Improved performance and prolonged lifetime of titania-based materials: sequential use as adsorbent and photocatalyst

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Received July 3, 2014; accepted August 20, 2014; published online April 13, 2015

Lifetime is a key index in the evaluation of environmentally functional materials. Although it is well known that adsorption is the first step in photocatalysis, very little work has been done on the sequential use of materials as both adsorbents and photocatalysts. In this work, two titania-based materials, TiO$_2$ xerogel and TiO$_2$ photocatalyst nanoparticles, were fabricated and evaluated as adsorbent and photocatalyst for the remediation of contaminated water with an azo dye, Acid Orange 7 (AO7), as the modeling pollutant. The TiO$_2$ xerogel showed a high adsorption capacity to AO7 (769 mg/g) and could be regenerated easily with diluted NaOH solution (0.01 mol/L) for several cycles. The exhausted xerogel was calcined at 400 °C for 3 h and used as a photocatalyst for the degradation of AO7. Compared to the nanoparticles directly prepared from fresh TiO$_2$ xerogel, the TiO$_2$ nanoparticles from adsorption exhausted xerogel showed a much higher photocatalytic activity upon both UV and visible light irradiation. Thus the titania-based materials were endowed with improved performance as well as prolonged lifetime.

taxtium dioxide, adsorbent, reuse, photocatalyst, azo dye

1 Introduction

Dyestuff effluent is one of the main pollution sources in industrial wastewater because of the potentially pathogenic, mutagenic and carcinogenic properties of synthetic dyes [1]. Even at low concentrations, dyes may greatly alter the water quality. The removal of azo dyes, which are highly stable in aqueous media and resistant to light and oxidative agents, is a major challenge in wastewater treatment [2,3]. Typical methods for dyeing wastewater treatment include physical, chemical and biological processes, such as adsorption [4], advanced oxidation processes (AOPs) [5–7] and biological treatment [8,9].

Physical adsorption is widely used because of its high efficiency and low cost. Various adsorbing materials for soluble dyes have been studied, such as ion exchanger [10], activated carbon [11], modified bamboo charcoal [12], and titania aerogel [2]. Most of these spent adsorbents can be regenerated by concentrated acids/bases/salts for repeated use [13,14]. However, after several adsorption/desorption cycles, the adsorption capacities are inevitably reduced. Replacement of the material constitutes a large portion of the cost in the field of water treatment.

In recent years, photocatalysis has become a hot topic in the field of AOPs. TiO$_2$ is a well-known and widely used photocatalyst due to its good photocactivity, low cost, and non-toxicity. As the first step in photocatalysis, adsorption on the photocatalyst surface is of great significance [15]. Nevertheless, only a few studies have been reported on the interactions between organic pollutants and the surface of photocatalysts [15–18].

Due to the large band gap, the energy harvesting of TiO$_2$ is limited in the UV region. A great deal of attempts, such as metal ion doping [19], non-metal doping [20], organic dyes anchoring onto the surface of TiO$_2$ [21], and TiO$_2$...
anchoring onto carbon-based materials [22,23], have been made to extend the absorption edge of TiO$_2$ to the visible region for improved energy utilization and photocatalytic efficiency. However, deactivation of TiO$_2$ photocatalysts over time is still an inherent obstacle for their commercialization [24].

In our previous work, we reported a type of TiO$_2$ xerogel with acetylacetonato anchors as the photo-responsive sites for reversible sorption of azo dyes, which build a bridge between adsorption and photochemistry [25]. Herein, a TiO$_2$ xerogel prepared with the same sol-gel process was investigated as an adsorbent. Both the pristine and adsorption-saturated xerogels were employed as precursors for TiO$_2$ photocatalyst nanoparticles. An azo dye, Acid Orange 7 (AO7), was used as a model pollutant for the performance evaluation of these materials. A prolonged lifetime of titania-based materials was proposed based on the sequential use in adsorption and photocatalysis.

2 Experimental

2.1 Materials and synthesis

2.1.1 Chemicals
Tetra-$n$-butyl titanate (TNBT, Ti(OC$_4$H$_9$)$_4$), acetylacetone (AcAc, CH$_3$COCH$_2$COCH$_3$), ethanol and nitric acid were all of analytical purity grade and were used as received. AO7, Methyl Orange, Rhodamine B, Methylene Blue, and all of analytical purity grade and were used as received. TiO$_2$ was supplied by Evonik Degussa Co. (45x394), Sulforhodamine B were obtained from Sangon Biotech Co. (45x406), AO7, Methyl Orange, Rhodamine B, Methylene Blue, and all of analytical purity grade and were used as received. AO7, Methyl Orange, Rhodamine B, Methylene Blue, and all of analytical purity grade and were used as received. TiO$_2$ was supplied by Evonik Degussa Co. (45x394), Sulforhodamine B were obtained from Sangon Biotech Co. (45x406).

2.1.2 Synthesis of the TiO$_2$ xerogel
The TiO$_2$ xerogel was prepared with the sol-gel process. Firstly, 10 mL TNBT was added dropwise to a mixture of ethanol (20 mL) and AcAc (1.5 mL) under a magnetic stirring for 30 min. The diluted nitric acid (0.5 mL) was added to a mixture of ethanol (10 mL) and ultrapure water (3.0 mL). The nitric-containing mixture was then added dropwise to the TNBT-ethanol-AcAc solution. After stirring for another 30 min, a yellowish sol was obtained which slowly turned to gel during the next few hours. The gel was aged and dried under ambient conditions until a constant weight was obtained.

2.1.3 Synthesis of the TiO$_2$ photocatalyst nanoparticles
Both the as-prepared (pristine) and AO7-saturated TiO$_2$ xerogels were calcined at 400 °C for 3 h in a multi-segment programmable muffle furnace (3216 PID Temperature Controller, Eurotherm Ltd., UK) in which the temperature ramping rate was 5 °C/min. The resultant TiO$_2$ nanoparticles from the as-prepared and AO7-saturated TiO$_2$ xerogels were named TiO$_2$-A and TiO$_2$-S, respectively.

2.2 Characterization
Fourier transform infrared (FTIR) spectra were recorded with the standard KBr pellet method on a Thermo Nicolet 870 spectrometer (Nicolet Inc., USA). Before tableting, the TiO$_2$ xerogel (0.2 g/L) was firstly equilibrated with a 100 mg/L AO7 solution, and then was filtered and dried in a vacuum freeze dryer.

The point of zero charge (PZC) was determined by potentiometric titration experiments with a computer-controlled automatic titration system (T50, Mettler Toledo Co., Switzerland) equipped with a combined glass electrode (DGi115-SC). Zeta potential was measured with a Malvern Zetasizer 3000 Hsa (England). The solution pH was determined after shaking the mixture of 0.05 g TiO$_2$ nanoparticles and diluted NaNO$_3$ solution in dark for 24 h.

The Brunauer-Emmett-Teller (BET) surface area was determined from nitrogen adsorption-desorption isotherms collected at 77 K with a surface area and porosity analyzer (ASAP 2020, Micromeritics Co., USA). Prior to analysis, the xerogel sample was firstly vacuum-dried at 35 °C for 48 h and then was degassed at 80 °C for 48 h. The TiO$_2$ nanoparticles were degassed at 100 °C for 24 h.

Particle size analysis was conducted with a static laser scattering analyzer (Winner 2008, China) with a detection range of 50 nm to 2000 μm. All suspensions of the samples were sonicated for 30 min with an ultrasonic oscillator (200 W and 40 kHz, KQS200DE, Kun Shan Ultrasonic Instruments Co., Ltd, China) prior to analysis.

The phase composition and crystallinity of the TiO$_2$ were studied by an X’TRA (ARL Co., Switzerland) XRD diffractometer using Cu Kα ($\lambda=1.5406$ Å) radiation. The transmission electron microscopy (TEM) was conducted on a JEM-100CXII electron microscope (JEOL, Japan). Carbon-coated copper grids were used as sample holders.

The UV-Vis spectra of the TiO$_2$ samples were recorded using an integrating sphere (ISR2600, Shimadzu, Japan) attached to a Shimadzu 2700 UV-Vis spectrometer with BaSO$_4$ as the reference.

An X-ray photoelectron spectrometer (PHI 5000 Versa-Probe, ULVAC-PHI Co., Japan) with an Al Kα radiation (1486.6 eV) source was employed for composition analysis. The binding energies were adjusted with the adventitious C1s of binding energy at 284.6 eV. Element contents were determined with an elementary analyzer (CHN-O-Rapid, Heraeus Co., Germany).

2.3 Adsorption experiments
Adsorption experiments were conducted in shaking conical flasks at 150 r/min for 72 h, which contained TiO$_2$ xerogel of exact weight and dye solutions of various concentrations. The pH of the solution was adjusted with 0.1 mol/L NaOH or HNO$_3$. After adsorption equilibrium was reached, the TiO$_2$ xerogel was separated from the solution by centrifuga-