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Hydrogen peroxide generation during regeneration of granular activated carbon by bipolar pulse dielectric barrier discharge plasma

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ABSTRACT

Hydrogen peroxide (H_2O_2) is one of the pivotal reactive species produced in dielectric barrier discharge (DBD) plasma. We studied the characteristics of H_2O_2 generation during DBD regenerating granular activated carbon (GAC) process driven by a bipolar pulse power. A range of measurements were conducted to explore the effects of different conditions like pulse voltage, air support rate, and GAC water content on H_2O_2 formation on the GAC. The rate constant and energy efficiency of H_2O_2 generation were also calculated to investigate kinetics. The results indicated that the greater discharge intensity and air supply rate were beneficial to H_2O_2 production, and there was a moderate value of GAC water content (20%) for its formation. The highest H_2O_2 amount was 297.8 μmol/kg GAC under the parameters of pulse voltage of 28 kV, air flow rate of 1.2 L/min and GAC water content of 20%. Meanwhile, the efficiencies of phenol removal on GAC and GAC regeneration were promoted with the treatment time, which reached 93.3% and 88.5% after 100 min, respectively. The main degradation byproducts such as catechol, hydroquinone, and benzoquinone formed on GAC were increased firstly and then decreased with the treated duration.

1. Introduction

Activated carbon (AC) adsorption is a simple and effective way for the treatment of industrial organic wastewater, that becomes hazardous material after saturated with pollutants [1,2]. Regeneration for exhausted AC has been regarded as a necessary technical from the point of economical cost and environmentally sustainable development. The most common method is thermal regeneration which still presents several drawbacks, such as high mass loss, high cost and energy consumption [3,4]. For improving the property of AC regeneration, many technologies have been developed, including microwave, electrochemical, solvent extraction regeneration [5–8]. These techniques put forward to some basic and important demands for the regeneration process: first, it should be capable of removing contaminants from AC, without damaging pore structure and adsorption capability; second, it should be able to mineralize the adsorbed organic compounds to small organic and inorganic molecules, without secondary pollution for environment [9,10].

To attain above objectives, advanced oxidation technologies (AOTs) have attracted great attention. Among these ways, non-thermal plasma (NTP) was proved to be a remarkably effective AOT [11–13]. During NTP process, a very large amount of active species are produced by the NTP-induced reactions and responsible for contaminant decomposition in gas and liquid phases, for instance, hydrogen peroxide (H_2O_2), hydroxyl radicals (·OH), ozone (O_3), and other radicals and molecular species. Hence, it is generally considered that the generated active species in NTP is the key for the pollutants removal [14,15].

In our previous work, we applied a DBD reactor to regenerate GAC, and investigate different parameters on the effects of GAC regeneration, such as applied voltage, gas flow rate and water content of GAC [16,17]. Besides, other scholars have also researched AC regeneration by NTP in similar ways [18,19]. Published documents related to AC regeneration by discharge plasma mainly concentrated on the effects of AC regeneration and contaminants decomposition, and the various characterization of the AC before and after NTP treatment. In these studies, the operational parameters are considered as the key factors influencing the regeneration process.

However, seldom references discussed the major mechanism of NTP regeneration, and just speculated that the produced chemically species penetrated into AC pores and oxidized pollutants, emptying adsorption site and then regenerating AC. And even few research concerned with the characteristics of active species formation and relationship between generated reactive substances and pollutants. Especially, the reactions of plasma materials and AC are a complex gas–solid phase process, and it is hard to detect ·OH radicals due to its short lived time in the NTP regeneration.

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Former investigation suggested that a double of ·OH could be combined to generate a H_2O_2 molecule [20], thus ·OH amount could be estimated indirectly by identifying the content of H_2O_2 in the discharge system [21]. Moreover, H_2O_2 can chemically react with pollutants through direct and indirect effects. Firstly, H_2O_2 itself is a strong oxidizing agent, which can degrade most of organic compounds directly. Secondly, the indirect process could promote ·OH formation, as H_2O_2 could be reacted with O_3 and decomposed by high energy electron bombardment and UV irradiation [22,23]. We can therefore conclude that the H_2O_2 concentration could serve as a token parameter and reflect the oxidation reaction in DBD approach. So it is necessary to study the detailed H_2O_2 generation features on the GAC during DBD regeneration, which is beneficial to the improvement of AC regeneration efficiency and energy efficiency of the DBD system.

The main aim of this work was to research the characteristics of H_2O_2 generation in the DBD reactor during the process of GAC regeneration. Pulse voltage, air support rate, and GAC water content on H_2O_2 formation on GAC were determined to search the effects of various operational conditions. Generation kinetics were investigated by calculating the rate constant and energy efficiency of H_2O_2 generation. The phenol degradation also its main intermediates and GAC regeneration efficiency were studied to evaluate the roles of H_2O_2 during the process of the reaction. This research could provide a meaningful reference to explore organic compounds decomposition and GAC regeneration by NTP plasma.

2. Experimental

2.1. Materials

The GAC used in this study was a kind of column (2.0 mm in diameter and 1.0–5.0 mm in length) purchased from Shenyang Huagong Shiji Factory, China. It was thoroughly soaked with deionized water, and desiccated in an oven at 105 °C for 12 h, and then stored in a dry vessel prior to use. Phenol, titanium potassium oxalate, and the other reagents were analysis reagent and bought from the Tianjin Kwangfu Fine Chemistry Industry Research Institute and used as received.

2.2. DBD reactor

The sketches of the DBD reactor and bipolar pulse power for GAC regeneration were illustrated in Fig. 1. The reactor was form of dual dielectrics made by quartz glass. Two stainless steel plates were attached to the outside of the quartz glass as high voltage discharge electrode and grounding electrode, respectively. A Plexiglass cylinder was used as the GAC packed bed and put in the medium of the two dielectrics. Dried air was obtained by passing a home-made silica gel column after the air compressor, and pumped into the reactor as the discharge carrier gas. The detailed sizes of the reactor and operation parameters were same as our previous research [24]. For each experiment, approximately 4.6 g GAC were spread in the packed bed before DBD treatment.

The bipolar pulse power was utilized to generate a positive–negative pulsed high-voltage discharge, which consisted of two couples of capacitors to charge, and the discharge process was conducted by a pair of vertical rotary spark gap switches (RSG). The pulse power repetitive rate was adjustable by the motor rotational speed. The pulsed capacitance (C_p) and the pulsed repetition were 3 nF and 50 Hz, respectively. The pulsed raise time was minor than 100 ns, and the pulsed width was 100–300 ns. The peak voltage of the pulse power was adjustable in 0–80 kV. A voltage probe (Tektronix P6015A) and a current probe (Tektronix P6021) were equipped with an oscilloscope (Tektronix TDS2014) to record the discharge waveforms. The discharge power of the reactor was counted by the integration of voltage and current under time.

2.3. Methods and analysis

The DBD treatment started while the supply power was switched on, and a series of discharge treatments were conducted under different operating conditions. The methods of GAC adsorption and regeneration, and phenol extraction and determination were identical with previous publications [17,24]. The H_2O_2 generated on the GAC was determined by the titanium potassium oxalate method [25]. At first, 136.0 mL concentrated sulfuric acid was slowly added into 150 mL deionized water, and then 17.7 g titanium potassium oxalate was added, and the final volume was adjusted to 500 mL to prepare the solution of titanium potassium oxalate. After different discharge treatment, the GAC samples were extracted with 30 mL deionized water in a conical flask and placed on a water bath oscillator for 60 min (150 rpm, 25 °C). After that, 2.0 mL titanium potassium oxalate solution and 2.0 mL extracted liquid were blended together and dissolved with deionized water to 10.0 mL. Finally, the absorbancy of extracted solution was determined by a UV–vis spectrophotometer (UV-2102C, Unico, Shanghai Instrument Co., Ltd., China) under the wavelength of 400 nm. The TOC of the phenol extracted solution was determined by a TOC Analyzer (Shimadzu-V), and the main phenol degradation intimidate products, such as catechol, hydroquinone, and benzoquinone were measured by a High Performance Liquid Chromatography (HPLC, Shimadzu, LC-10Avp) with an external standard method.

3. Results and discussion

3.1. Influence of pulse voltage

Pulse voltage is an important control parameter in discharge plasma, and it affects directly the discharge energy input and chemically active agents generation during the DBD regeneration. Fig. 2 indicated the change trends of H_2O_2 formation at different pulse voltages. Experiments were performed at the following pulse voltage: 18, 23 and 28 kV. Other operating parameters employed in this treatment were conducted as follows: air flow rate 0.8 L/min and GAC moisture content 10%. As shown in Fig. 2, the production of H_2O_2 improved with increasing pulse voltage due to the more energy injection into the DBD reactor. When the pulse voltage was 28 kV, the amount of H_2O_2 was 260.9 μmol/kg GAC after 100 min. With the reduction of pulse voltage, the H_2O_2 yields only achieved 245.6 and 221.7 μmol/kg GAC at 23 kV and 18 kV respectively.

In the present DBD system, the H_2O_2 on the surface of GAC would be generated through a series of reactions. The principle for H_2O_2 production could be mainly due to the excitation and dissociation of the H_2O molecules in NTP, and this progress has much resemblance to that by procedures of photochemical reaction, electron emission, and radiolysis [26–28]:

$$H_2O \xrightarrow{e} \cdot OH + \cdot H$$

$$2H_2O \xrightarrow{e} H_2O_2 + 2H$$

$$H_2O \xrightarrow{e} H_2O^+ + e$$

$$H_2O^+ + H_2O \rightarrow \cdot OH + H_3O^+$$

$$OH + \cdot OH \rightarrow H_2O_2$$