Separation and Purification Technology 197 (2018) 63–69

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Magnetic $Pr_6O_{11}/SiO_2@Fe_3O_4$ particles as the heterogeneous catalyst for the catalytic ozonation of acetochlor: Performance and aquatic toxicity

Junliang Wang[a], Yuanyang Lou[a], Xiaowei Zhuang[b], Shuang Song[a], Weiping Liu[c], Chao Xu[a,*]

[a] College of Environment, Zhejiang University of Technology, Hangzhou 310032, China
[b] Key Laboratory of Forest Resources Utilization of Zhejiang, Zhejiang Forestry Academy, Hangzhou 310023, China
[c] College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, China

ARTICLE INFO

Keywords:
Catalytic ozonation
Acetochlor
Praseodymium
Magnetic particles
Aquatic toxicity

ABSTRACT

A magnetic core–shell $Pr_6O_{11}/SiO_2@Fe_3O_4$ catalyst using chemical precipitation was prepared. Its structure was confirmed by X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, and energy-dispersive X-ray spectrum. The catalytic activity was evaluated by the catalytic ozonation of acetochlor. The results showed that the catalyst could effectively improve the acetochlor removal and mineralization. The total organic carbon removal reached 37.3% with the catalyst at 120 min, whereas the removal was 14.1% with ozonation alone. The catalyst was proved to be stable and recyclable by determining the concentration of the leaching praseodymium ions and the catalyst's activity after repeated use. The effect of the radical scavengers indicated that the catalytic ozonation process followed an $^{\cdot}OH$ reaction mechanism. In addition, we employed *Chlorella* and zebrafish as model organisms to investigate the aquatic toxicity of the treated solution and the dissolved praseodymium ions. We found that the aquatic toxicity of the reaction solution decreased with an increase in the degradation time, and no obvious toxicity was found for the dissolved praseodymium ions.

1. Introduction

Catalytic ozonation, especially heterogeneous catalytic ozonation, has attracted significant attention in recent years because it can enhance the removal of insoluble and refractory compounds with a relatively high efficiency [1,2]. The difficulties associated with separation in a catalytic ozonation system, however, limit its further application in wastewater treatment fields [3]. To overcome this drawback, magnetic catalysts were developed. Compared to conventional heterogeneous catalysts, magnetic catalysts offer easy separation and recyclability. Recent studies have identified magnetic catalysts such as Fe_3O_4 [4,5], MFe_2O_4 (M = Mn, Cu, Co, and Ni) [6–10], magnetic carbon spheres [11,12], and active substances like metal oxides (e.g., CeO_2, Co_3O_4, TiO_2, CuO, and Ru_2O_3) with a magnetic core (e.g., Fe_3O_4, Fe_2O_3, or pyrite cinder) [13–18]. In these catalysts, Fe_3O_4 was usually employed as a core or support, due to its remarkable magnetic properties and low toxicity [17,19], and silica was used to cover the surface of Fe_3O_4 to avoid oxidation [20,21]. The lanthanide oxide Pr_6O_{11} proved to be promising for catalytic ozonation because of its chemical and biological inertness, recyclability, and extended stability against chemical corrosion. Notably, the praseodymium ion can move between its trivalent and tetravalent states to release and absorb oxygen [22]. He et al. prepared a series of praseodymium-modified $\gamma\text{-}Al_2O_3$ and found the catalyst was more active than metal oxides (Mn, Ni, Fe, Zn) in the ozonation of succinic acid [23]. In our previous work, the presence of a Pr_6O_{11} catalyst significantly improved the removal and mineralization of diethyl phthalate in an aqueous solution [24].

The process of heterogeneous catalytic ozonation is an effective method for degrading organic contaminants. However, it is difficult to achieve complete mineralization, especially for refractory organic pollutants, which could inevitably generate oxidation by-products; these compounds may be more toxic than the original pollutant [25]. In addition, metal oxides, as the active substances of a heterogeneous catalyst, would be leached during catalysis. It is well known that most metal ions, such as copper, zinc, lead, and chromium, have an aquatic toxicity at low concentrations. Thus, the toxicity of leaching metal ions from the catalyst cannot be ignored. As a result, a treated solution is a complex mixture. Its ecotoxicological impact cannot be predicted by simple chemical determinations, not to mention the potential interactions among pollutants [26]. Thus, ecotoxicological bioassays of the treated solution are necessary to provide a holistic direct estimation. For example, Wen et al. tested the acute toxicity of the O_3/H_2O_2 degradation of DEP and its intermediates with Gram-negative luminescent bacteria [27]. Hou et al. examined the variation in the acute toxicity during the

---

* Corresponding author.
E-mail address: chaoxu@zjut.edu.cn (C. Xu).

https://doi.org/10.1016/j.seppur.2017.12.052
Received 13 July 2017; Received in revised form 23 December 2017; Accepted 27 December 2017

US/Fe_3O_4/O_3 process for the degradation of sulfamethoxazole from an aqueous solution using *Daphnia magna* [28]. Guo et al. measured the acute toxicity of BP-3 and the treated solution with the unicellular green microalgae *Chlorella vulgaris* [29]. Wang et al. investigated the change in the acute toxicity of a chloramphenicol solution after ozonation using zebrafish embryos [30]. Although different toxicity evaluation results were obtained when different test organisms were employed to evaluate the aquatic toxicity of the treated effluent [31,32], fish and algae play an important ecological role in the aquatic ecosystems and are widely used as model organisms in the evaluation of aquatic toxicity since they are present throughout the aquatic environment and play an important ecological role in the aquatic ecosystems.

Acetochlor is a U.S. Environmental Protection Agency approved selective, chloroacetacetanilide herbicide used to control most annual grasses and certain broadleaf weeds. It is one of the most widely used herbicides in the world and belongs to a group of broadly used weed killers along with alachlor, metolachlor, propachlor, propisochlor, and MG-84 [33]. Because of its extensive application, there is some concern regarding its possible toxic effects upon nontarget organisms.

In this study, a magnetic catalyst was prepared with a ternary structure consisting of a Fe_3O_4 magnetic core, a silica membrane midlayer, and a lanthanide oxide Pr_6O_{11} outer layer. Its catalytic ozonation activity and stability were evaluated by the degradation of acetochlor. A possible catalytic ozonation mechanism at the solid-liquid interface was investigated. In addition, we employed zebrafish and *Chlorella* to evaluate the aquatic toxicity of the reaction solution during the degradation of acetochlor.

2. Materials and measures

2.1. Reagents and chemicals

Praseodymium (III) nitrate tetrahydrate was purchased from Aladdin Reagent Co., Ltd. (China). Acetochlor (purity > 90%) was obtained from Zhejiang Dayou Chemical Reagent Co., Ltd. (China), and the radical scavenger *Tert*-butyl alcohol (TBA) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (China). The ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), potassium hydroxide (KOH), potassium nitrate (KNO_3), trisodium citrate ($NaC_6H_5O_3$), ammonium hydroxide ($NH_3{\cdot}H_2O$), ethyl alcohol (C_2H_5OH), and tetraethyl orthosilicate (TEOS) used for the preparation of Fe_3O_4@SiO_2 were purchased from Huadong Medicine Co. (Hangzhou, China). All the other reagents used in this study were of analytical reagent grade. Deionized water produced with a Milli-Q water purification system (Millipore) was used to prepare all solutions.

2.2. Preparation and characterization of the Pr_6O_{11}/SiO_2@ Fe_3O_4 catalyst

We synthesized magnetic porous Pr_6O_{11}/SiO_2@ Fe_3O_4 via a chemical precipitation and subsequent calcination process followed a previous report [24]. By placing drops of each sample on a copper grid, the morphologies of the Fe_3O_4, Fe_3O_4@SiO_2, and Pr_6O_{11}/SiO_2@Fe_3O_4 particles were characterized by transmission electron microscopy (TEM). We determined the element composition of the samples by the energy-dispersive X-ray spectrum (EDX) and recorded the powder X-ray diffraction (XRD) of the catalyst on a Thermo ARL SCINTAG X'TRA diffractometer at room temperature using Cu Kα irradiation at 45 kV and 40 mA. The specific surface areas were measured using a Brunauer-Emmet-Teller (BET) apparatus (Micromeritics ASAP 2020, Norcross, GA). The X-ray photoelectron spectroscopic (XPS) tests were conducted on an RBD upgraded PHI 5000C ESCA system (PerkinElmer, Waltham, MA) with Mg KR radiation (300 W, 14.0 kV, and 93.9 eV). We calibrated the binding energies by using contaminated carbon (C1s = 284.6 eV) and measured the magnetic properties at room temperature with a vibrating sample magnetometer (VSM7407, Lake Shore Cryotronics, Westerville, OH). The pH value at the point of zero charge (pH_{PZC}) was measured by the drift method, as described elsewhere [34].

We analyzed the structures and characteristics of the catalyst particles. Our results showed that the catalyst had a spinel and ternary structure with an Fe_3O_4 magnetic core, a SiO_2 shell, and a Pr_6O_{11} outer layer. The catalyst was composed of Si, O, Fe, and Pr, and the mass percentage of the elements was 27.40%, 23.37%, 3.05%, and 46.16%, respectively; it also exhibited a strong attraction to magnetic fields with a close coercivity of ~4.5 Oe at room temperature. The diameter of the catalyst was about 200 ~ 300 nm, and the BET and pH_{pzc} were 58.9 m^2/g and 11.01, respectively.

The details of these syntheses and characteristics of the catalyst were reported in our previous study [24] (for detailed information, see Figs. S1–S4).

2.3. Catalytic ozonation activity measurements

The experimental apparatus in this study included a cylindrical Pyrex glass reactor, an O_3 supply system, a temperature control system, a magnetic stirring device, and an exhaust treatment system. The ozone diffuser was a bubble-column reactor, which was fixed at the bottom of the glass reactor. The catalysts could be diffused well in the aqueous solution by mixing. The experiments were conducted at room temperature in a water bath. Simulated wastewater that contained 20 mg/L acetochlor and 0.4 g (0.5 g/L) of the catalyst was added to the reactor. The reaction was started when the ozone was added. Samples were withdrawn at predetermined time points from the top of the reactor, and these samples were filtered through a 0.22 µm pore size membrane filter before analysis. The concentration of acetochlor was determined by high-performance liquid chromatography (Jasco, Tokyo, Japan) with a Hypersil ODS2 column (250 mm × 4.6 mm internal diameter, 5 µm film thickness). The mobile phase was water and acetonitrile (25:75, v/v) at a rate of 1.0 mL/min. The wavelength was 215 nm. The concentration of the total organic carbon (TOC) was analyzed by a TOC-VCPH analyzer (Shimadzu, Kyoto, Japan) and the concentration of O_3 in the O_2/O_3 mixture was determined by iodometry [35].

2.4. Aquatic toxicity tests

2.4.1. Chlorella

We obtained a nonaxenic unialgal culture of *Chlorella* from the Institute of Hydrobiology at the Chinese Academy of Sciences (China). We selected the test organism according to its ecological relevance and ease of culture in the laboratory [36]. Cultures were grown in a No. 4 aquatic medium, at pH 8.0. *Chlorella* was cultured in a light incubator by shaking the culture 3 times a day at regular intervals until the optical density of *Chlorella* reached OD_{680} = 1.0. We performed the bioassays according to the methods sanctioned by the Organization for Economic Co-operation and Development (OECD) for testing chemicals soluble in water with some modifications [37]. In 100 mL cotton-gauge plugged bioassay flasks, we aseptically inoculated 8 L *Chlorella* of exponentially growing cells. Then, the reaction solution was withdrawn at different times and added to the No. 4 aquatic medium. Three parallel samples were used for each concentration.

2.4.2. Zebrafish embryos

Adult zebrafish (*Danio rerio*) were obtained from the Institute of Hydrobiology at the Chinese Academy of Sciences (China). To investigate the developmental toxicity of the reaction solution at different times on the zebrafish embryos, we randomly distributed fertilized embryos in 24-well plates (Costar, Corning Inc., NY) containing a reaction solution for 72 h. The procedural details were consistent with those specified by the OECD test guidelines [38]. Briefly, newly fertilized embryos were first exposed to chambers with known concentrations of acetochlor and its degradation solutions. Half an hour later, any