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Enhanced generation of oxidative species and phenol degradation in a discharge plasma system coupled with TiO_2 photocatalysis

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Abstract

In this paper, the streamer formed during a pulsed discharge process was used as a lamp house to induce the photocatalysis of TiO_2 in a pulsed discharge plasma system. A synergistic effect of plasma and TiO_2 photocatalysis was revealed through a comparison of the generated amounts of oxidative species ($^{\bullet}OH$, $^{\bullet}O$, H_2O_2) and phenol decomposition in the plasma system with and without supported TiO_2. A spectral analysis of oxidative radicals such as $^{\bullet}OH$ and $^{\bullet}O$ identified a higher emission intensity of the radicals in the plasma/TiO_2 system than in the plasma alone system. Both the H_2O_2 concentration and the phenol degradation in the plasma/TiO_2 system were higher than those in the plasma alone system. Furthermore, higher energy efficiency of phenol decomposition and total organic carbon (TOC) removal was achieved in the plasma system coupled with TiO_2 photocatalysis. Moreover, the streamer was proved to be in existence by measuring the power in the systems of plasma alone and plasma-photocatalysis system. This coupling process can be further studied to identify and exploit the existence of streamers in plasma channels.
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Keywords: Discharge plasma; Pulse streamer; TiO_2 photocatalysis; Synergistic effect; Oxidative species; Phenol degradation

1. Introduction

As one of the potential advanced oxidation processes (AOPs), non-thermal plasma production during discharge in the liquid or hybrid liquid–gas phase has long been exploited for water and wastewater purification, since the investigation of pre-breakdown phenomena of discharge in aqueous solutions was first reported by Clements et al. in 1987 [1]. Owing to its virtue of producing in situ oxidative species for decomposing toxic compounds, its operational simplicity (realized under the conditions of an ambient temperature and pressure), its variable reactor configuration, and its good-performance degradation of low-concentration organic compounds, this discharge technique has been of great interest in the field of environmental protection for the past two decades [2–12].

Because of the potential industry applications of pulsed corona discharges, many studies have been carried out using discharge plasma for biorefractory contaminants removal. In these researches, the chemical effects of active species ($^{\bullet}OH$, $^{\bullet}H$, $^{\bullet}O$, O_2^{-}, $^{\bullet}HO_2$, H_2O_2, O_3) produced in plasma channels have always accounted for most of the decomposition of organic compounds in wastewater [13–19]. By contrast, the physical effects formed during the pulsed discharge process, such as strong electric fields, streamer (including UV light), electro-hydraulic cavitations and supercritical water oxidation, have received little attention.

Heterogeneous photocatalysis of TiO_2 is also a promising AOP for wastewater treatment, attracting researchers since Honda studied the decomposition of water molecules on TiO_2 electrodes in 1972 [20]. When the surface of TiO_2 (particles or films) is irradiated with light of wavelengths shorter than ~387 nm, the generated holes (h^+) and electrons (e^-) can react with ambient water molecules to produce reactive species (O_2^{-}, $^{\bullet}OH$). The $^{\bullet}OH$ radicals and h^+ themselves serve as the pivotal species aiding in assuring the degradation of organic compounds in the photocatalytic system.

The spectral analysis of Sun et al. [15] proved that there was a discharge radiant in far ultraviolet to near infrared spectral

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ranges in the pulsed corona discharge system, as well as intensified light during the discharge process. Therefore, the streamer spectra in the ultraviolet region may excitated the photocatalytic activity of TiO_2. Lukeš et al. [21] and Hao et al. [22] similarly proved the enhancement of contaminants degradation in a pulsed discharge plasma process in combination with TiO_2 powder.

The present work investigates the synergistic effect of plasma and TiO_2 photocatalysis on oxidative species generation and organic compound degradation, by establishing a hybrid liquid–gas phase pulsed discharge system coupling with TiO_2 photocatalysis, streamer is used as a new lamp house to induce the photocatalysis of supported TiO_2 in the plasma system. Coupling the two AOPs should permit higher energy efficiency and further practical applications.

2. Experimental

2.1. The plasma-photocatalysis reaction system

Fig. 1 displays a schematic diagram of the plasma-photocatalysis (plasma/TiO_2) reaction system. The system consisted of a pulsed high-voltage power supply and a reactor, with parameters of the pulsed discharge system the same as those of our previous work [23]. A cooling system maintained a constant temperature throughout the experiment. The pulse peak voltage, the pulse frequency, and the capacitance were kept at 21 kV, 50 Hz, and 4 nF (the corresponding energy was 538 mJ per single pulse, which is the integral value of the wavelength of the product of the voltage and current waveforms with single pulse) in all reaction processes. A digital oscilloscope (Tektronix TDS2024), a high-voltage probe (Tektronix P6015A) and a current probe (Tektronix P6021) were used to monitor the discharge parameters. A Plexigas^{TM} cylinder (75 mm diameter and 100 mm length) served as the reactor vessel. The electrode system inside was with seven-needle-to-plate geometry, and the electrode was made of stainless steel with a distance (*d*) 15 mm.

2.2. Spectral analysis system

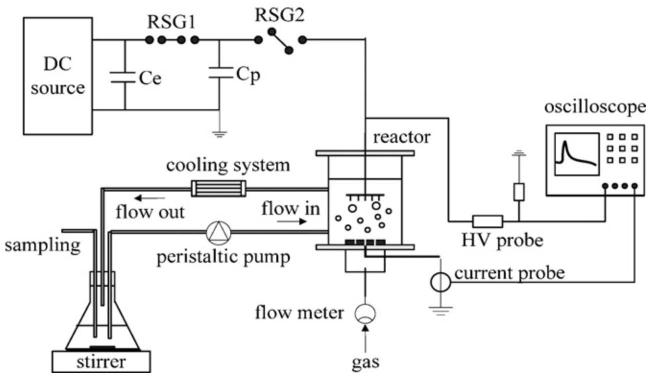

Fig. 1. Schematic diagram of the experimental system.

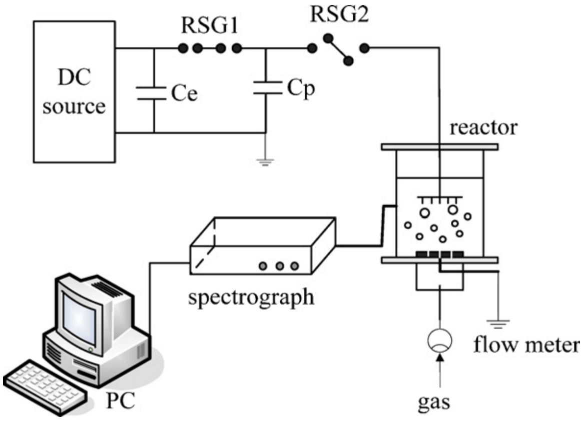

Fig. 2. Schematic diagram of the spectral analysis apparatus.

A spectrum testing system within the interim reaction system (Fig. 2) detected the emission intensities of $^{\bullet}OH$ and $^{\bullet}O$. The spectral plot was recorded by a spectrograph (Inspectrum 300, Acton Research Corporation) combined with a computer. The head of an optical fiber 1 mm in front of a quartz window (5 mm in diameter) and parallel to the tips of needle electrodes collected the light signal. The light signal was detected from the gas phase plasma in water. The operational parameters of the spectrum system used to record the spectral plot were adjusted to a 1200 mm/g grating and a 500 μm slit width.

2.3. Materials

All reagents used in this study were of an analytical grade and were used as received; analytical eluents were HPLC grade. All experiments were conducted in deionized water at room temperature. A sol–gel process deposited photocatalytic TiO_2 films on soda-lime glass beads of 5–6 mm particle size [24]. The formed precursor solution reached $Ti(OC_4H_9)_4:C_2H_5OH:H_2O:NH(C_2H_4OH)_2 = 1:26.5:1:1$ in molar ratio. All experiments used a supported TiO_2 film photocatalyst prepared through eight dipping–lifting processes. X-ray diffraction (XRD) analysis identified the prepared TiO_2 particles about 6 nm in diameter, and scanning electron microscopy (SEM) indicated a uniform TiO_2 film on the glass beads.

2.4. Experimental method

Phenol at an initial concentration of 100 mg/L (an initial pH of about 7) was chosen as the target contaminant. A peristaltic pump circulated 250 mL of distilled water or phenol through the reactor at a solution flow rate of 100 mL/min. Adding a 1-mol/L KCl solution adjusted the initial electrical conductivity of the testing solution to100 μS/cm. 100 glass beads supported with TiO_2 were packed in the reactor as photocatalyst in the plasm/TiO_2 system. Fig. 3 shows the packed state of the photocatalysts. The formed discharge plasmas do not change in the reaction systems with or without the photocatalysts. Throughout the experiments, O_2 with a 5 L/min flow rate was continuously bubbled into the reactor through the orifices of the stainless-steel ground electrode. Samples were taken for analysis at given intervals. All experiments were carried out under a consistent input power.