Kinetic analysis of acid orange 7 degradation by pulsed discharge plasma combined with activated carbon and the synergistic mechanism exploration

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HIGHLIGHTS

- Synergistic effect of PDP and AC for the AO7 degradation is confirmed.
- The synergistic mechanism for A07 degradation by the PDP/AC process is proposed.
- •OH and •O were the two important radicals for the AO7 degradation in the synergistic system by the spectra analysis.

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ABSTRACT

The synergistic technique of pulsed discharge plasma (PDP) and activated carbon (AC) was built to investigate the kinetics of acid orange 7 (AO7) degradation under different conditions of AC addition, electrode gap, initial pH value of solution, gas variety and gas flow rate. Emission spectra of •OH and •O, UV−vis absorption spectra of the AO7 solution and TOC removal were measured to illustrate the synergistic mechanism of the PDP and the AC. The obtained results indicated that the kinetic constant of AO7 degradation increased from 0.00947 min^{-1} to 0.01419 min^{-1} when 4 g AC was added into the PDP system; AO7 degradation was higher in the case of alkaline solution when oxygen was used as the flow gas in the PDP/AC system, 2 L/min oxygen flow was more favorable for the degradation. Results of the relative emission intensities of •OH and •O indicated the catalytic effect of the AC on the active species formation as well as the important role of the two radicals for the AO7 degradation. There was no new peaks appeared by the UV−vis analysis of the AO7 solution after 60 min treatment. The highest TOC removal in the PDP/AC system was 30.3%, which was achieved under the condition of 4 L/min air flow rate and 3 initial pH value.

1. Introduction

Acid orange 7 (AO7) is one kind of azo dyes, which is widely used in textile industries. However, AO7 is difficult to be degraded by conventional methods due to its non-negligible toxicity, low biodegradability and dark colors (Wang et al., 2016b). With the development of wastewater treatment technology, many advanced oxidation technologies (AOTs), such as sonochemistry (Velegraki et al., 2006), UV photolysis (Bessekhouad et al., 2006),

photocatalysis (Stylidi et al., 2004), ozone oxidation (Li et al., 2006b), electron-beam irradiation (Zhang et al., 2005), electrical discharge plasma technology (Du et al., 2008; Li et al., 2007a,b; Sugiarto et al., 2003; Wang et al., 2016a), have been employed successfully in oxidizing AO7 in water.

As one of AOTs, pulsed discharge plasma (PDP) is a kind of complex advanced oxidation technology, which combines the effects of optical, electrical, acoustic and chemical oxidation processes. Degradation of organic compounds in the PDP system are mainly due to the oxidative chemical specials, including active molecules (H$_2$O$_2$, H$_2$, O$_3$, etc.) and oxygen free radicals (•O, •OH, etc.), which generated during the discharge process in water. However, there are some problems restricting the application of PDP, such as lower energy utilization and unclear degradation of

organic compounds in the PDP system. Therefore, research on the application of the combined system of PDP with other technologies for pollutants degradation has become a hot topic for the development of the PDP technology. Activated carbon (AC) has been used as an adsorbent widely in wastewater treatment due to its large specific surface area and pore structure. It has been proved that AC can adsorb many kinds of benzene compounds, phenolic compounds and petroleum in solution (Świątkowski, 1999; Mohan and Pittman, 2006). Studies have reported that the combined process of PDP and AC could enhance the overall removal of organic compounds in solution and the AC acted as the catalyst primarily in the synergistic process (Qu et al., 2013; Grymonpré et al., 1999; Zhang et al., 2011a,b). In the catalytic process, AC can accelerate ozone decomposition and then lead to the more formation of •OH in the system (Jans and Hoigné, 1998; Beltrán et al., 2002). The researches by Zhang et al. and Jiang et al. have also proved that the combination of PDP and activated carbon fiber has a synergistic effect on the degradation of dyes in wastewater (Zhang et al., 2010; Jiang et al., 2013).

Although many studies have proved the positive effect of AC addition on the removal of organic compounds in the PDP system, the effect of AC addition on the production of activated species, especially for the formation of •OH and •O has not been investigated thoroughly. Furthermore, change of the two active radicals before and after the degradation process has not been sufficiently clarified. Therefore, it is necessary to detect the relative amount of the two radicals produced in the synergistic system of PDP/AC and analyze the important role of the two radicals for the organic compounds degradation.

In the present work, a multi-needle-to-plate electrode geometry PDP system with hybrid gas-liquid phase was established to investigate the kinetics of AO7 degradation in the synergistic system. The effect of AC addition, electrode gap, initial pH value of the AO7 solution, gas varieties and gas flow rate on the AO7 degradation was determined according to the pseudo first-order reaction kinetic mode. The emission spectra of •OH and •O was detected with a spectrometer to investigate their role on the degradation process; the UV—vis absorption spectra of the treated AO7 solution as well as the TOC analysis was also carried out to confirm the synergistic degradation and the mineralization level of the AO7 solution.

2. Experimental

2.1. Materials

The AO7 solution was prepared by AO7 and deionized water. The initial concentration of AO7 used in this study was 50 mg/L and initial pH value of the AO7 solution was about 6.9. AC used in present study was obtained from Shuangyuan AC Factory in Liyang, Jiangsu. The purchased AC was firstly sieved into uniform size of 2—3 mm firstly. Secondly, powder was removed from the sieved AC by rinsing with deionized water. Thirdly, the pure AC was dried at 105 °C for 24 h thirdly. At last, the preprocessed AC was stored in a desiccator before use. All chemicals used in this research were of an analytical grade unless special instructions.

2.2. PDP system and emission spectrum detection system

The experimental equipment was composed of a pulse power supply, an electric monitoring system and a circulatory reaction system. The schematic diagram of whole experimental system adopted in this research is shown in Fig. 1. The power supply was made up of a DC power supply, a storage capacitance, an adjustable trim capacitance and a rotating spark-gap switch. The frequency of the power supply was 0—150 Hz adjustable and the voltage was

0—60 kV adjustable. The electric monitoring system consisted of a voltage probe (Tektronix P6015A), a current probe (Tektronix P6021) and an oscilloscope (Tektronix TDS3032B). The circulatory reaction system was a connection of a reactor, a peristaltic pump (Longer pump BT600-2J) and a magnetic stirrer (Ronghua 85-2). The reactor contained a gas bubbling chamber and a discharge chamber. The inner diameter of the reactor was 80 mm. The total height of the reactor was 140 mm. The high voltage anodes located in the upper of the discharge chamber were seven syringe needles (type 12#, length 100 mm), one needle was in the center and the other six needles distributed uniformly around a circle of 30 mm radius. The ground cathode located on the bottom of the discharge chamber was a stainless steel plate (80 mm diameter, 3 mm thickness). AC was put on the stainless steel plate. Air flew into the reactor through the needles by an air-blowing pump (Hailea ACO-318) and the gas flow rate was adjusted by a gas flow meter (Kere LZB-6WB). The peristaltic pump was used to make the solution flow into the reactor recurrently. Flow rate of the peristaltic pump was controlled at 100 mL/min. When 300 mL AO7 solution flew into reaction system, one cycle would be completed at 3 min.

The emission spectrum detection system was similar with the reaction system applied for the AO7 degradation. Besides the pulse power supply and the electric monitoring instruments, it also consisted of a spectrometer (Avantes Avaspec-2048L), a laptop (lenovo G460) and a reactor without circulation. The reactor used for emission spectrum analysis was same as the reactor applied for the AO7 degradation. The only difference was the quartz plate embedded on the wall of the reactor, which was fixed for exploring the emission light in the PDP system. The optical probe was set outside the reactor and the location was directly to the tip of the needles.

2.3. Analytic methods

Degradation of AO7 was calculated according to the absorbance of AO7 solution measured by an ultraviolet—visible spectrophotometer (Ruili UV-9600). The absorbance of AO7 solution was measured every 15 min during the treatment process and the total treatment time was controlled at 60 min. The pH values of the solution were adjusted with 0.1 mol/L NaOH and 0.1 mol/L HCl. The pH value was detected by a pH meter (Thermo Orion 828). The emission spectra of •OH and •O was tested with the spectrograph mentioned in 2.2. Fig. 2 shows the typical emission spectrum detected from the PDP/AC system with distilled water in the reactor. From Fig. 2, it can be seen that •OH could be produced during the pulsed discharge process and one of the characteristic peaks of the •OH appeared at 309 nm (Wang et al., 2007). The characteristic spectrum were formed due to the transitions of $A^2\sum{}^+ (v' = 0) \rightarrow X^2II (v'' = 0)$. The main transitions for generating the characteristic spectrum of the •O at 777 nm were based on $3p^5P^o \rightarrow 3s^5S$ (Wang et al., 2011). Therefore, the relative emission intensities at the wavelengths of 309 nm and 777 nm in the PDP system and PDP/AC system were detected for illustrating the synergistic effect of the PDP and the AC.

The absorption spectra of the AO7 solution was measured by a spectrophotometer (Shimadzu UV-9600). TOC values of the AO7 solution were measured by a TOC analyzer (Shimadzu TOC-L$_{CPH}$). In the paper, all experiments were carried out by three time measurements and the final values shown in the paper were the average values.

Kinetic analysis of the AO7 degradation was fitted according to the following pseudo first-order equation (Hsieh et al., 2014; Yan et al., 2008):