

# Microwave assisted photocatalytic degradation of pentachlorophenol in aqueous TiO<sub>2</sub> nanotubes suspension

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## Abstract

TiO<sub>2</sub>/SiO<sub>2</sub> (Ti:Si = 10:1) nanoparticles were first prepared by ultrasound-assisted hydrolysis and then treated by 10M NaOH at 110°C for 20 h to form titania nanotubes. The formed samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N<sub>2</sub>-adsorption, UV–vis absorption spectra and ESR spectrometer. Result indicates that the samples prepared are nanotubular structure with opened ends. The diameter of nanotubes is about 10 nm and their length is about 100 nm. The surface area of TiO<sub>2</sub> nanotubes is 286 m<sup>2</sup>/g. The ESR signals show that there are more •OH on the surface of TiO<sub>2</sub> nanotubes than that on the surface of TiO<sub>2</sub>/SiO<sub>2</sub> nanoparticles. The photocatalytic degradation of PCP on TiO<sub>2</sub> nanotubes assisted by microwave in aqueous solution was investigated. The result indicates that the degradation rate in the microwave assisted photocatalysis process (MPC) is faster than that in other processes including microwave assisted photolytic (MDP), microwave alone process (MP) and dark process (DP). The photocatalytic activity of TiO<sub>2</sub> nanotubes is higher than that of P25 and TiO<sub>2</sub>/SiO<sub>2</sub> nanoparticles. It may be contributed to the capacity of absorption to the UV–vis irradiation and specific surface area among the photocatalysts. PCP is effectively degraded in the MPC on TiO<sub>2</sub> nanotubes. The removal of 40 mg/L PCP is 93.5% and the COD<sub>cr</sub> decrease is 51.8% in 20 min. Along with the degradation of PCP, pH of solution decreases from 10.32 to 7.5 and the dechlorination is completed in 12 min. The major intermediates of PCP in MPC on TiO<sub>2</sub> nanotubes were identified by GC/MS, including tetrachlorophenols, trichlorophenols, tetrachlorocatechol, tetrachlorohydroquinone. Based on the results, the possible photocatalytic degradation pathways of PCP on TiO<sub>2</sub> in MPC were proposed.

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## 1. Introduction

As an advanced oxidation processes (AOPs), the semiconductor photocatalytic oxidation can effectively degrade environmental organic pollutants, which can be mineralized to CO<sub>2</sub>, H<sub>2</sub>O and other small molecules [1,2]. Because of its nontoxicity, strong oxidizing power, chemical inertness and inexpensive, TiO<sub>2</sub> has been broadly used. However, in the application of TiO<sub>2</sub>, there still are some problems to be solved, such as its low specific surface area and poor quantum efficiency.

To improve its photocatalytic activity, TiO<sub>2</sub> was modified with doping metal ion and nonmetal anions, depositing heavy metal, decreasing the size of TiO<sub>2</sub> particle. In recent years, it is noticed to enlarge the specific surface area of semiconductor

to improve efficiency of photocatalysis [3,4]. The surface area of the photocatalysts plays an important role in the photocatalytic process. An increase in the surface area can be related to an increase in the number of the reactants adsorbed which may imply an increase of activity. TiO<sub>2</sub> nanotubes have larger surface area and larger pore volume than TiO<sub>2</sub> nanoparticles, so it is expected to improve the activity of photocatalyst [5,6]. Many researchers have prepared TiO<sub>2</sub> nanotubes using different techniques, such as hydrothermal reaction [7–9] and templating synthesis [10] and the reports about nanotubes are mostly focused on the preparation and turning to the application in the degradation of pollutants gradually in recent years. Yang et al. [11] had prepared TiO<sub>2</sub>/Ti nanotube-like electrodes and investigated their photoelectrocatalytic activity for the degradation of PCP in aqueous solution, the result showed the kinetic constant of photoelectrocatalytic processes for degradation of PCP using electrode was 64.7% higher than that using TiO<sub>2</sub> film electrode.

It had been found that microwave irradiation not only can excite the electrodeless discharge lamp (MWL) to generate

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ultraviolet (UV) radiation [12] which can excite TiO<sub>2</sub> for photocatalysis, but also could significantly improve the photocatalytic activity of TiO<sub>2</sub> for removing pollutants [13,14]. Photocatalysis assisted by microwave powered MWLs has been used to treat polluted waters recently [15]. But there is no report about photocatalysis on TiO<sub>2</sub> nanotubes assisted by microwave powered MWLs at present.

Pentachlorophenol (PCP) was widely used throughout the world. Because of its hypertoxicity, PCP has been listed as a priority pollutant by the U.S. Environmental Protection Agency [16]. Attention has been focused on its presence in and removal from the environment. The conventional treatment technologies include biological treatment and the chemical hydrodehalogenation methods. The degradation of chlorophenols mediated by microbes is well documented. However, the process is slow, even worse at high concentrations [17]. The chemical hydride halogenation methods are only suitable to the compounds containing one or two carbon atoms [18,19] and have to suffer slow reaction rate [20,21]. Therefore, it is necessary to develop more effective processes for removing PCP. One emerging and very promising technology is photocatalysis [22]. Quan et al. [23] have investigated the photoelectrocatalytic degradation of PCP on TiO<sub>2</sub> nanotubes electrode and found that PCP was mineralized 70% in PCP.

The main objective of the present study was to prepare TiO<sub>2</sub> nanotubes with large surface area and study the degradation of PCP assisted by microwave and MWLs on TiO<sub>2</sub> nanotubes.

## 2. Experimental

### 2.1. Materials

The reagents used were pentachlorophenol (98% purity, Supelco Chemical Company), tetrabutylorthotitanate (CP, Tianjin Chemical Company), ethyl silicate (AR, Shenyang Chemical Company), NaOH (AR, Lingfeng Chemical Company), HCl (AR, Nanjing Chemical Company), P25 (consisting of 75% anatase and 25% rutile with a specific BET-surface area of 50 m<sup>2</sup>/g and primary particle size of 20 nm).

### 2.2. Preparation of TiO<sub>2</sub> nanotubes

TiO<sub>2</sub>/SiO<sub>2</sub> particles were prepared by ultrasound-assisted hydrolysis. 38.29 mL of tetrabutylorthotitanate and 2.51 mL of ethyl silicate were stirred until they were homogeneous. The mixture was added into 900 mL of distilled water at the condition of strenuous stir. After addition, the product was stirred and irradiated in the ultrasonic bath for 1 h, respectively, before aged in a closed beaker at room temperature for 24 h. After aging, the sample was evaporated to dryness to obtain TiO<sub>2</sub>/SiO<sub>2</sub> nanoparticles (TS). 2.5 g TS was put into a Teflon vessel with 35 mL 10 M NaOH solution. The vessel was then placed in a stainless steel vessel, which was closed tightly, and held at 110 °C for 20 h in the muffle furnace. The treated powders were washed well with 0.1 M HCl solution and distilled water until pH of the solution was about 7 and dried at 80 °C for 10 h to obtain TiO<sub>2</sub> nanotubes (TN). Then TS and

TN were calcined at 400 °C for 1 h to obtain TS-400, TN-400, respectively.

### 2.3. Characterization of TiO<sub>2</sub> nanotubes

The morphology of the TiO<sub>2</sub> nanotubes was characterized using transmission electron microscopy (TEM; Hitachi-600). The crystallinity of the TiO<sub>2</sub> nanotubes was determined by X-ray diffraction (XRD) using a diffractometer with Cu K $\alpha$  radiation (Model, Shimadzu LabX XRD-6000). Nitrogen adsorption–desorption isotherms were measured on a Micromeritics TRISTAR 3000 analyzer at –195 °C over a wide relative pressure range from 0 to 1.0. Light absorption properties were measured using a UV–vis spectrophotometer (UV-2401) with a wavelength range of 190–900 nm, the •OH forming in the degradation process were trapped using the DMPO spin-trap technique and analyzed by a JEOL JES-TE200 ESR spectrometer.

### 2.4. Photocatalytic experiment

The microwave assisted photocatalysis experiments were conducted using a MW assisted MWLs system, as referred the previous study [24]: In the MW oven (330 mm  $\times$  330 mm  $\times$  200 mm, 900 w maximal MW output, made in Midea Company), there is a flat bottom flask (250 mL), with which a 600 mm long water reflux condenser is connected through a communication pipe. The limit on the safe stray leakage of MW power density is kept below 0.5 mW/cm<sup>2</sup> at 2450 MHz measured at 200 mm distance from the aperture.

All the experiments were performed under the following conditions: the flat bottom flask was filled with 5 mL of aqueous solution of PCP and the initial concentration of PCP solution was 40 mg/L, pH was 10.32. Then two MWLs (10 mm  $\times$  50 mm, in the wavelength range 250–300 nm, 4.5 mW/cm<sup>2</sup>) [24] containing mercury vapor and 0.05 g TN-400 (or TS-400, P25) were placed into the reactor vessel. Microwave oven was timing when reaction began.

### 2.5. Analytical methods

The samples after reaction were filtered with 0.20  $\mu$ m Millipore to remove photocatalysts. The determination of PCP concentrations was performed by ultraviolet spectrophotometer (V2550, Japan) at 220 nm [25,26]. pH was measured with pH meter (PHS-2C, China). The concentration of Cl<sup>–</sup> was measured by Chloride Ion-Selective Electrode (pCl-1, China). The chemical oxygen demand (COD<sub>Cr</sub>) was analyzed by dichromate method. The solutions were extracted with 25 mL dichloromethane plus 0.2 mL 30% HCl (shaking at 150 rpm for 4 h). The above procedure was repeated three times. The solvent fractions were combined and concentrated to 1 mL. Identification of intermediates was carried out with a GCQ coupled with a capillary column (DB-5MS, 30 m). The temperature ramp was as follows: 60 °C for 2 min, 65–120 °C at 35 °C min<sup>–1</sup>, 120–300 °C at 7 °C min<sup>–1</sup> and at 300 °C hold for 5 min.

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