of phenol was not changed significantly under mercury lamp irradiation/ Fenton oxidation treatment compared to the ordinary Fenton oxidation treatment. But the UV irradiation can help the oxidation treatment of phenol wastewater with Fenton reagent. In order to get the optimal condition for the removal of phenol, the orthogonal experiment for light enhanced Fenton treatment was designed and processed. The optimal conditions for the removal of phenol were: the amount of hydrogen peroxide of 4.03 mmol, pH value of 2.8, amount of ferrous sulfate of 0.1543 mmol, the maximum phenol removal rate was 98.2 %

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