



Improved photodegradation and detoxification of 2,4,6-trichlorophenol by lanthanum doped magnetic TiO₂



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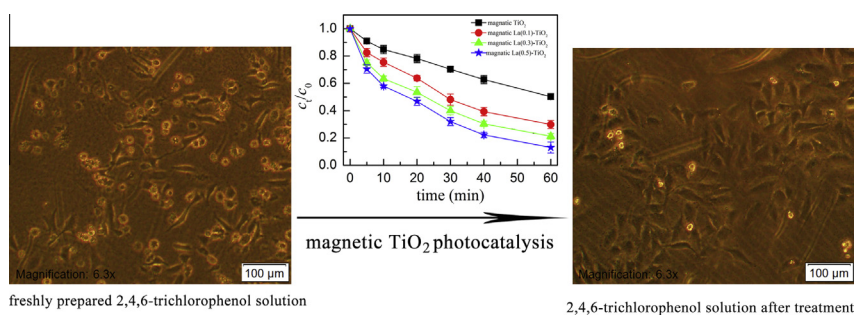
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HIGHLIGHTS

- Lanthanum ion doped magnetic TiO₂ is synthesized and characterized.
- Magnetic La doped TiO₂ shows highly photoactivity under UV–vis irradiation.
- The treated 2,4,6-trichlorophenol showed no obvious toxicity to HeLa cell.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetic lanthanum doped TiO₂ (Fe₃O₄/SiO₂/La-TiO₂, referred to magnetic La-TiO₂) and undoped magnetic TiO₂ (Fe₃O₄/SiO₂/TiO₂, referred to magnetic TiO₂) hybrid microspheres with uniform magnetic cores (Fe₃O₄/SiO₂) were synthesized and characterized in this work. The results indicate that the photoactivity of the magnetic La-TiO₂ is much higher than that of the magnetic TiO₂ for the degradation of 2,4,6-trichlorophenol (10 μM) under UV–visible light irradiation (λ ≥ 340 nm). The initial degradation rate (R₀, μM/min) for the photodegradation of 2,4,6-trichlorophenol (10 μM) in a 2 g/L magnetic La-TiO₂ dispersion is 0.45 μM/min, which is 1.8 times larger than the value obtained in a 2 g/L magnetic TiO₂ dispersion. The activities of these two catalysts decreased after seven cycles use, probably due to the reduction of surface hydroxyl groups and reaction sites. Carboxylate acids and Cl⁻ were detected as advanced oxidation products. Thus, after 120 min of degradation, the treated 2,4,6-trichlorophenol solution showed no toxicity to HeLa cells. The results clearly demonstrate that the magnetic TiO₂ particularly magnetic La-TiO₂, would be an effective catalyst for the treatment of solutions polluted with chlorophenols.

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1. Introduction

Chlorophenols are widely used in pesticides, antiseptics and wood preservers and can enter the environment when these products are being made or used. Currently, chlorophenols are widely

found in environmental water, soil and sediment samples, as well as in living organisms, including humans [1,2]. Chlorophenols can cause undesired effects on organisms even at trace levels [3]. Findings obtained from a 2 years toxicity studies showed that 2,4,6-trichlorophenol (2,4,6-TCP) was carcinogenic to laboratory animals, causing liver tumors in mice and inducing forms of leukemia/lymphoma in male rats [4]. It is generally accepted that the primary toxic effects of chlorophenols are a result of the

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destruction of cellular membranes and the inhibition of oxidative phosphorylation [3]. Therefore, chlorophenols have been characterized as first priority pollutants by many governments. Various methods, such as adsorption [5,6], biodegradation [7], and advanced oxidation processes (AOPs) [8–10], have been applied to remove chlorophenols from aqueous solutions.

Most types of toxic pollutants including organic compounds, metal ions, bacteria and viruses can be successfully removed by using TiO_2 as a photocatalyst due to the photo-generated electron–hole pairs and the subsequently produced reactive oxygen species (ROS) [11–15]. However, the slurry operation method limits the practical application of TiO_2 photocatalysis due to the high cost of the post-removal of the TiO_2 after the reaction [16]. Additionally, there have been concerns about the environmental risks of nano-sized materials caused by their direct and indirect toxicities [17–19]. In recent decades, magnetic TiO_2 has offered an alternative method to facilitate the reuse of the catalyst [20–22].

However, its high recombination rate of photo-generated electron–hole pairs and low ability to utilize visible light make TiO_2 a relatively inefficient catalyst. Efforts including doping TiO_2 with metal ions or nonmetallic elements, ligands or polymers post modification were carried out to improve TiO_2 's efficiency. Recently, doping with rare earth metals has attracted attention. The reported work proved TiO_2 doped with rare earth metals including platinum, ruthenium and lanthanum showed significant increases in visible light absorption and could also facilitate the electron–hole separation, and their photoactivities were highly improved [23–25]. Therefore, rare earth metals-doped magnetic TiO_2 could meet the need for both immobilization and high photoactivity. Our previous work showed platinum doped magnetic TiO_2 ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{La-TiO}_2$) showed higher activity than the undoped magnetic TiO_2 ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$) in removal of acid orange [26]. Lanthanum doped magnetic TiO_2 ($\text{Fe}_3\text{O}_4/\text{La-TiO}_2$) also showed higher activity than $\text{Fe}_3\text{O}_4/\text{TiO}_2$ in removal methyl orange [27]. Compared with the application of rare earth metals including platinum, ruthenium and lanthanum doped TiO_2 or magnetic TiO_2 in removing dyes or other pollutants from aqueous solutions [23–28], the investigation of rare earth metals doped magnetic TiO_2 in the removal of chlorophenols has been quite limited.

Lanthanum doped magnetic TiO_2 , $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{La-TiO}_2$ (magnetic La- TiO_2) was synthesized in this work, and its structure was well characterized. The TiO_2 or La- TiO_2 layer was chosen to attach on the SiO_2 layer rather than directly on Fe_3O_4 because SiO_2 layer could provide a larger surface area than the Fe_3O_4 core for further coating of titania layer [26]. Moreover, it has been reported that the presence of a SiO_2 layer between the magnetic core and TiO_2 layer can prevent electrons from being transferred to the Fe_3O_4 core thus avoiding iron leaching [21]. The photoactivities of the magnetic TiO_2 samples were assessed by their ability to remove 2,4,6-TCP under UV–visible light irradiation ($\lambda \geq 340$ nm). In addition, we also studied the cytotoxicities of treated 2,4,6-TCP aquatic solutions by morphological methods in an attempt to investigate the possible toxic side effects of intermediates generated during the photodegradation and further display the superiority of magnetic TiO_2 as a photocatalyst.

2. Materials and methods

2.1. Reagents

2,4,6-Trichlorophenol (98%) was obtained from the Aladdin Reagent Corporation (Shanghai, China) and was used as a representative of chlorophenol pollutants. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, sodium acetate ($\text{NaAc} \cdot 3\text{H}_2\text{O}$), tetraethyl orthosilicate (TEOS), ethylene glycol, absolute ethanol, concentrated aqueous ammonia solution and

hydrochloric acid were purchased from the Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All of these reagents were of analytical grade and were used without further purification. Titanium isopropoxide and diethylenetriamine were purchased from Alfa-Aesar and used as received. Lanthanum nitrate was a commercial product of the Aladdin Reagent Corporation (Shanghai, China) and was used as the metal ion precursor. Deionized water (resistivity > 18.0 M Ω cm) was used during sample preparation.

2.2. Synthesis of La doped magnetic TiO_2 (magnetic La- TiO_2)

The synthesis method for the Fe_3O_4 core, SiO_2 coated Fe_3O_4 ($\text{Fe}_3\text{O}_4/\text{SiO}_2$) and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ (magnetic TiO_2) nanocomposites was described in our previous work [26]. In a typical synthesis of La doped magnetic TiO_2 (magnetic La- TiO_2), 0.1 g of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ was dispersed in 41.5 mL of iso-propyl alcohol and was sonicated for 1 h. A 30 μL aliquot of diethylenetriamine was added into the above dispersion and gently stirred for 5 min, which was followed by the addition of 2 mL of titanium isopropoxide and lanthanum nitrate (atom ratios of La to Ti are 0.1:100, 0.3:100 and 0.5:100) [25]. The resulting mixture was then transferred to a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was placed into a 200 °C oven for 24 h and then cooled to room temperature. The obtained magnetic La- TiO_2 was washed with ethanol and water six times and then dried under vacuum at 60 °C for 6 h. Finally, the products were calcined in argon at 500 °C for 4 h (warming rate of 5 °C/min). From the mass balance, the contents of TiO_2 or La doped TiO_2 in the corresponding magnetic TiO_2 composites were both approximately 0.3 g/g. Unless otherwise specified, magnetic TiO_2 and magnetic La- TiO_2 stand for the undoped magnetic TiO_2 and lanthanum (atom ratio of La to Ti is 0.5:100) doped magnetic TiO_2 , respectively.

2.3. Characterization of the synthesized magnetic materials

The compositions of the synthesized magnetic TiO_2 samples before and after 7 cycling uses were analyzed on a X-ray fluorescence (XRF) spectroscopy (S4PIONEER, Bruker AXS). The XRD patterns of the prepared products were recorded with a Dmax-rA powder diffractometer (Rigaku, Japan) that used, with $\text{Cu K}\alpha$ as a radiation source at a scanning rate of 2° min^{-1} . The Brunauer–Emmett–Teller (BET) surface area was determined by using a Micromeritics ASAP 2020 setup. The scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed with a FEI-QUANTA 200 microscope. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM 2010HT microscope (Japan Electronics, Japan) at an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) analysis of magnetic La- TiO_2 before and after 7 cycling use was recorded on a Kratos XSAM 800 X-ray photoelectron spectrometer operated in the FRR mode using nonmonochromatic $\text{Mg K}\alpha$ (1253.6 eV) radiation. The applied voltage and current was 11.7 kV and 17 mA, respectively. The peak curve fitting was accomplished by XPS peak 4.1 software.

2.4. Photodegradation of 2,4,6-trichlorophenol using magnetic TiO_2 and magnetic La- TiO_2

The photodegradation of 2,4,6-trichlorophenol was investigated to assess the photoactivities of magnetic TiO_2 and magnetic La- TiO_2 . The experimental details were described in a previous work [29]. The degradation ratio (%) of 2,4,6-trichlorophenol was calculated from Eq. (1):

$$R = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (1)$$

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