Available online at www.sciencedirect.com
ScienceDirect
Journal of Electrostatics 66 (2008) 16–24
Journal of ELECTROSTATICS
www.elsevier.com/locate/elstat

Using a novel pulsed high-voltage gas–liquid hybrid discharge continuous reactor for removal of organic pollutant in oxygen atmosphere

Lecheng Lei*, Yi Zhang, Xingwang Zhang, Yongjun Shen

Institute of Environmental Pollution Control Technologies, Xixi Campus, Zhejiang University, Hangzhou 310028, PR China

Received 8 August 2006; accepted 21 June 2007
Available online 19 July 2007

Abstract

A novel continuous reactor with gas–liquid hybrid discharge system was designed in order to remove abundant of contaminated water. The effects of pulsed high voltage, repetition frequency, liquid flow rate, initial concentration of 4-CP and oxygen flow rate on 4-CP removal and energy yield were investigated. At the initial concentration of 60 mg/l, the optimum conditions were pulsed high voltage of 16 kV, pulse repetition frequency of 100 Hz, liquid flow rate of 40 ml/min and oxygen flow rate of 0.4 m^3/h. The removal efficiency of 4-CP was 88.3% and energy yield was 5.39×10^{-9} mol/J. It was found that this continuous reactor is beneficial to degrading 4-CP efficiently with a high-energy yield. Ozone and hydrogen peroxide were largely formed and utilized efficiently for 4-CP removal. A model was established to predict the degradation of 4-CP and formations of intermediates (hydroquinone and 4-chlorocatechol) within each unit of the reactor.

Keywords: Continuous reactor; Gas–liquid hybrid discharge; 4-CP removal; Energy yield; Model prediction

1. Introduction

In the past few decades, several advanced oxidation technologies (AOTs), such as TiO_2 photocatalysis [1–2], electron-beam irradiation [3], sonochemistry [4], electrochemical oxidation [5] and UV/Fenton oxidation [6], have been utilized for degrading organic pollutants in wastewater. The AOTs are essentially based on highly reactive chemical species, especially hydroxyl radical ($^{\bullet}OH$) to react with pollutants [7].

Pulsed high-voltage discharge technology, as one of newly developed AOTs, has been used for the degradation of pollutants in aqueous solutions [8]. With this method, energy is injected into the aqueous solution through the plasma channel formed by pulsed high-voltage discharge between electrodes. In the discharge process, physical processes (the strong electric field, ultraviolet light and shock waves [9–11]) and chemical processes (the formation of various reactive chemical radicals such as $^{\bullet}OH$, $^{\bullet}H$, $^{\bullet}O$, $^{\bullet}HO_2$ and molecular species such as H_2O_2, O_3 [12–16]) occurred simultaneously to directly or indirectly degrade pollutants. A number of parameters, such as the flow rate of the gases bubbling, the electrode material and shape, and power supply voltage, played important roles in the degradation of pollutants and variation of the solution pH and conductivity [17–19].

Initial works have only been done in batch reactors for degradation of pollutants, with a pulsed high-voltage discharge produced by point–plane electrode system [8,10,11]. In our previous studies, a batch reactor with gas–liquid hybrid discharge was explored [20,21], which utilized ground electrode above water level and high-voltage electrodes submerging in water with gas bubbling through anode electrodes. The main advantage of this reactor is the combination of gas phase non-thermal plasma with liquid phase spark discharge to enhance the overall efficiency for removal of pollutants in water. However, for large-scale applications, such kind of batch

*Corresponding author. Tel.: +86 571 88273090; fax: +86 571 88273693.
E-mail address: lclei@zju.edu.cn (L. Lei).

0304-3886/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.elstat.2007.06.003

reactor would be inadequate due to the incontinuous treating process and the long preparing time. Compared to the batch reactor, the continuous reactor is more suitable for treating large volume pollutants. The continuous reactor with wire–plate electrodes system has been extensively used for treatment a wide range of hazardous air pollutants by gas pulsed corona discharge [22,23]. However, the application of the continuous reactor in wastewater treatment by pulsed high-voltage system was rarely studied [24], especially for the experimental investigations on optimum of parameters, formation of active species, variety of intermediates, and utilization of energy yield.

In the present study, a continuous reactor containing ten single point–plane electrode units with gas–liquid hybrid discharge was designed. The effects of pulsed high voltage, repetition frequency, initial concentration of 4-CP and gas flow rate of oxygen on 4-CP removal and energy yield were investigated. In addition, the degradation mechanism focusing on formations of active species, such as ozone and hydrogen peroxide were also studied. An improved model was estimated by classical basic chemical engineering principles to predict 4-CP degradation and intermediates formations.

2. Setup

The experimental apparatus is shown in Fig. 1. The electrical source was similar with that used in our previous work [25,26]. Electrical energy is formed from a large pulse-forming capacitance (4 nF). Energy is released as a pulsed electrical discharge using a double rotating spark gap. The pulsed high voltage varies from 14 to 16 kV, and the repetition frequency changes from 25 to 100 Hz. The values of pulsed output voltage and current were measured using a digital oscilloscope (Lecroy LT264) with a high-voltage probe (INC P150-GL/5 k) and a current transducer (Pearson Electronic M411). Typical voltage and current waveforms from the experimental process is shown in Fig. 2.

The continuous reactor (270 mm × 45 mm × 100 mm) was made of Plexiglas and contained a needles–plane geometry electrode system. The reactor was divided into 10 units uniformly by nine vertical baffles (5 mm × 45 mm × 20 mm). The baffle was alternatively fixed on the bottom of reactor or 5 mm higher than the bottom. The treated solution was pumped from a reservoir. And the liquid flow was alternatively upwards or downwards between compartment partitions, so the wastewater was effectively mixed at the base of each unit. The liquid flow rate was 10, 13.3, 20, 40 and 80 ml/min and the corresponding hydraulic retention time (HRT) was 20.0, 15.0, 10.0, 5.0 and 2.5 min, respectively. Pulsed high-voltage electrode was a stainless-steel injection needle (No. 7 with ∅ 0.7 mm) fixed uniformly in the center of each unit in the liquid phase. Silicone insulation encased the needle tips protruding from the reactor bottom. The needle tips were only 2.0 mm of length exposed beyond the silicone insulator. The ground electrode was a stainless-steel plate (250 mm × 25 mm × 3 mm) above the water level. The total distance between high-voltage electrodes and ground electrode was 20 mm, and the distance between ground electrode and water level was about 10 mm. In this study, the needle electrodes were shortened about 1.0 mm at average after 10 times experiments caused by discharge. And we termly adjusted the needle electrodes to eliminate the effect of erosion. Oxygen was continuously injected into the reactor through the tip of needle electrodes to maintain the discharge in pure oxygen atmosphere. The gas flow rate was adjusted to 0.2, 0.3, 0.4, 0.5 and 0.6 m^3/h, respectively. 4-CP was dissolved in distilled water at initial concentration of 30, 60, 90 and 120 mg/l, initial conductivity of 1.45 μS/cm and initial pH of 5.4. In addition, the solution was enclosed within a cooling water jacket to maintain the reactor temperature at 25 °C.

For the continuous reactor, when the applied voltage was input, the experiment was startup and the effluent sample was performed. It took about 5.0, 10.0, 20.0, 30.0 and 40.0 min to reach steady state at the HRT of 2.5, 5.0, 10.0, 15.0 and 20.0 min, respectively. The steady-state time was one time longer than HRT due to the backmixing effect. Other operation conditions such as pulsed high voltage, pulse repetition frequency, initial concentration of 4-CP and oxygen flow rate had little effect on the steady-state time. The data of steady effluent concentration were calculated by the average value of the samples detected after steady state. All experiments were conducted no less than twice.

The concentrations of 4-CP, 4-chlorocatechol (4-Cl-CC) and hydroquinone (HQ) in the solution were analyzed by Knauer HPLC with a reversed phase C18 column and ultraviolet detector setting wavelength of 278 nm. The volume ratio of mobile phase of deionized water (containing 1% phosphoric acid) and methanol was 50:50. The concentration of dissolved ozone in distilled water was determined with the indigo method [27]. The concentration of hydrogen peroxide was determined colorimetrically using the reaction of H_2O_2 with titanyl ions by the analysis of the maximum absorbance of the yellow peroxotitanium (IV) complex at wavelength $\lambda = 410$ nm [28]. The liquid conductivity was measured by a DDS-11 A conductivity meter. The solution pH was measured by a pHS-25 m.

The removal efficiency of 4-CP is defined as the ratio of the removed concentration to the initial concentration

$$\eta = \frac{X_0 - X}{X_0} \times 100\% = \left(1 - \frac{X}{X_0}\right) \times 100\%, \quad (1)$$

where X_0 (mol/l) is the initial 4-CP concentration, X is the 4-CP concentration after treatment.

In order to compare the discharge energy yield under different conditions, G yield values (mol/J) are evaluated by the converted amount of 4-CP molecules divided by