Study on the factors influencing phenol degradation in water by dielectric barrier discharge (DBD)

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Abstract. Dielectric barrier discharge (DBD) is an effective method to produce active species including ozone for remediation of pollutants in water, gas, etc. In the present work, a DBD type surface discharge system was utilized to degrade phenol in solutions. The influence of experimental conditions including solution pH values, initial concentration of phenol and applied voltage on the degradation rate of phenol, the removal of COD and the byproducts was examined and discussed as well as the concentration change of ozone during phenol was examined. Experimental results reveal that high pH value advanced the degradation of phenol and COD removal, which maybe contributed to the enhanced generation of hydroxyl radicals under higher pH value; applied voltage influenced the transformation of phenol to byproducts which could be demonstrated by the different COD removal under different applied voltages. Under an optimization condition, the degradation rate of phenol reached 100% in 80 minutes and COD removal reached 68% in 120 minutes.

1. Introduction
Electrical discharge technologies have attracted many attentions for the degradation of organic compounds in aqueous solutions in the past decades [1]. As a high efficiency method, DBD is an effective method to removing biorefractory organic compounds in aqueous solutions. The most abundant oxidizing species produced by dielectric barrier discharge plasmas is ozone that is formed in the gas phase, although small amounts of other species such as hydrogen peroxide, hydroxyl radicals, and hydroperoxyl radicals are also produced in the water phase [2]. Therefore, in order to efficiently utilize ozone for removing the water contaminants, it is very important to study the factors affecting the ozonation efficiency.

Phenol has been widely used as an object pollutant to elucidate the complex discharge reaction mechanisms and to evaluate the performance of many reactors designs [3]. Moreover, a high content of phenols wastewater exhibiting high chemical oxygen demand (COD) is still less effective treated through conventional biological processes due to their poor biodegradability. Their toxic effects on human health are well documented, being related to severe illnesses and some serious human organ malfunctions.

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In this study, we investigated the application of a DBD reactor submerged in water to degrade phenol. Meanwhile, several factors affecting the degradation efficiency of phenol were studied in detail, such as pH values, initial concentration of phenol and applied voltage.

2. Experimental

2.1. Experimental Apparatus

The DBD reactor was made with a quartz glass cylinder (inner diameter: 10 mm; outer diameter: 12.5 mm; length: 280 mm) and a stainless steel wire, in which the wire coiled inside of the cylinder was supplied with an AC high voltage power supply. The wastewater was grounded. The volume of the wastewater contained in the reactor vessel was 600 mL. The flow rate of dry air fed into the DBD reactor was 2 L min⁻¹.

The AC high voltage applied to the DBD reactor was varied from 6 to 10 kV (peak value) to change the discharge power, and eventually to change the concentration of ozone. For measurement of the voltage applied to the DBD reactor, a 1000:1 high voltage probe (Tektronix P6015A) and a digital oscilloscope (Tektronix TDS2014) were used.

2.2. Experimental Methods

The chemical oxygen demand (COD) was measured by potassium dichromate titration method.

The percentage removal of the parameters evaluated (degradation) was determined using the following equation (1):

\[ \eta_{\text{COD}}\% = \left( \frac{m_0 - m}{m_0} \right) \]

where \( \eta \): degradation efficiency of COD, \( m_0 \) and \( m \) are initial and final values of COD in the synthetic wastewater.

The concentration of ozone in the gas was analyzed by the iodometric method [4].

The determination of phenol concentrations was measured by HPLC. The degradation of phenol was determined by equation (2):

\[ \eta_{\text{p}} = \left( \frac{C_0 - C}{C_0} \right) \]

where \( \eta \): degradation efficiency of phenol, \( C_0 \) and \( C \) are the initial concentration of phenol and the concentration of phenol at any time in the synthetic wastewater.

3. Results and discussion

3.1. Effect of solution pH

Since pH is a key parameter for both ozone stability and the production of hydroxyl radicals in aqueous solution, it is important to examine the influence of pH on ozonation of phenol-contained water. Figure 1 shows the COD removal efficiency of phenol solution with an initial concentration of 80 mg L⁻¹ and a different initial pH values at 3.0, 6.0, 9.0 and 11.0, respectively. It is obvious that the degradation efficiency of COD increased with discharge time. The degradation efficiency reached the high value of 54.32% during 80 min in the solution with pH 9.0. For the solutions with pH 3.0 and 6.0, the degradation efficiencies were more and more close to 65% in 120 min. However, the degradation efficiency decreased in the solution with pH 11.0, which only reached 12.60%.

It was well known that ozone decomposes into hydroxyl radicals more easily in basic solution than neutral or acid circumstances because hydroxide ions may play a role of initiator of the chain reaction [5]. The variations of ozone at different pH can be observed in table 1, the results show that the higher pH was, the lower the amount of ozone was, which maybe attributed to the production of hydroxyl radicals in basic solution through ozone decomposition. Because hydroxyl radicals were a less selective and more powerful, more phenol molecules can be oxidized in a basic pH solution since the concentration of hydroxyl radicals is much higher than acid solution. Therefore, the COD removal efficiency reached the high value at pH 9.0. However, the COD removal efficiency was close at pH=3, 6 and 9 after 80 min, especially in 120 min. As shown in figure 2, there is a tendency toward a decrease in pH with the ozonation time; the decrease in pH may be due to phenol molecules being
oxidized by ozone, resulting in small organic molecular fragments, such as acetic acid [6], aldehydes, ketones and so on. pH was almost same in 120 min with different initial pH values at 3.0, 6.0 and 9.0. The main reactions taking place in the acid aqueous solution were those between ozone and phenol. So the COD removal efficiency was close at 120 min. However, the COD degradation efficiency decreased in pH 11.0. In the above experiments, the working gas was dry air, which includes CO$_2$. In basic solution condition, CO$_2$ can generate carbonate ions which are the suitable •OH scavengers. So phenol decomposition in the synergistic system of DBD was decreased.

Figure 1. Effect of pH on COD removal efficiency (applied voltage 7 kV, initial concentration 80 mg L$^{-1}$, frequency 7 kHz)

Figure 2. pH variations of the solutions (Initial concentration 80 mgL$^{-1}$, applied voltage 7 kV, frequency 7 kHz).

| pH    | Ozone (mg$^{-1}$) |
|-------|-------------------|
| 3     | 0.459             |
| 6     | 0.445             |
| 9     | 0.364             |
| 11    | 0.315             |

Table 1. Ozone variations of different pH.

3.2. Effect of initial concentration of phenol
The results of the COD removals at an initial concentration of 60, 80, 150, 200 mg L$^{-1}$ are shown in figure 4. A maximum phenol conversion of 68 % attained at an initial concentration of 60 mg L$^{-1}$. As shown in figure 3, the removal rate of phenol reached to 100 % after 80 min discharge treatment, while the COD removals efficiency was 45 % which was much less than the removal rate of phenol. It may be due to phenol molecules being easily oxidized by ozone, resulting in small organic molecular fragments, which are not completely mineralized under the oxidative conditions described. So the degradation efficiency of pollutants through examination of the COD removal is more reasonable.

The initial concentration of phenol had the lowest effect on its degradation. An increase in the initial amount of the pollutant from 60 to 150 mg L$^{-1}$ in solution led to a decrease in the degree of COD conversion only by 6.3 %, while a decrease of 26.3 % occurred when initial concentration changed from 60 to 200 mg L$^{-1}$. It may be there was plenty of ozone for removal of phenol below 150 mg L$^{-1}$. So the amount of ozone was a constant under certain conditions, the COD removals efficiency was also certain.
3.3. Effect of applied voltage

The effects of applied voltage on COD decomposition were revealed in figure 5. It could be observed that the COD decomposition decreased with the applied voltage. At applied voltage of 7 kV, about 69% of COD was removed, while approximately 75%, 22%, and 19% of phenol could be degraded at pulse voltages of 6, 8, and 8.8 kV under the same condition, respectively.

As shown in table 2, higher applied voltage would generate more ozone, which should result in increasing COD removal, but the result is not accord with it. This can be explained as follows: the degradation pathways of phenol in different voltages are diverse. Figure 6 shows the UV/visible spectra of the samples after being treated for 60 min at different applied voltages. These spectra of phenol degradation at the applied voltage of 7 kV were much different from that at the applied voltage
of 8 kV, which indicates the by-products of the applied voltage at 7 kV are different from that at 8 kV. It may be that the by-products produced at higher voltage are more refractory. The main intermediates detected in the phenol oxidation were ring compounds and short chain acids. The ring intermediates mainly included catechol, hydroquinone and benzoquinone [7]. So the ring compounds are likely to the main by-products of higher applied voltage. In all cases, maximum absorbance occurred at around 210 nm, which is attributed to the presence of the byproducts produced from the phenol. In this study, the byproducts were not fully identified, but these spectra indicate that most of the benzene and naphthalene rings existing in the original phenol molecules were destroyed.

**Table 2.** Ozone variations of different applied voltage.

|          | 6 kV  | 7 kV  | 8 kV  | 8.8 kV |
|----------|-------|-------|-------|--------|
| Ozone (mg l⁻¹) | 0.2853 | 0.415 | 0.473 | 0.603  |

4. Conclusions

The aim of the present work was to investigate the factors affecting the COD degradation efficiency of phenol. The optimal conditions for the COD removal are as follows:

1. The optimum pH for phenol degradation was about 6, although the degradation efficiency reached the high value in the solution with pH 9.0, but degradation efficiency at pH =6.0 were slightly less than at pH =9.0, especially the innate pH of phenol is about 6. So the degradation effect of phenol is good at pH =6.0, and the operation of experimental system is easy.

2. The best range of initial concentration is from 80 mg L⁻¹ to 150 mg L⁻¹ in this reactor. The amount of ozone in this reactor is abounding within this limit.

3. The highest value of COD degradation efficiency was 75 % at 6 kV. However, voltage instability may occur at 6 kV. The value of COD degradation efficiency was 69 % at 7 kV, so there was a high COD degradation efficiency at 7 kV.

Acknowledgments

This work is partially supported by the Fundamental Research Funds for the Central Universities [Grant NO. DUT12RC (3)12].

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