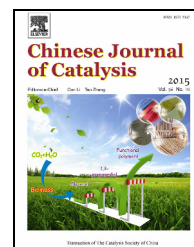


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Article

Influence of synthesis conditions on physical properties of lanthanide-doped titania for photocatalytic decomposition of metazachlor



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ABSTRACT

Heterogeneous photocatalysis is a very effective method for the decomposition of a whole range of water pollutants. In this work, the influence of synthesis conditions on the physical properties and photocatalytic activity of lanthanide-doped titanium dioxide photocatalysts was evaluated. Titanium dioxide was prepared via sol-gel synthesis followed by a solid state reaction under different conditions, including different temperatures (450, 550, and 650 °C) and reaction times (4, 8, and 12 h). The crystalline phase of the products was determined to be solely anatase using X-ray diffraction, and this result was confirmed by Raman spectroscopy. The structure, as well as particle size, of the samples was examined using scanning electron microscopy, and their specific surface area was calculated using Brunauer-Emmett-Teller analysis. The band gap energy of the samples was examined using ultraviolet-visible spectroscopy from diffuse reflectance measurements. Doping with lanthanide species, dysprosium and praseodymium, caused the absorption edge to shift towards higher wavelengths and enhanced photocatalytic activity in comparison with pure titania. The photocatalytic activity of the samples was studied in terms of the degradation of the commonly used herbicide metazachlor. The decomposition was carried under UV light and the decrease in metazachlor concentration was measured using high performance liquid chromatography. The best performance was obtained for samples treated at 550 °C for 8 h during the solid state reaction step.

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1. Introduction

Metazachlor belongs to the organochlorine pesticide group and was the fifth most used herbicide in the Czech Republic in 2010, with a consumption of nearly 200 000 kg [1]. Generally, residues of various pesticides and herbicides are able to leach from agricultural soil to deeper ground or to ground water, where they can remain for long time owing to their nondegradable properties. Consequently, such species can cause different serious problems even at very low doses of nanograms per cubic decimeter [2]. Metazachlor has been

found to be moderately toxic to different aqueous organisms, especially daphnia, carp, and bluegill sunfish. The highest sensitivity was discovered in trout, where it can cause damage to liver or kidneys [3]. Because of its toxicity, metazachlor, as with many other pesticides, belongs to large group of endocrine disrupting chemicals (EDCs) [4]. Many of these compounds pass through wastewater treatment plants [5,6] that are not designed for removing such contaminants [7], and therefore many of them reach the surface water unchanged [8].

Many different techniques have been studied in the effort to remove micropollutants from water, from physical processes,

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such as sorption or membrane filtration, to biological processes, using bacteria or enzymes [9]. Nowadays, one very promising group of treatment techniques is that based on advanced oxidation processes, particularly heterogeneous photocatalysis. The main feature of this method is the production of hydroxyl radicals, which initiate subsequent reactions that lead to the decomposition and removal of organic compounds [10]. This technology is also non-selective and versatile, which are useful and necessary in wastewater treatment [11]. Titanium dioxide is one of the most commonly used photocatalysts because of its high activity, biological and chemical inertness, high photostability, excellent optical and electrical properties, and nontoxicity. However, its absorption only in the UV region and quite narrow band gap energy, which brings about fast back recombination of the electron-hole pair, are its main disadvantages. Many authors have attempted either to shift the absorption edge of titania towards higher wavelength, or to suppress the recombination process, which may be achieved by doping the titania [12]. Nevertheless, most studies concentrate their photocatalytic investigations on model compounds [13,14] such as phenol or dyes [15,16].

In this work we successfully prepared lanthanide-doped titanium dioxide, which has been reported to exhibit better photocatalytic activity in comparison with that of pure titania [17], and investigated its suitability for the photocatalytic decomposition of metazachlor because of the current need to remove this species from wastewater. Furthermore, we investigated the effects of different process conditions and compared the photocatalytic activity of doped and undoped samples with commercial titania P25.

2. Experimental

2.1. Catalyst preparation

Preparation of lanthanide-doped titanium dioxide was performed by sol-gel synthesis using titanium propoxide as the precursor. The titanium propoxide (0.125 mol) was added dropwise under continuous stirring to isopropanol (0.5 mol), which was used as a solvent. Afterwards, acetylacetone (0.06 mol) was added to the mixture as a stabilization agent. Dysprosium (Dy) and praseodymium (Pr) doped TiO₂ (0.3 mol% [18]) samples were synthesized by first dissolving the oxides of the corresponding elements in nitric acid (20 cm³), and the obtained solutions were poured into the propoxide dispersions. The sols were left to age at room temperature for 7 d to form a gel structure, after which they were heated at 120 °C until xerogels were formed. The xerogels were then subjected to solid state reaction at various temperatures ($T = 450, 550, \text{ and } 650 \text{ }^\circ\text{C}$) for different time periods ($t = 4, 8, \text{ and } 12 \text{ h}$). The obtained lanthanide-doped TiO₂ samples were denoted as Dy-TiO₂ T/t and Pr-TiO₂ T/t .

2.2. Catalyst characterization

Thermogravimetric analysis (TGA) was carried out on the heat-treated powders using a thermoanalyzer (Seiko Instru-

ments 6300 TG-DTA) in an atmosphere of argon-air (volume ratio 1:1). The analysis was performed over the temperature range 35–1000 °C, with a gas flow rate of 400 cm³/min and a temperature ramp rate of 20 °C/min. The crystalline phase of the prepared powders was examined using X-ray diffraction (XRD; X-ray diffractometer SmartLab, Rigaku), using a Cu K_β radiation source and a 2θ scan range of 20°–60°. The results of the XRD measurements were confirmed by Raman analysis (Renishaw inVia), which was carried out using a 633 nm laser at an output power of 30 mW and measured range of 0–1600 cm⁻¹. Crystallite size was calculated from the XRD results using the Scherrer equation $d = B\lambda/(\beta\cos\theta)$, where d is the size of the crystallites in the direction vertical to the corresponding lattice plane, B is a constant equal to 0.94, λ is the wavelength, equal to 0.157 nm, and β is the width of the selected peak at half of its height.

The structure of the prepared powders, as well as their particle size, was investigated using scanning electron microscopy (SEM; Carl Zeiss Ultra Plus). The influence of synthesis conditions on the band gap energy was examined from diffuse reflectance measurements (UV-Vis spectrometer Avaspec-2048). Nitrogen adsorption/desorption analysis was carried out to determine the specific surface area of the samples (BET).

2.3. Photocatalytic experiments

The aim of this study was to determine optimal solid state reaction for the preparation of photocatalytically active nanopowders that could be useful for decomposition of pesticides in water. The photocatalytic experiments were performed on metazachlor. All experiments were carried out in a flow reactor (Fig. 1), which was composed of a borosilicate glass tube with inner diameter of 0.6 cm placed at a distance of 1 cm from the light source. The decomposition reaction was performed using UV-LED (370 nm) irradiation with an optical power density of 22 mW/cm². The flow rate in the reactor was 2.5 cm³/s. Before each experiment, the Dy-TiO₂ or Pr-TiO₂ sample (1 g/L) was dispersed in 70 cm³ of an aqueous solution of metazachlor (10 mg/L), and the resulting suspension was kept in darkness for 6 min under continuous stirring to reach adsorption/desorption equilibrium. 1 cm³-aliquots of the reaction solution were sampled at certain intervals, and the concentration of remaining metazachlor was determined by HPLC (Shimadzu LC-20) after filtration (pore size 0.45 μm). The HPLC conditions were as follows: Luna 5u C18 (2) 100A (250 mm × 4.6 mm) column, the eluent was a mixture of water-acetonitrile (volume ratio 1:1) with a flow rate of 1.8 cm³/min, column temperature 40 °C, injection volume 0.25 μL, and detector wavelength 210 nm.

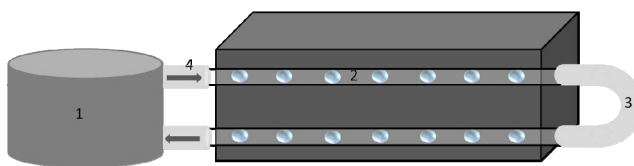


Fig. 1. Flow tube reactor. 1, beaker containing reaction mixture; 2, UV-LED source; 3, borosilicate tube; 4, direction of flow.

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