Journal of Environmental Management xxx (2018) 1–8

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

A magnetically separable and recyclable Ag-supported magnetic TiO_2 composite catalyst: Fabrication, characterization, and photocatalytic activity

Woo Jin Chung [a, 1], Dinh Duc Nguyen [a, 1], Xuan Thanh Bui [b], Sang Woo An [c], J. Rajesh Banu [d], Sang Moon Lee [a], Sung Su Kim [a], Dea Hyun Moon [a], Byong Hun Jeon [e], Soon Woong Chang [a, *]

[a] Department of Environmental Energy Engineering, Kyonggi University, 94 San, Iui-dong, Youngtong-gu, Suwon-si, Gyeonggi-do, 16227, Republic of Korea
[b] Faculty of Environment and Natural Resources, University of Technology, Vietnam National University, Ho Chi Minh City, Vietnam
[c] Wizinnotek Co. Ltd, 452 Nohae-ro, Nowon-gu, Seoul, 01762, Republic of Korea
[d] Department of Civil Engineering, Regional Campus of Anna University, Tirunelveli 627007, Tamil Nadu, India
[e] Department of Earth Resources and Environmental Engineering, Hanyang University, Seoul 04763, Republic of Korea

ARTICLE INFO

Article history:
Received 30 September 2017
Received in revised form
12 February 2018
Accepted 16 February 2018
Available online xxx

Keywords:
Ag-supported magnetic TiO_2 catalyst
Photocatalytic activity
Photocatalytic degradation
Methyl orange dye
Recyclability

ABSTRACT

In this study, a magnetically separable, highly active, and recyclable photocatalyst was synthesized by physico-chemical incorporation of Ag, TiO_2, and Fe_3O_4 into one structure. The physical and chemical properties of the catalysts were evaluated by X-ray diffraction, X-ray fluorescence spectrometry, scanning electron microscopy, field emission transmission electron microscopy, energy dispersive X-ray spectroscopy, and diffuse reflectance spectroscopy. The Ag-supported magnetic TiO_2 composite demonstrated desirable properties and features such as a narrow band gap of 1.163 eV, modifiable structure, and high degradation efficiency. The activity and durability of the synthesized photocatalyst in the degradation of methyl orange (MO) in aqueous solutions under visible light irradiation and different experimental conditions were evaluated and compared to those of commercial TiO_2 and Ag/TiO_2 composites. It was found that the synthesized composite showed a much higher MO photodegradation efficiency than the other composites under visible light irradiation. Moreover, it exhibited a high photocatalytic activity and was recoverable and durable; its photocatalytic efficiency in MO removal was consistently higher than 93.1% after five reuses without any evident signs of deactivation. Thus, the developed photocatalyst is a very promising material for practical applications in environmental pollution remediation.

1. Introduction

Significant attempts have been made over the past several decades to improve wastewater treatment and reclamation technologies with remarkable results (Neoh et al., 2016; Nguyen et al., 2014). Unfortunately, these technologies are expensive and still incapable of thoroughly handling recalcitrant contaminants in wastewater such as estrogenic chemicals, pharmaceuticals, antibiotics, pesticides, and dyes (Aziz et al., 2012; Mohapatra et al., 2014; Teixeira et al., 2017). Therefore, one of the most important objectives related to the prevention and control of environmental pollution is the development of a suitable solution that can be applied multiple times to quickly treat these recalcitrant pollutants in water and wastewater.

Recently, advanced oxidation processes (AOPs) have become attractive methods to achieve a cleaner environment. In particular, photocatalytic processes generate a variety of strong reactive oxidation species ($OH^{\bullet}$, $O_2^{\bullet-}$ $O_2^{\bullet-}$, H_2O_2, etc.) as a result of excitation with ultraviolet (UV) and/or visible light (Dewil et al., 2017; Sillanpää et al., 2018). Generally, these species can completely oxidize and destroy environmental pollutants and a wide range of dissolved organic pollutants in wastewater, converting them into carbon dioxide, water, inorganic compounds, or biodegradable intermediates that can be degraded easily via biological processes

* Corresponding author.
E-mail addresses: nguyensyduc@gmail.com (D.D. Nguyen), swchang@kyonggi.ac.kr (S.W. Chang).
[1] These authors contributed equally to the manuscript.

https://doi.org/10.1016/j.jenvman.2018.02.064
0301-4797/

(Jaafar et al., 2012; Mohapatra et al., 2014; Neoh et al., 2016). Therefore, it is necessary to develop materials that exhibit high photocatalytic activity under solar irradiation. Additionally, photocatalytic processes have been reported in the literature as being chemically stable and environmentally friendly (Zhang et al., 2016).

Titanium dioxide (TiO_2) has been extensively studied and utilized for the photodegradation and mineralization of various organic pollutants since Fujishima and Honda reported the photosplitting of water in 1972 (Fujishima and Honda, 1972). Owing to the numerous desirable attributes such as high photocatalytic activity, stability, resistance, non-toxicity, and widespread availability, TiO_2 has been recognized as one of the most promising and efficient photocatalysts (Aziz et al., 2012). However, TiO_2 also has a high band gap energy of ~3.2 eV and a high photoelectron-hole pair recombination rate. This limits its photocatalytic activity, since photoexcitation can only occur in the UV wavelength region, which only accounts for less than 6% of the total solar spectrum (Khaki et al., 2017; Narayana et al., 2011). Therefore, research efforts directed toward the production of high-activity photocatalysts that can absorb UV and visible light (Yan et al., 2017) are essential in order to utilize solar energy. Furthermore, the activity of photocatalysts after recovery and recycling should also be considered.

Photocatalysts that are commonly used in the treatment of water pollutants can be classified as either suspended (powder) or immobilized (supported) photocatalysts. Suspended photocatalysts are more effective in treating pollutants compared to those immobilized on carriers (Yan et al., 2017). However, suspended photocatalysts need to be separated and recovered from treated water to avoid secondary pollution, which can increase the process complexity and cost.

In order to address the abovementioned concerns and enhance the photocatalytic activity under both UV and visible light irradiation, efforts have been made to develop TiO_2-based variants with superior properties and high separability. With regard to separation and reuse after photocatalysis/photocatalytic degradation, magnetic TiO_2-based photocatalysts have recently generated interest (Aziz et al., 2012; Jia et al., 2017; Xu et al., 2007). Generally, such photocatalytic composites feature TiO_2 and a magnetic material, which can be recovered easily by applying an external magnetic force (He et al., 2012). Magnetic composites featuring Fe_3O_4, gamma-Fe_2O_3, or $NiFe_2O_4$ cores and a TiO_2 shell have been extensively reported as their combination with TiO_2 has solved problems associated with photocatalyst recovery (Álvarez et al., 2010; Jia et al., 2017; Rana et al., 2005; Yu et al., 2011). In addition, photocatalysts featuring magnetic TiO_2, such as TiO_2/Fe_3O_4 and $TiO_2/SiO_2/Fe_3O_4$, have already been tested and applied for the photodegradation of pollutants (Hu et al., 2011; Shi et al., 2011a). Unfortunately, these magnetic TiO_2 catalysts still have drawbacks like low photocatalytic activity and nanosecond-scale charge carrier lifetimes (Xu et al., 2005).

In order to improve their activity, photocatalysts have been loaded with different metals and/or non-metals. Among the various metals used for this purpose, silver (Ag) is the most attractive in terms of photocatalytic performance, economics, ease of preparation, the lifetimes of the electron-hole pairs, and antimicrobial activity (Jia et al., 2017; Zhan et al., 2014). Lai et al. (2010) reported that Ag/TiO_2 shows improved photocurrent generation, while Li et al. (2009) and Albiter et al. (2015) demonstrated that a Ag/TiO_2 sample with an appropriate Ag content showed high photocatalytic activity because of a high rate of formation of photoinduced electron-hole pairs and inhibited recombination thereof, which facilitated pollutant degradation. Recently, Zhao et al. (2017) reported that Ag/TiO_2 shows better surface plasmon resonance and photocatalytic performance than pure TiO_2.

Therefore, it is reasonable to expect that a magnetic photocatalyst obtained through the incorporation of three heterogeneous components, Ag, TiO_2, and Fe_3O_4, may display superior photocatalytic properties, thus leading to improved photocatalytic activity and quantum size (photocurrent density, band gap energy, flat band potential), in addition to easy recovery by magnetic separation, and stability. Although the feasibility of a three-component $Ag/TiO_2/Fe_3O_4$ composite has been investigated and evaluated, an effective reaction strategy to implement such a composite still needs to be developed and elucidated (Zhang et al., 2016).

Consequently, in this study, a Ag-supported magnetic TiO_2 nanoparticle catalyst was synthesized from Ag, TiO_2, and Fe_3O_4 (denoted as $Ag/TiO_2/Fe_3O_4$ hereafter), and its physicochemical properties and features were thoroughly examined using various analytical techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), and diffuse reflectance spectroscopy (DRS). Then, its photocatalytic activity in the degradation of methyl orange (MO) under visible light irradiation was evaluated, in addition to its recyclability and recoverability. The relationship between the physicochemical properties and photocatalytic activity of the synthesized composite has also been discussed. In addition, the effect of irradiation time, solution pH, and contaminant (MO dye) concentration in an aqueous solution on the photocatalytic efficiency (decolorization of MO) under visible light irradiation was carefully evaluated.

2. Experimental methods

2.1. Preparation of photocatalysts

Silver nitrate ($AgNO_3$, 5.1 g) was dissolved in 500 mL of distilled water. Ammonium hydroxide (NH_4OH, 0.1 M) was added dropwise to the $AgNO_3$ solution with vigorous stirring until it turned colorless. This was followed by the addition of 100 mL of a 0.1 M glucose ($C_6H_{12}O_6$) solution, 50 mL of a 0.2 M sodium dodecylsulfate (SDS) solution, and 75 mL of distilled water. Subsequently, a 0.1 M sodium hydroxide (NaOH) solution was added to adjust the pH to 11.5 and the reaction mixture was stirred for 10 min. The prepared Ag nanoparticles were used for further experiments without any additional modifications. The Ag nanoparticles (0.1 g) were rinsed thrice with ethanol and then suspended in ethanol (20 mL) under sonication for 2 h. The Ag nanoparticles were then resuspended in distilled water (100 mL) and the mixture was acidified with HCl (0.5 M, 1.10 mL) The synthetic procedures of these catalysts were modified based on the methods described by Wan et al. (2011) and Shi et al. (2011b).

Ag/TiO_2 nanoparticles were prepared from Ag nanoparticles in water/oil (W/O) microemulsions consisting of hexadecyltrimethylammonium bromide ($[(C_{16}H_{33})N(CH_3)_3]Br$, CTAB) as the surfactant, 1-pentanol as the co-surfactant, and hexane as the oil phase. In a typical experimental procedure, the microemulsion was prepared by dissolving 1.0 g of CTAB in 15 mL of hexane and 1 mL of 1-pentanol, and then stirring vigorously for 30 min until it became homogeneous. Commercial TiO_2 (5 g, P25, Degussa Crop.) with a composition of 75% anatase and 25% rutile, a particle size of 22.3 nm, and a surface area of ~55 m^2/g, was then added to the microemulsion, and the solution was sonicated for 30 min. The reaction was left to stir for 10 h and the Ag/TiO_2 nanoparticles were subsequently separated by centrifugation, dried at 100 °C for 24 h in air, and calcined at 300 °C in air for 2 h. This provided the Ag/TiO_2 nanoparticle samples.

Magnetite nanoparticles as a support material were prepared using a coprecipitation method. Ferrous sulfate heptahydrate

Please cite this article in press as: Chung, W.J., et al., A magnetically separable and recyclable Ag-supported magnetic TiO_2 composite catalyst: Fabrication, characterization, and photocatalytic activity, Journal of Environmental Management (2018), https://doi.org/10.1016/j.jenvman.2018.02.064