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Immobilization of S, N-codoped TiO_2 nanoparticles on glass beads for photocatalytic degradation of methyl orange by fixed bed photoreactor under visible and sunlight irradiation

Hajar Khalilian [a,*], Mohsen Behpour [a], Vajiheh Atouf [a], Seyed Nezam Hosseini [b]

[a] Department of Analytical Chemistry, Faculty of Chemistry, University of Kashan, 87317-51167 Kashan, Iran
[b] Pasteur Institute of Iran (IPI), Tehran 13164, Iran

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Abstract

This research focused on photodegradation of organic compound by a fixed bed photoreactor. The photoreactor consists of a cylindrical glass tube, was filled by TiO_2 coated glass beads codoped with sulfur and nitrogen (S, N). The photoactive layer of TiO_2 was deposited on glass beads using the sol–gel dip-coating technique. The S, N-codoped TiO_2 film after thermal treatment at 500 °C for 1 h, was characterized by XRD, XPS, SEM and EDX analyses. The XRD analyses exhibited an anatase structure of TiO_2 with particle size about 35 nm. The photocatalytic activity was determined by degradation of methyl orange (MO) (7 mg/L, pH 2). The effective parameters of photocatalyst efficiency were investigated in laboratory and large volume scales under visible and sun light irradiations. The results showed that visible-light photocatalytic activity of TiO_2 was extremely increased through adding thiourea (Tu) as a source of nitrogen and sulfur into TiO_2 sol, which conducted to degradation of MO solution up to 95% in sunlight irradiation after only 2 h. Overall, the photoreactor of immobilized S, N-codoped TiO_2 on glass beads was found to be a promising technology for water treatment.

Keywords: Reactor design; Photocatalytic degradation; X-ray photoelectron spectroscopy (XPS); Sunlight irradiation

1. Introduction

In the future, reuse of treated water is the best solution for managing of water crisis in countries that have water leakage problem. Numerous concepts have been developed for removal of organic and inorganic toxic contaminants from water and wastewater. One of the developed and promising technology is TiO_2 photocatalytic degradation, which destructed the organic compound pollutants and final products are CO_2 and H_2O (Fox and Dulay, 1993; Hoffmann et al., 1995). Eliminating pollutants from water and wastewater by the TiO_2 photocatalyst has been discussed in the literature since 1970s (Frank and Bard, 1977). In general, TiO_2 as a catalyst for photocatalytic degradation process, can be divided into two forms of suspension (slurry) and immobilized on inert-solid supports (Lee et al., 2003).

Bahnemann's work presented several reactor concepts for the solar photocatalytic water treatment such as: parabolic trough reactor (PTR), thin film fixed bed reactor (TFFBR), compound parabolic collecting reactor (CPCR) and double skin sheet reactor (DSSR). It was observed that in every case, the efficiency of the TFFBR was superior to

* Corresponding author.
E-mail address: h.khalilian316@gmail.com (H. Khalilian).

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that of the PTR in the same conditions (Bahnemann, 2004). So the development of thin film fixed bed photoreactors has attracted special interest for large-scale wastewater treatment (García et al., 2010). Also a review of all types of photoreactors are reported in Fujishima's work (Ochiai and Fujishima, 2012). Some general types of fixed catalyst reactors include: fixed bed reactors, fluidized bed reactor, photocatalytic reactor with a rotating disk and spiral photoreactor system (Wu et al., 2012). An appropriate photoreactor condition presented by (Hanel et al., 2010), according to the presented characteristics, the fixed bed photoreactor has been chosen as the best photoreactor.

In the fixed-bed systems, the photocatalyst is immobilized on a support and many materials for support have been studied, including glass, glass microspheres, sand grains, steel net, steel plates, ceramics such as alumina, perlite, poly (dimethylsiloxane) and (Chan et al., 2001; Hosseini et al., 2007; Jiang et al., 2013; Kabra et al., 2004; Niu et al., 2006; Sakthivel et al., 2002; Yao et al., 2009). The characterizations of an appropriate support is mentioned in the Miranda-Garcia's work (García et al., 2011). According to the mentioned characterizations, the glass bead has been chosen as the best support.

To eliminate water contaminations, beside immobilized TiO_2 photocatalysis, a UV source is required; which can be sunlight or artificial UV source. For high-volume water treatment, using the sun light is more affordable than UV lamps (Bokare et al., 2013; Rodriguez et al., 2012). However, wide band gap of titanium (3.2 eV) was a restriction for photocatalytic applications, that does not cover main part of solar spectrum; for an efficient use of solar energy, titanium band gap should be less than 3 eV (Etacheri et al., 2012).

To improve the photocatalytic activity of TiO_2 in the solar spectrum, many attempts have been made such as doping other atoms to the titanium structure, that decrease the absorption edge and improve degradation efficiency (Bokare et al., 2013; Rengifo-Herrera and Pulgarin, 2010).

The purpose of this paper is evaluating performance of solar photocatalytic degradation of MO at low concentrations (7 mg/L) as the pollutant model of water. So in this work at first, the sol–gel dip-coating technique was used for S, N-codoped TiO_2 immobilization on glass beads, then the photocatalytic activity was tested in a fixed-bed photoreactor. Afterwards, the effective parameters of photocatalyst efficiency were investigated in laboratory scale under visible and sun light irradiation. Finally, the performance of photoreactor for MO photocatalytic degradation in large volume was studied under sun light irradiation.

2. Experimental

2.1. Preparation of TiO_2 precursor sol

All the chemicals were purchased from Merck and used as received without any further purification. The glass beads used as a support material (with 0.5 mm diameter) and the deionized (DI) water which used for preparing solutions, was achieved by an ultra-pure water system, type smart-2-pure, TKA, Germany. The TiO_2 sol was obtained by hydrolyzing tetrabutyl ortho titanate (TBOT) in acidic conditions. In this method, 2.5 mL TBOT, 10 mL ethanol and 2.5 ml acetylacetone (acac) were mixed. Acac which acts as chelating agent in the solution, is added to can prevent from the precipitation of the TBOT. By magnetic stirring with magnetic force for 30 min, the clear and yellow solution was achieved. Then 2.0 mL of DI water was added to the above solution and the sample was magnetically stirred for more than 10 min. The pH of the sol was adjusted at about 1.8 by adding concentrated HCl solution. Tu (CH_4N_2S) was used as a source of nitrogen and sulfur that can transfer the photocatalytic activity of TiO_2 to visible light. In our previous work (Behpour and Atouf, 2012), the amount of Tu/TiO_2 has been adjusted to 0.25 g, then added into prepared sol. Inclusion of Tu/TiO_2 in the sol leads to the photocatalytic activity improvement of the material due to the synergetic effect between TiO_2 sources and porosity by eliminating organic compound during calcination. In addition pore size and pore volume were increased. After stirring the sol for 2 h, the stable sol was obtained. This solution is prepared for deposition on substrate. For the activity comparison, pure TiO_2 and TiO_2 doped with Tu films were prepared by the same procedures. The sample with optimum ratio of Tu has been shown as Tu–TiO_2.

2.2. Precipitation of thin films

Before coating operations, the beads were cleaned by detergent and etched for 24 h in diluted hydrochloric acid, then washed completely with deionized water and dried at 105 °C for 2 h. Dip coating technique was used to immobilize the TiO_2 on the glass beads. Subsequently, they were dried at 60 °C in an oven for 4 h and then calcinated at 500 °C for 1 h Fig. 1.

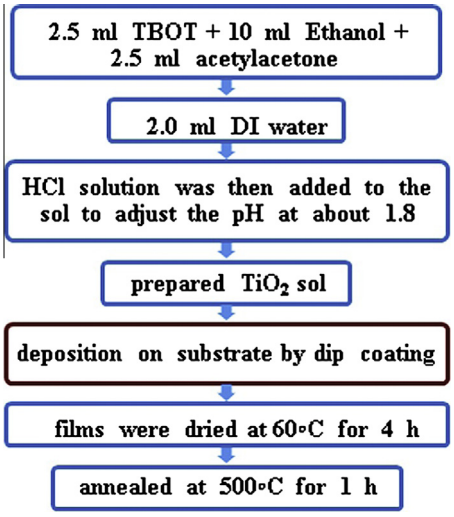

Fig. 1. Preparations of TiO_2 solution by sol–gel method.