

Degradation of Phenol in Wastewater with Ozone Produced by Self-design Ozone Generator

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Abstract. The optimized tube's structure of the self-design ozone generator was made with the double dielectric inner electrode and small metal cones were embedded in the outside electrode. This ozone generator was used for the degradation of phenol in wastewater. The research was studied from ozone gas flow rate, reaction time, the initial pH and concentration of the phenol in wastewater. In addition, the article also discusses the reaction mechanism of ozone degraded the phenol in wastewater. The results illustrate that the ozone concentration of self-design ozone generator under the pure oxygen flux (1.0 L/min) were 7.06 mg/L, compared with the unoptimized ozone, the optimized ozone generator's efficiency was improved 56.89%; the phenol removal rate was increased as the initial pH increased in wastewater, when pH was 12, the phenol removal rate was 80.17%; GC-MS analysis was adopted to analyze and determine the phenol intermediates. The results illustrate that the major oxidation degradation products of phenol may be p-benzoquinone benzenequinone, 4-cyclopentene-1, 3-dione and diacetone alcohol.

1 Introduction

Phenolic compounds were biodegradable and widely existed in industrial waste water which has a high toxicity. Phenol is a typical kinds of phenolic compounds with high biotoxicity. [1] The discharge of phenol in wastewater under strict control in water pollution management. So developing an effective method to deal with phenol in wastewater has important meaning to environmental protection and peoples' health.

At present, several methods was reported to treat the phenol in wastewater. Wastewater with high concentration of phenol is usually treated by an extraction process to reuse phenol. [2,3] In addition, some advanced technologies had been adopted to deal with wastewater with a low concentration of phenol, such as chemical processes, [4,5] ozonation, [5-8] ultrasonic processes, [9,10] fenton reaction, [11] compound oxidation process. [12,13] It is effective for ozone to sterilize, decrease chromaticity and smell, increase the biodegradability of refractory organics and improve the flocculent effect with its strong oxidation characteristics which is due to the high oxidation potential (2.08 V). [14-16] However, in the process of ozone generating, the high consumption of energy and low concentration of ozone limited the application in wastewater treatment in industry, so to improve the efficiency of ozone generation is the key to gain a broad prospect of applications in wastewater treatment of

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ozonation technology. At present, the research in ozone generator mainly focuses on the following aspects: (1) The power system turns high voltage power frequency to medium voltage high frequency or uses the high-voltage bipolar pulsed corona etc.; (2) With thin and high dielectric constant of the dielectric materials; (3) Using the narrow discharge gap; (4) An improved cooling system with dual cooling system.

On the basis of development and insufficiency of ozone generator and treatment of phenol in wastewater. In this study, the phenol was selected as a model of toxic organic contaminant in solutions. The self-design ozone generator was optimized for its tube structure and electrode, which was applied as ozone source to removal phenol in wastewater. Finally, the ozone concentration of self-design ozone generator and the influence of operational conditions such as the initial concentration and pH of the water, the concentration of ozone on the phenol degradation and the intermediate products were evaluated.

2 Experiments and methods

2.1 Reagent and instrument

Reagent: Phenol was purchased from Tianjin Bodi Chemical Reagent Co., Ltd. 4-aminoantipyrine was purchased from Chengdu Kelong Chemical Reagent Co., Ltd. Sulfamic acid (AR grade, purity $\geq 99.5\%$). Potassium ferricyanide was purchased from Tianjin Fengfan Chemical Reagent Co., Ltd. Potassium iodide was purchased from Tianjin Guangfu Fine Chemical Research Institute. Co., Ltd.

Main equipments: electronic scales (FA/JA); hot type constant temperature magnetic stirrer (DF-101s) ; ozone analyzer (PTM400-O3) ; self-design ozone generator; Gas Chromatography-Mass Spectrometer (PerkinElmer Clarus SQ 8, Clarus 680).

2.1.1 Self-design ozone generator

Ozone generator was assembled according to the standard of CJ/T322-2010 《Water Treatment By Ozone Generator》, the structure of ozone generator's tube had been ameliorated on the premise of other parts didn't change, the materials of tube's dielectric and electrode is quartz glass and stainless steel, respectively. The optimized tube's structure of the self-design ozone generator was made with the double dielectric inner electrode and small metal cones were embedded in the outside electrode, and the bottom radius and height of the small metal cone is 0.1 cm and 0.1 cm, respectively, as the pattern in Figure 1. The double-dielectric barrier discharge was occurrence in the inner electrode of ozone generator.

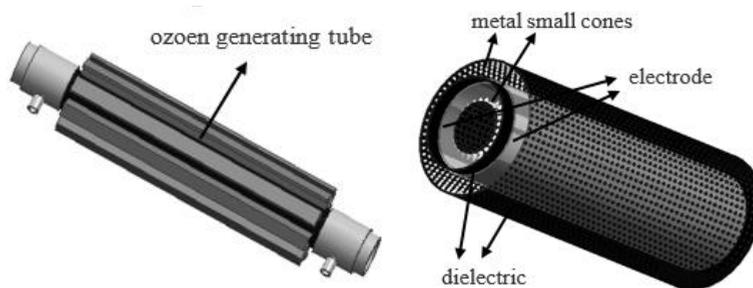


Figure 1. Ozone generating tube and its inner structure.

2.1.2 Preparation of the phenol wastewater

Dissolve phenol (analytically pure) in distilled water, and dilute with distilled water to 2000 ml in the brown glass flask.

2.1.3 Preparation of the 4-aminoantipyrine solution

Dissolve 2 g 4-aminoantipyrine in distilled water, and dilute with distilled water to 100 ml. The prepared solution was kept in the refrigerator to avoid the loss of potency.

2.1.4 Preparation of the potassium ferricyanide solution

Dissolve 8 g potassium ferricyanide in distilled water, and dilute with distilled water to 100 ml. The prepared solution was kept in the refrigerator to avoid the loss of potency.

2.2 Experimental method

The graph of ozone generator's laboratory equipment was shown in Figure 2. Ozone generator used pure oxygen to produce ozone under DBD ionization, and ozonization degraded wastewater with high concentration of phenol in 20 °C. The samples of phenol wastewater were examined and analyzed for a period of time. Ozone concentration was detected by ozone analyzer, and the concentration of phenol was detected by direct spectrophotometric method. A variety of degraded products were identified by GC-MS analysis.

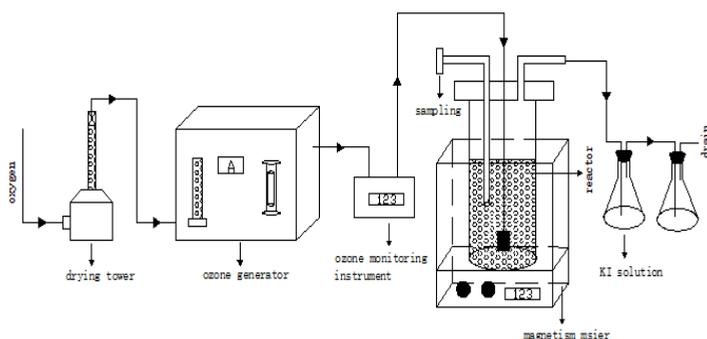


Figure 2. Stimulated phenol wastewater treatment device.

3 Results and discussion

3.1 Effect of pure oxygen flux on ozone concentration

The variation of ozone concentration with pure oxygen flux is presented in Figure 3 and other operating parameters remain the same. It could be found that with the pure oxygen flux increased the concentration of ozone first increased then decreased. As the concentration of pure oxygen was 1.0 L/min, the highest concentration of ozone was 7.06 mg/L. Compared with the traditional ozone generator, the concentration of ozone was only 4.5 mg/L in the same condition. The efficiency of the optimized ozone generator was improved 56.89%. The phenomenon might due to the corona discharge capacity of ozone generator was limited by DBD. The double dielectric barrier discharge could expand the discharge space of the ozone generator's tube thus raised discharge efficiency. Small metal cones were embedded in outside electrode which is advanced to increase the discharge efficiency and produced more oxygen atoms then improved the ozone concentration. The results indicated that the optimized self-design ozone generator was effective.

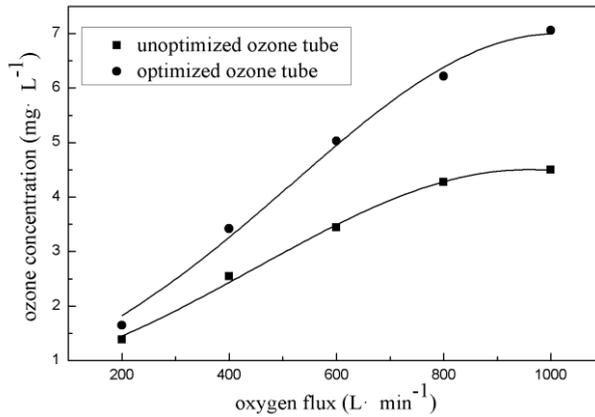


Figure 3. Effect of the oxygen flux on ozone concentration.

3.2 Effect of mixed ozone gas flux on phenol wastewater treatment

Prepared 2 L wastewater with 6 g phenol as phenol wastewater, the effective of mixed ozone gas flux (0.5 L/min, 1.0 L/min and 1.5 L/min) on ozone treated phenol wastewater was evaluated as the other operation conditions remained the same and the reaction continued for 240 min. The removal ratio of phenol in wastewater by different mixed ozone gas flux was showed in Figure 4. It could be fined that the best condition of the treatment was the mixed ozone gas flux was 1.5 L/min. After the reaction for 240 min, the removal ratio of phenol reached 75.8% under the reactive condition with 1.5 L/min of mixed ozone gas flux. This phenomenon was consistent with the highest concentration of ozone in the optimized ozone generator with the pure oxygen flux in 1.5 L/min. It was founded that the solubility of ozone in wastewater was related to the on concentration of ozone, the solubility of ozone increases with the concentration of ozone increased. As the time goes by, the removal ratio of phenol in wastewater increased, which was corresponded to the first-order kinetics equation in the reaction for 240 min.

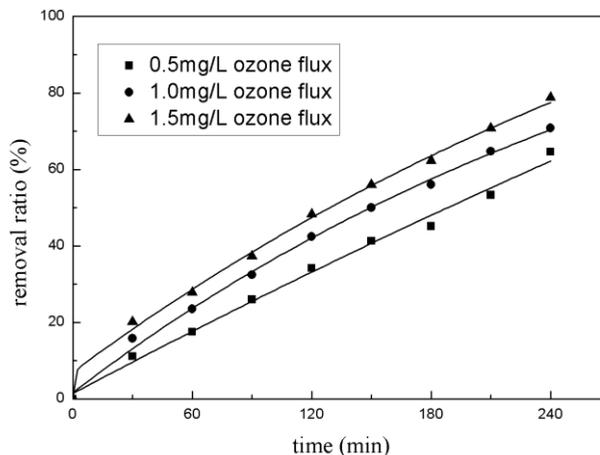


Figure 4. Phenol removal rate in wastewater by different ozone flux (reaction for 240 min, the concentration of phenol wastewater was 3000 mg/L).

3.3 Effect of the initial concentration of phenol wastewater on phenol wastewater treatment

The initial concentration of wastewater with phenol removal rate was presented in Figure 5, in the condition of mixed ozone gas flux was 1.5 L/min. When the concentration of wastewater was 100 mg/L, the phenol removed 99.9% in the oxide time for 30 min. While the concentration of wastewater was 3000 mg/L, the phenol removed 98.6% in oxide time for 480 min. In Figure 5, the results showed that the phenol removal rate increased as the reaction time increased, and the removal rate of phenol was near 100%. It illustrated that the removal efficiency of ozone generator produced by self-design was favorable for phenol wastewater treatment in a short time, and the removal rate of phenol was near 100%, even the wastewater with high concentration of phenol.

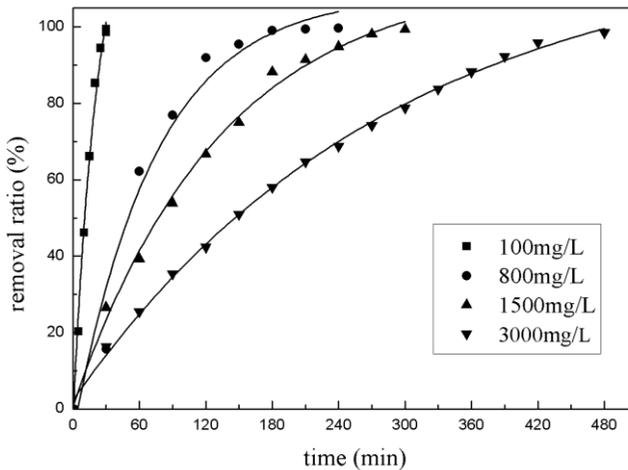


Figure 5. Reaction time on phenol removal rate at different concentration of phenol wastewater.

3.4 Effect of pH on phenol wastewater treatment

The relation shape between phenol removal rate and pH of initial wastewater was shown in Figure 6, and other operating parameters remain the same. The removal rate of phenol increased with the increasing pH value. The results illustrated that the removal of phenol was better in alkaline condition, and the phenol removal ratio was 80.2% with a pH of 12. However, when the pH was 2 the removal ratio of phenol was 64.6%. It might be because of the neutral reaction of phenol with alkalis, according to the weak acid property of phenol, moreover, improved the initial pH of wastewater was favorable for the production of hydroxyl radical ($\bullet\text{OH}$). [17] In this condition, compared with the reaction rate constant of hydroxyl radical and the ozonation, the former was seven times bigger than the latter one, this change caused the phenol removal ratio increased. Fortunately, the removal rate of phenol was 64.6% when the pH was 2. It demonstrated that the self-design ozone generator could effectively treat the phenol wastewater whatever the pH condition was.

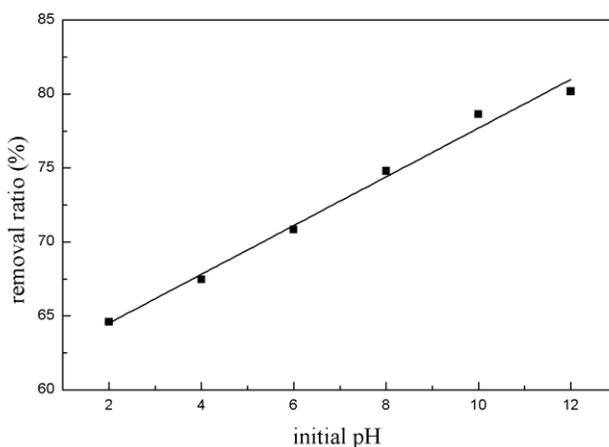
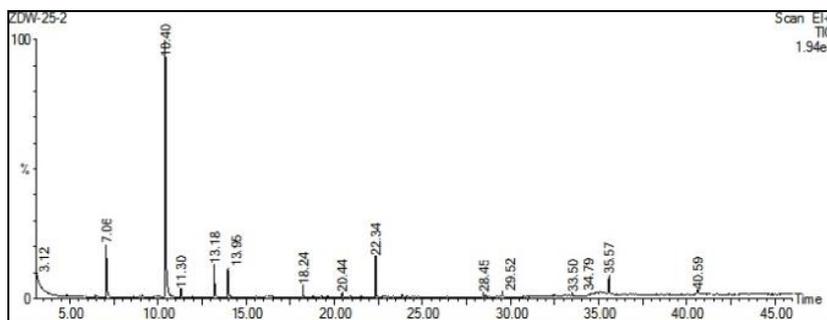


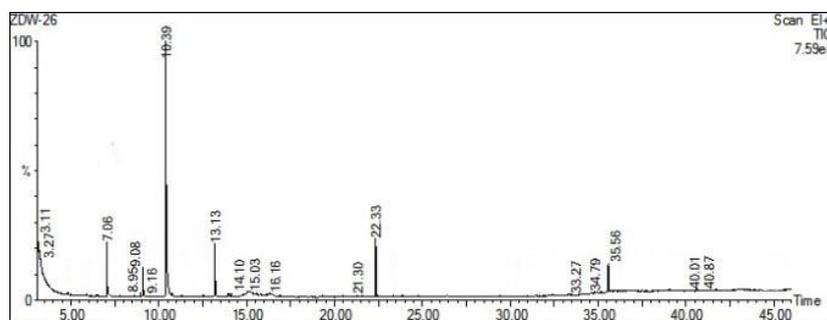
Figure 6. Initial pH on phenol removal rate (the concentration of phenol was 300 mg/L, reaction for 240 min).

3.5 Degradation analysis

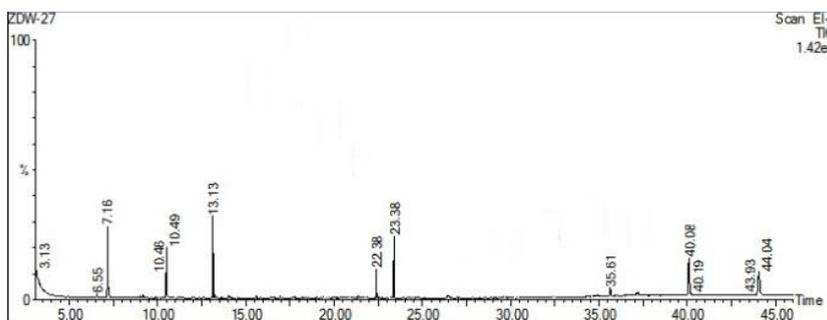
The degradation products of oxidized phenol in wastewater reactor were analyzed by gas chromatography-mass spectrometer (GC-MS). The concentration of the phenol wastewater was 100 mg/L. As the phenol was totally degraded by ozone for 30 min, so during wastewater treatment process there are 4 periods time (5 min, 10 min, 20 min and 30 min) were measured by GC-MS. The peak of phenol appeared at about 10.4 min in the Figure 7 (a, b, c). Compared the Figure 7 (a) with (b), the peak of p-benzoquinone just appeared at about 9.1 min in the Figure 7 (b) and disappeared in the Figure 7 (c). The peak of 4-cyclopentene-1, 3-dione appeared at about 13.13 min in the Figure 7 (a, b, c, d), and the intensity of the peak increased as the reaction time increased. The peak of diacetone alcohol appeared at about 7.1 min in the Figure 7 (a, b, c and d), and the intensity of the peak also increased as the reaction time increased. The rest of peaks was impure peaks. In the Figure 7 (c), the peak of p-benzoquinone and phenol did not appear and only left the peak of diacetone alcohol and the peak of 4-cyclopentene-1, 3-dione in the Figure 7 (d). Besides, the peak of 4-cyclopentene-1, 3-dione gradually decreased and the peak of diacetone alcohol gradually increased, these results showed that the phenol and p-benzoquinone were oxidized by ozone and new intermediate products emerged. This conclusion was in consistent with the phenomenon that the golden solution turned to be colorless transparent solution after reaction for about 20 min, which was shown in Figure 8. Presumably, the phenyl structure of the p-benzoquinone were destroyed, p-benzoquinone was degraded into diacetone alcohol by ozone or hydroxyl radical, and then, the further oxidation products of diacetone alcohol might be the diacetone alcohol. To sum up, p-benzoquinone, 4-cyclopentene-1, 3-dione and diacetone alcohol were the intermediate products, which were degenerated from phenol by ozone in wastewater solution. And this degradation mechanism could be expressed by an equation was shown in Figure 8.



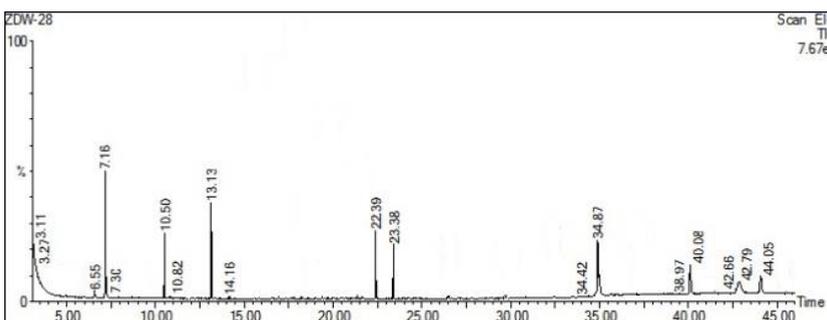
(a)



(b)



(c)



(d)

Figure 7. GC-MS spectrum of the degradation of phenol at 4 reaction periods, 5 min (a), 10 min (b), 20 min (c) and 30 min (d).

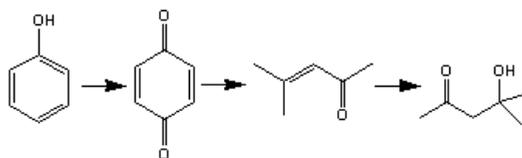


Figure 8. The degradation mechanism of phenol.

4 Conclusions

1. As the concentration of pure oxygen was 1.0 L/min, the highest concentration of ozone might be 7.06 mg/L. The concentration of ozone was increased by optimizing ozone generator in a range of pure oxygen gas flux. The concentration of ozone depended on discharge space and efficiency, as all the other conditions remained the same. It is effective for the optimization that the inner electrode of double dielectric and small metal cones were embedded in the outside electrode.

2. The concentration of ozone and the initial concentration of phenol have significant effect on the degradation of phenol. The increase in the initial concentration of phenol as the removal time increased, and as the time went on, the phenol removal ratio in wastewater was increased nearly 100%, which was in keeping with the first-order kinetics equation.

3. The self-design ozone generator can effectively treat phenol whatever the pH conditions was.

4. The intermediate products of the oxidation degradation of phenol were detected by GC-MS. According to a preliminary inspection, the intermediate products were p-benzoquinone, 4-cyclopentene-1, 3-dione and diacetone alcohol.

Acknowledgement

The authors acknowledge the research grant provided by the national science and technology major project for water pollution control and management (Project No. 2014ZX07105-001). And the major science and technology program of Yunnan Province, China (Project No. 2012ZB005) .

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