Detection of hydroxyl radicals during regeneration of granular activated carbon in dielectric barrier discharge plasma system

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Abstract. To understand the reactions taking place in the dielectric barrier discharge (DBD) plasma system of activated carbon regeneration, the determination of active species is necessary. A method based on High Performance Liquid Chromatography with radical trapping by salicylic acid, has been developed to measure hydroxyl radical (•OH) in the DBD plasma reactor. The effects of applied voltage, treatment time, and gas flow rate and atmosphere were investigated. Experimental results indicated that increasing voltage, treatment time and air flow rate could enhance the formation of •OH. Oxygen atmosphere and a suitable GAC water content were contributed to •OH generation. The results give an insight into plasma chemical processes, and can be helpful to optimize the design and application for the plasma system.

1. Introduction
To understand the reaction mechanisms taking place in the dielectric barrier discharge (DBD) plasma system of activated carbon regeneration, the determination of active species is necessary [1]. It gives a perception into plasma chemical processes, and can be helpful to optimize the design and application for the plasma system.

The hydroxyl radical (•OH) is an important reactive agent in various plasma applications. It has extremely high oxidation potential (2.8 V), which is only lower than that of F2 (3.0 V) [2]. The existence of •OH in the aquatic systems and the atmospheric phase has been universally believed [3]. •OH is also believed to be the key reactive species for the oxidation of environmental contaminants in the plasma system [4].

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To analyze the mechanism of pollutants removal in plasma reactions, a diagnosis technique of the atmospheric pressure non-thermal plasma process is very important to develop in practice [1]. One of the plasma diagnoses is the detection of radicals and active species produced in the atmospheric pressure plasma. Though the importance of •OH in the pollutants’ decomposition by plasma have been affirmed, •OH measurement techniques have long been a difficulty due to its short lifetime. In recent studies, several methods have been developed to detect •OH in non-thermal plasma systems, including electron spin resonance (ESR) [5], laser-induced fluorescence (LIF) [6], colorimetric spectrophotometry [7], a radiocarbon method [8], and quantitative analysis of •OH by oxidating CO to CO₂ [9]. However, these reported methods have lots of limitations for actives species determination.

Because •OH has an extremely short lifetime (<10^{-3} s), it is difficult to determine it directly. In this paper, salicylic acid (SA, o-hydroxybenzoic acid) was chosen as the molecular probe to capture •OH. When •OH exists in the solution, it will rapidly react with SA and produce 2, 3-dihydroxybenzoic acid (2, 3-DHBA) or 2, 5-DHBA, which can be determined by High Performance Liquid Chromatography (HPLC). Jen [10] first applied the HPLC method to determine •OH concentration in an advanced oxidation process, which proves to be a simple and sensitive way as the measurement of •OH in a biological system [11]. Guo and Liao [12, 13] employed the HPLC method to detect •OH in non thermal plasma system.

Our previous bench-scale work reported that using the DBD reactor to regenerate granular activated carbon (GAC) exhausted with organic pollutants, and the experiments yielded desirable results. However, there is little information available in literature about generation of active species in the DBD regeneration reactor, and the pollutants’ degradation mechanisms have not been fully understood. The present work aimed to detect the generation of •OH by HPLC method in DBD regeneration system, and to study the effect of applied voltage, treatment time, gas flow rate, gas type and water content of GAC on •OH production.

2. Experimental

2.1 DBD plasma system
The schematic diagram of the DBD plasma regeneration system was shown in figure 1. It mainly consisted of alternating current high-voltage power supply and the DBD reactor. The frequency of high-voltage power of this experiment was 1000 Hz. The voltage was 0-50 kV adjustable. The DBD reactor (as shown in figure 1) was comprised of two parallel-plate stainless steel electrodes (φ45×2 mm) as the high-voltage and ground electrode respectively, and each electrode was covered by one quartz glass dielectric (150×150×2 mm). The distance between two dielectrics was 6 mm. One Plexiglas chamber (φ40×6 mm), between the two dielectrics, was used as the GAC packed bed. A Plexiglas TM cylinder (φ4 mm) was embedded in GAC to provide air as reaction gas source for the DBD reactor. In each experiment, adsorbed GAC (approximately 2.8 g, moisture content 10 %) was introduced into the reactor and evenly filled up the packed bed, and then the DBD process began when the AC power supply was turned on.

2.2 Materials
The GAC (approximately 2.0 mm diameter and 1.0-5.0 mm length) used in this study was columned
coal-based carbon and was manufactured by Shenyang Chemical Reagent Factory, China. Prior to use, the GAC was immersed in deionized water for 24 h, and then liberally rinsed with deionized water to remove fine particles and impurities, at last dried in an oven at 378 K overnight and then kept in a desiccator. All chemical reagents used in this study were analytical grade reagents supplied by Tianjing Beilian Fine Chemical Product Co. Ltd, China.

Salicylic acid (SA, 99.5 % purity) was purchased from Shanghai Chemical Reagent Company, China. 2, 3-DHBA (Sigma) and 2, 5-DHBA (Sigma) were prepared as standard solution according to desired concentration.

2.3 Experimental procedures and analysis

For •OH determination, the aqueous solution of SA with an initial concentration of 5000 mg L\(^{-1}\) for experiments was prepared from deionized water and SA reagent. Then, 20 g of GAC were added into the sealed flasks with SA solution and placed in the water-bath shaker with an agitation speed in the range of 150 rpm to adsorb SA on GAC. The adsorption capacity \((q, \text{mg g}^{-1})\) was calculated using the following equation:

\[
q = \frac{(C_o - C_t) V}{m}
\]  

Where \(q\) (mg g\(^{-1}\)) is the adsorption capacity of GAC, \(C_o\) (mg L\(^{-1}\)) is the initial concentration of SA in aqueous solution, \(C_t\) (mg L\(^{-1}\)) is SA concentration in aqueous phase at time \(t\), \(V\) (L) is the solution volume and \(m\) (g) is the mass of the adsorbent. After that, the adsorbed SA GAC were dried in an oven under very mild condition (313 K) until a constant certain mass was achieved. After that, a definite mass of prepared GAC (approximately 2.8 g) was introduced into the DBD reactor and was evenly spread over the packed bed. The DBD process began when the AC power supply was turned on, and the regeneration would last for different experimental conditions.

During the DBD process, the adsorbed SA on GAC would be reacted with •OH generated in the discharge space. After each discharge experiment, the SA residues on GAC samples were extracted in a conical flask using a 50 mL ethanol solution. The conical flask was kept shaking at 150 rpm at 298

![Figure 1. Schematics of experimental setup.](image-url)
K for 60 min, and then ultrasonic extracting for 30 min. The extraction procedures were repeated for three times, and the extract was collected finally. The recoveries were about 85 % for SA on GAC samples in this study. The determination of SA concentrations in solution were performed by a High Performance Liquid Chromatography (LC-10A vp Shimadzu) using a Hypersil ODS (25 μm, 4.6×250 mm) reverse phase column. The DHBA yields represented hydroxyl radicals’ concentration.

3. Results and discussion

3.1 Effect of applied voltage on •OH production
Discharge voltage has a significant effect on the generation of plasma (such as active radicals, high-energy electrons and ultraviolet light, etc.) [14]. Therefore, the discharge voltage was regarded as one of the most important parameters for the degradation of pollutants loaded on GAC and regeneration of GAC. The effect of applied voltage on •OH production was determined, and the results were revealed in figure 2. The other operation conditions were as follows: air flow rate 0.8 L min⁻¹ and water content of GAC 10 %. Three levels, 18, 23, 28 kV, were investigated. It was found that •OH production increased with the applied voltage. At pulse voltage of 28 kV, about 47.1 μmol DHBA was generated within 100 min of treatment, while approximately 46.6 and 44.8 μmol DHBA could be measured at voltages of 23 and 18 kV within the same time, respectively. It is generally believed that more energetic electrons are produced at higher voltage, leading to the accelerated formation of active species. Furthermore, •OH radicals and hydrogen peroxide can be generated by DBD due to the humidity on GAC samples [15]. On the other hand, ozone reacts with hydrogen peroxide and finally readily dissociates into •OH radical [16]. These active radicals are strong oxidants, which play a significant role in contaminates’ degradation [17]. Hence, the increase in applied voltage contributes to the increase in active species, which in turn enhances the degradation of pollutants adsorbed on GAC.

![Figure 2](image2.png)
**Figure 2.** Effect of applied voltage on •OH production.

![Figure 3](image3.png)
**Figure 3.** Effect of air flow rate on •OH production.

3.2 Effect of gas flow rate on •OH production
The effect of air flow rate on DHBA yields was studied in this part, and the experimental result was
illustrated in figure 3. The other operation conditions were as follows: applied voltage 28 kV and water content of GAC 10 %. When air flow rate increased from 0.4 to 1.2 L min\(^{-1}\), DHBA yields increased from 43 to 47 μmol after 100 min of discharge time. However, the maximal DHBA yield at 1.2 L min\(^{-1}\) has little differences than 0.8 L min\(^{-1}\).

It could be suggested that with the increasing of air flow rate, the generation of •OH radicals are correspondingly increased. In contrast, the residence time of active species is shortened and their utilization efficiencies on GAC are correspondingly decreased. So, the combined effects of above two aspects resulted in that there is a preferable compromise flow rate 0.8 L min\(^{-1}\) for DBD plasma reactor.

### 3.3 Effect of gas type on •OH production

The varieties and numbers of oxidative species are considerably different during discharge processes under different gas atmospheres [18]. In order to investigate the roles of different gas atmospheres in •OH production, experiments were conducted separately under oxygen, nitrogen, and air atmospheres. The experimental results for •OH production under different gas atmospheres were shown in figure 4. The other operation conditions were as follows: applied voltage 28 kV, gas flow rate 0.8 L min\(^{-1}\) and water content of GAC 10 %. The DHBA yields obtained under oxygen and air atmospheres were much higher than those under nitrogen atmosphere. DHBA yields of 57.0 and 47.1 μmol were achieved in oxygen and air atmospheres after 100 min of discharge treatment, respectively; while only 21.3 μmol DHBA was obtained in nitrogen atmosphere at the same treatment time.

**Figure 4.** Effect of gas type on •OH production.

**Figure 5.** Effect of GAC water content on •OH production.

Under oxygen atmosphere, the input energy was mainly consumed to produce the O-reagents, whose concentrations were larger than those under air atmosphere, resulting in the greater generation of •OH radicals under oxygen atmosphere than those under air atmosphere. In general, N\(_2\) is inactive and cannot participate in many chemical reactions. However, when discharge occurred in gas atmosphere containing N\(_2\), it can be dissociated to the atomic N, N\(_2^+\) and N\(^+\) [19]. The bond dissociation energy of N\(_2\) (9.82 eV) is higher than that of O\(_2\) (5.12 eV), and thus it is much easier for O\(_2\) to dissociate than N\(_2\) when discharge occurs under air atmosphere. Therefore, more •O and •OH radicals can be generated under air atmosphere than N\(_2\). Furthermore, the oxidative potentials of •O
and •OH radicals are much stronger than those of atomic N, N$_2^+$ and N$^+$, so the DHBA yield was higher under air atmosphere that under N$_2$ atmosphere.

3.4 Effect of GAC water content on •OH production

Under different water content of GAC, the concentration of •OH radical was detected, and the results are shown in figure 5. The other operation conditions were as follows: applied voltage 28 kV and air flow rate 0.8 L min$^{-1}$. The humidity of GAC increased from 1 % to 35 %. It shows that •OH radical increased with the increase of GAC water content within 100 min discharge treatment.

Water plays a very important role in the reaction since it decomposes into •OH and H free radicals in the plasma system. The initiating reactions involving the H$_2$O excitation are given in reactions (2)–(5) [20]. When the humidity is high, more H$_2$O molecules collide with high-energy electrons, and •OH radicals are formed.

$$\text{H}_2\text{O} \rightarrow \text{H}, \text{e}_{\text{aq}}^{-}, \text{OH}, \text{H}_2, \text{H}_2\text{O}_2, \text{H}_3\text{O}^+, \text{OH}^-$$ (2)

$$\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \quad K = 1.2 \times 10^{10}$$ (3)

$$\text{e}_{\text{aq}}^{-}\text{O}_2 \rightarrow \text{O}^- \quad K = 1.9 \times 10^{10}$$ (4)

$$\text{HO}_2 + \text{O}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad K = 9.7 \times 10^{7}$$ (5)

However, water also has an adverse effect on pollutants’ removal due to its electronegative characteristics. Increasing the humidity limits the electron density in the system and quenches some activated chemical species. Therefore, the optimal water content of GAC for •OH generation is 20 % rather than 35 % in this experiment.

4. Conclusions

A HPLC method with radical trapping salicylic acid, was used to detect indirectly the concentration of •OH radical on granular activated carbon in the DBD regeneration system. Under the studied conditions, increasing applied voltage and treatment time resulted in higher •OH generation, due to the enhancement of energy input. The quantity of •OH increased with an increase of gas flow rate. The role of gas atmosphere for •OH formation was identified. The highest •OH yield was achieved with a GAC water content of 20 %. At a higher humidity, the concentration of •OH declined because of a decrease in electron mean energy by water molecules. This work supplies a simple and rapid determination method for the generation of •OH in the DBD regeneration system. As •OH is an active and environmental friendly oxidant, it will have great significance in the fields of green chemistry, environmental protection, and other related fields.

Acknowledgments

The authors thank the Ministry of Science and Technology, P.R. China (Project No. 2008AA06Z308) and the National Natural Science Foundation, P.R. China (Project Nos. 51177007 and 40901150) for their financial supports to this research.

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