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Journal of Hazardous Materials 141 (2007) 475–482

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Non-thermal plasma-induced photocatalytic degradation of 4-chlorophenol in water

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Received 29 March 2006; received in revised form 6 July 2006; accepted 7 July 2006

Abstract

TiO_2 photocatalyst (P-25) (50 mg L^{-1}) was tentatively introduced into pulsed high-voltage discharge process for non-thermal plasma-induced photocatalytic degradation of the representative mode organic pollutant parachlorophenol (4-CP), including other compounds phenol and methyl red in water. The experimental results showed that rate constant of 4-CP degradation, energy efficiency for 4-CP removal and TOC removal with TiO_2 were obviously increased. Pulsed high-voltage discharge process with TiO_2 had a promoted effect for the degradation of these pollutants under a broad range of liquid conductivity. Furthermore, the apparent formation rates of chemically active species (e.g., ozone and hydrogen peroxide) were increased, the hydrogen peroxide formation rate from 1.10×10^{-6} to 1.50×10^{-6} M s^{-1}, the ozone formation rate from 1.99×10^{-8} to 2.35×10^{-8} M s^{-1}, respectively. In addition, this process had no influence on the photocatalytic properties of TiO_2. The introduction of TiO_2 photocatalyst into pulsed discharge plasma process in the utilizing of ultraviolet radiation and electric field in pulsed discharge plasma process enhanced the yields of chemically active species, which were available for highly efficient removal and mineralization of organic pollutants.

Keywords: Titanium dioxide; Non-thermal plasma; Pulsed high-voltage discharge electrical process; 4-Chlorophenol; Phenol; Methyl red

1. Introduction

Non-thermal plasma in aqueous media (pulsed discharge plasma (PDP) in aqueous solution), namely, is the plasma produced from a fast rise-time (<200 ns) pulsed high-voltage electrical discharge in aqueous solution. The process accelerates free electrons, and the energized electrons ultimately collide with and ionize, dissociate or excite the ambient molecules, thus develops non-thermal plasma to produce chemically active species, i.e. high-energy electrons, $^\bullet OH$, $^\bullet H$, $O^\bullet$, O_3, H_2O_2, neutral molecules (excited state), and ionic species. Simultaneously some phenomena occur, which are quite similar to UV photolysis, ultrasonic cavitations, UV-radiation, shock waves and supercritical water conditions [1,2]. Non-thermal plasma process by pulse discharges introduced into water for the effective removal of organic compounds, especially toxic organic compounds, which are hardly efficiently degraded by conventional technologies such as biotreatment, has attracted extensive attention [3,4–9].

Recently, to enhance the degradation efficiency of organic contaminant and energy efficiency of power supply, homogeneous catalysts (such as Fe^{2+} for Fenton's reactions) were introduced into the pulsed discharge plasma process to enhance the degradation of organic dye [8] and organic pollutant phenol [10], while homogeneous catalysts were difficult to separate from the treated solution and led to limit their practical application in wastewater treatment. Therefore heterogeneous catalysts, such as activated carbon [5], alumina, and silica gel [2] have been paid more attention to promoting the degradation of organic contaminants for their adsorptions and plasma-induced reactions, whereas these heterogeneous catalysts at high concentration would hinder the ultraviolet light radiation and plasma channels formation, resulting in poor degradation of organic pollutants.

For pulsed discharge plasma in aqueous solution exists positive electric field and ultraviolet light radiation (wavelength $\lambda = 75$–185 nm) [11], and TiO_2 is a semiconductor with a band gap of about 3.0 eV, UV light (with λ shorter than 400 nm) can excite pairs of electrons and holes [12]. When the TiO_2 photo-

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doi:10.1016/j.jhazmat.2006.07.012

catalyst is introduced into this system, these conditions should excite the dissipation of electrons and holes in TiO_2 particle for its photochemical and photoelectrochemical properties, leading to more amounts of chemically active species, especially $^{\bullet}OH$ radicals formed [13]. It was preliminarily reported by Lukes et al. that the phenol removal was enhanced in the presence of TiO_2 due to the increase of the yield of OH radicals [14]. However, there are few work reported in details about pulsed discharge plasma system in combination with TiO_2 catalyst for the decomposition of organic pollutants.

The objectives of this paper are to explore the enhancement of the decomposition rate and energy efficiency for the decomposition of organic pollutants, i.e., 4-CP, phenol and methyl red by the addition of TiO_2 photocatalyst into pulsed discharge plasma process, and compare the varieties of the primary intermediates and hydrogen peroxide formed between PDP with TiO_2 and without TiO_2 under different liquid conductivities during the degradation of 4-CP. Finally we present possible reasons of such enhancement by analyzing of the variances in the amounts of chemically active species (i.e. ozone and hydrogen peroxide).

2. Experimental section

2.1. Chemicals

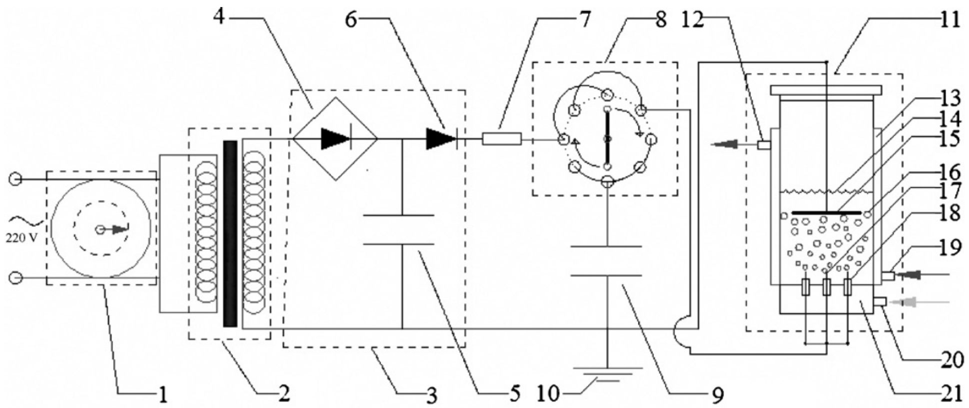
TiO_2 powder (Degussa P-25, Germany) had a surface area ($49.6\,m^2\,g^{-1}$) and contained anatase and rutile phases in a ratio of about 3:1. The reused TiO_2 was recycled from the final treated solutions containing TiO_2 by filtering though the 0.22 μm membrane filters, then it was regenerated in distilled water, and finally it was dried at 333 K for next use. The organic pollutant 4-CP is analytic grade purchased from Hangzhou Huadong Medicine Group Co., Ltd.

2.2. Equipments and procedures

The pulsed high voltage power supply used in the present study is identical to that in previous work [9]. The scheme of experimental set-up is shown in Fig. 1.The needle-plate reactor that used in this work consisted of a glass-cylinder chamber (Ø60 mm × 130 mm) with a water jacket to maintain the reactor at 298 K. The positive needle electrode was made from five stainless steel acupuncture needles (Ø0.30 mm × 75 mm, come from Suzhou medical instruments Co., Ltd.), which were placed in the center of these microtubules protruded 1.0 mm from the top of them and located at the bottom of gas chamber. Each microtubule was made of stainless steel microtubule (4.0 mm in length and 1.0 mm at diameter), which was connected with gas chamber at bottom of the reactor. When the gas bubbled through the microtubules, the gas surrounded the needle tip to form bubbles to homogenize the solution, and resulted in the hybrid gas–liquid phase electrical discharge. The ground plate electrode was made from stainless steel plate of 45 mm at diameter and located at the Teflon cap with four holes for gas output. The electrode distance was varied by moving the ground plate electrode. The standard $1000\,mg\,L^{-1}$ TiO_2 solution was sonicated to avoid the agglomeration of TiO_2 particles in the solution, then moved into 4-CP solution for treatment. The pH of mixed solution was adjusted by NaOH or HCl solution (0.01 M). Every sample is taken at interval of 6 min. Each series of samples had triplicates conducted. The experimental values were the averages of three samples, and reach over 95% confidence.

2.3. Analysis

The average output voltage and current were measured using an alternating current and voltage meter (Luguang instrument Group Co., Ltd., Shanghai). The applied voltage was 14 kV with a frequency of 150 Hz.



1: Slide transformer (0-220 V); 2: H.V. transformer (0-50 KV); 3: Voltage rectifying circuit;
4: Bridge diode rectifier 5: Filter capacitor (1 uF); 6: H.V.diode (100 KV/0.1 A);
7: Resistance (100 W/100 kΩ); 8: Rotating spark-gap switch; 9: Storage capacitor (3 nF);
10: Groundwire; 11: Reactor; 12: Cooling water outlet; 13: Water jacket; 14: Solution level;
15: Ground plate electrode; 16: Gas bubble; 17: Needle electrode; 18: Gas mirotubule;
19: Cooling water inlet; 20: Gas intake; 21: Gas chamber.

Fig. 1. Schematic diagram of experimental set-up.