ORIGINAL PAPER

Preparation of a filter bed coupled with Mn-TiO_2/ZnO nanocomposite for the treatment of micro-pollutants in municipal wastewater

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Date of submission: 19 Mar 2018, ***Date of acceptance:*** 03 Jul 2019

ABSTRACT

Technical advancement is urgently required for the degradation of micro-pollutants in municipal wastewater. The present study aimed to describe the preparation of a filter-bed Mn-TiO_2/ZnO nanocomposite and degradation of micro-pollutants in real-time municipal wastewater obtained from Kesare wastewater treatment plant in Mysore district, India. Activated carbon and sand were used for the preparation of the filter bed, and activated carbon was prepared using agricultural wastes (coconut shells). Meanwhile, the visible light-responsive Mn-TiO_2/ZnO composite was prepared using the mild sol-gel technique. The composites were characterized by scanning electron microscopy, Fourier-transform infrared spectroscopy, X-ray diffraction, and photocatalytic techniques. High crystallinity, considerable shift in the band gap energy, and adequate photocatalytic activity under the visible light range were observed. In addition, the filter bed coupled with the Mn-TiO_2/ZnO nanocomposite functioned efficiently in the degradation of the common pollutants under LED irradiation as the driving source of energy.

Keywords: Sol-gel, Composite, Sewage, Filter bed, Photocatalysis, Adsorption

Introduction

Semiconductor photocatalysis is a promising technology for wastewater treatment, which is associated with the production of no residues and secondary pollutants. In general, photocatalysis is defined as the process of generating minerals through the degradation of simple organic compounds in water and air in the presence of a catalyst. Titanium dioxide (TiO_2) has been widely used in wastewater purification technologies owing to properties such as strong oxidization power, cost-efficiency, and long-term stability against photochemical corrosion.[1-4] Meanwhile, zinc oxide (ZnO) is considered beneficial for similar purposes with its unique optical and electrical properties[5] and similarity to the physicochemical properties of TiO_2.[6, 7] The band gap of TiO_2 and ZnO is 3.2 and 3.37 eV, respectively, which limits their application since they could only be active under ultraviolet (UV) light irradiation.[8, 9] Therefore, several methods have been proposed to shift the optical sensitivity of TiO_2 and ZnO from UV to the visible-light range for the efficient use of solar energy; some of these methods include element doping, metal deposition, surface sensitization, and the coupling of composite semiconductors.[10-14] In addition, it is possible to enhance the activity of TiO_2 photocatalysts through ZnO coupling.[15] Among various coupled semiconductor composites, several studies have been focused on the integration of TiO_2 with other metal oxides, such as ZnO,[16] SnO_2,[17] Fe_2O_3,[18] ZrO_2,[19] Cu_2O,[20] WO_3,[21] SiO_2,[22] and MoO_3.[23] Moreover, it has been reported that TiO_2/ZnO nanocomposites have potent physical and chemical interactions with adsorbed species, as well as a variety of applications in gas sensing materials, thermoelectric materials, dye-sensitized solar cells, piezoelectric devices, and semiconductor photocatalysts.[16, 24, 25]

Several approaches have been developed for the production of TiO_2/ZnO composites using various precursors of titania and zinc; such examples are sol-gel, solvo/hydrothermal, and co-precipitation techniques. The structure and physiochemical properties of TiO_2/ZnO composites could be affected by changes in the

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Citation: Gopi M, Shivaraju HP. Preparation of a filter bed coupled with Mn-TiO_2/ZnO nanocomposite for the treatment of micro-pollutants in municipal wastewater. J Adv Environ Health Res 2019; 7(3): 187-196

temperature, calcination process, pH, stirring speed, water-to-precursor ratio, and reagent concentration. Depending on their size, shape, and crystallographic structure, TiO_2/ZnO systems exhibit variable physiochemical properties.[26] Moreover, ZnO has a slightly more negative band gap energy compared to TiO_2, which contributes to the injection of electrons from the conduction band of ZnO to TiO_2, favoring electron-hole separation.[27] Therefore, the incorporation of these materials into a combined structure is of utmost importance considering that the resultant products may possess improved physiochemical properties. In a study in this regard, Abdel Aal *et al.* prepared TiO_2/ZnO nanopowders with various TiO_2/ZnO ratios using the hydrothermal method for the photocatalytic degradation of 2-chlorophenol. The obtained results indicated the increased degradation efficacy of the TiO_2/ZnO composite with the ratio of 90:10.[28] In another study, ZnO nanoparticles were coated on titania nanotubes (TNT) and assessed in terms of the photocatalytic degradation of rhodamine B under UV irradiation. The findings clearly demonstrated that the ZnO-TNT nanocomposite exhibited superior degradation efficacy over pure TNTs, P25, and ZnO.[29] On the other hand, Liao *et al.* investigated the photocatalytic degradation of methyl orange using TiO_2/ZnO composite nanoparticles, reporting that the TiO_2/ZnO composite nanoparticles exhibited more prominent photoactivity compared to pure TiO_2.[16]

The present study aimed to describe the preparation of a filter bed coupled with a Mn-TiO_2/ZnO nanocomposite and evaluate its application in the degradation of micro-pollutants in real-time municipal wastewater within the visible range. Filtration was employed as the preliminary treatment for the removal of the suspended particles in sewage so as to enhance light penetration.

Materials and Methods

Synthesis of photocatalytic nanocomposites

The photocatalytic Mn-TiO_2/ZnO nano-composite was prepared using the mild sol-gel technique, with TiO_2 and ZnO as the precursors. During the preparation of the Mn-TiO_2/ZnO nanocomposite, TiO_2 was added to NaOH (1 M) with constant stirring on a magnetic stirrer. Following that, approximately 0.1 mg of $MnSO_4$ was dissolved in double-distilled water and added to the homogenous mixture drop-wise as a source of Mn dopant, forming solution A. Afterwards, ZnO was dissolved in NaOH to form solution B, which was slowly added to solution A under magnetic stirring (300-450 rpm) for 12 h at room temperature, followed by aging in darkness for 24 h. At the next stage, the aqueous mixture was washed repeatedly with deionized water and dried in a dust-free hot air oven at the temperature of 50 °C. The obtained powder was treated in a dust-free muffle furnace using a silica vessel provided with a lid at the temperature of 450 °C for 2 h. Finally, it was quickly quenched to the room temperature using a cooling system in order to obtain the desired crystallinity and active surface morphology. Fig. 1 illustrates the schematic preparation of the Mn-TiO_2/ZnO nanocomposite using the mild sol-gel technique.

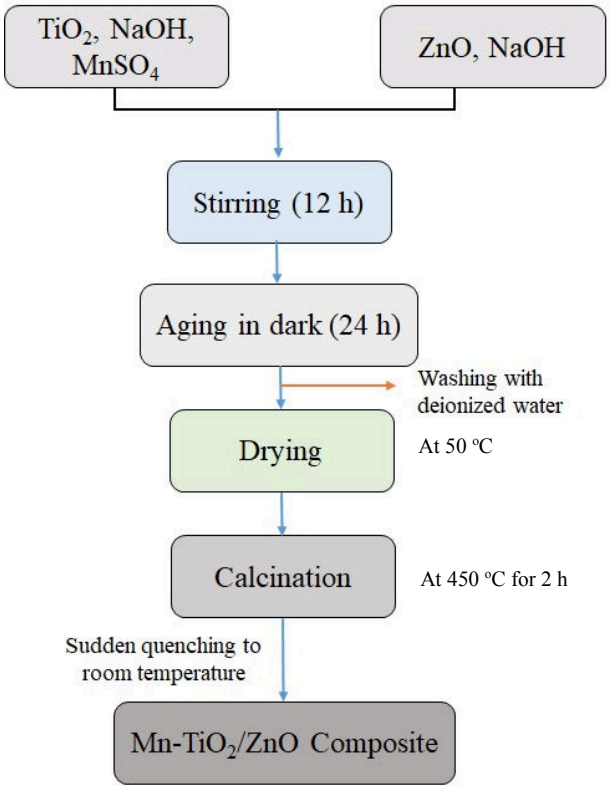

Fig. 1. Schematic of Mn-TiO_2/ZnO composite preparation through sol-gel process

SEM

The textural features of the prepared nanocomposite were investigated using SEM. As can be seen in Fig. 6, the nanocomposite demonstrated specific morphological changes, as well as a trend of surface particle agglomeration. This is consistent with the results obtained by Katarzyna *et al.*[37] Further particles with a granular morphology are also illustrated in Fig. 6.

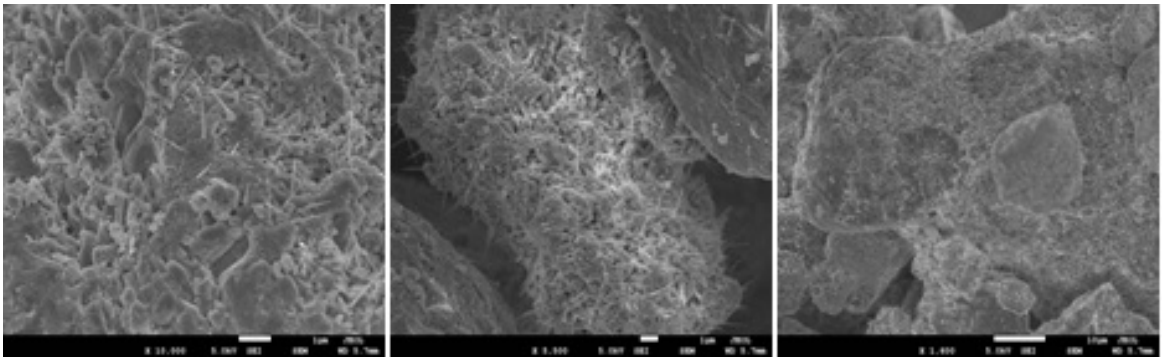

Fig. 6. SEM images of Mn-TiO_2/ZnO nanocomposite

Brunauer-Emmett-Teller (BET) surface area

The catalytic activity of the materials was determined based on several factors, such as the band gap energy and surface area. Surface area significantly influences the catalytic activity of every material. In the present study, the Brunauer-Emmett-Teller (BET) surface area of 105.6 m^2 g^{-1} was observed in the prepared composite, which was in line with the size and morphology of various nanoparticles in the TiO_2/ZnO composite. In addition, the pore volume of 0.149 cm^3 g^{-1} and pore size of 5.36 nanometers were obtained for the Mn-TiO_2/ZnO composite.[39]

Efficiency of the filter bed

Fig. 7 depicts the treatment efficacy of the filter bed utilized for the filtration of the real-time municipal wastewater collected from Kesare wastewater treatment plant located at Mysore, Karnataka (India). The initial characterization of the municipal wastewater is presented in Table 1. According to the findings, the suspended particles in wastewater inhibited the penetration of light, resulting in the hindrance of the photocatalytic process.

Therefore, the removal of the suspended solids was unavoidable prior to photocatalysis. The adsorption of the suspended particles by sand and activated carbon in the filter bed resulted in the removal of 92.2% of the suspended solids from the municipal wastewater. Furthermore, filtration was employed as a primary treatment technique for the removal of the suspended particles, which led to the degradation of micro-pollutants such as COD (88.43%), nitrate (77.03%), nitrite (40.42%), total dissolved solids (4.25%), and phosphate (3.97%) under the same experimental conditions. This could be explained by the elevated degradation efficacy of COD, nitrate, and nitrite due to the adsorption of the respective ions by activated carbon.[40-42]

In a study in this regard, Hassan and Azeema reported the possible mechanisms involved in the adsorption of ions by activated carbon. Accordingly, the adsorption sites in activated carbon could be divided into two major types, including graphene layers, which were hydrophobic in nature, and hydrophilic oxygen functional groups. As a result, the adsorption of anions occurred either by the p-orbitals of the graphene layers or through an ion exchange mechanism by the functional groups.[41-43]

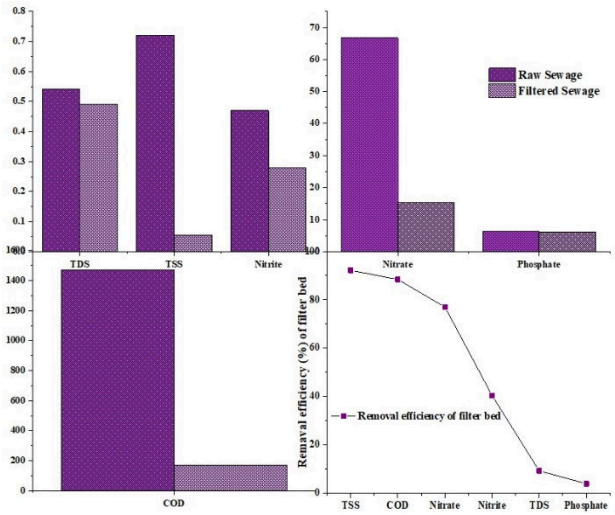

Fig. 7. Treatment efficacy of filter bed

Photocatalytic activity

The photocatalytic activity of the prepared nanocomposite was assessed using an aqueous solution of the model dye (methylene blue) with tungsten light irradiation for 4 h. Simultaneously, blank experiments were also maintained without the addition of photocatalysts (Fig. 8). The results of the blank experiments indicated that methylene blue could not be degraded without the addition of photocatalysts. Moreover, these results indicated the degradation efficacy of 86.3% with tungsten light irradiation, which was attributed to the band tuning toward the visible range, as well as the increased surface area, and increased pore size of the prepared nanocomposite.

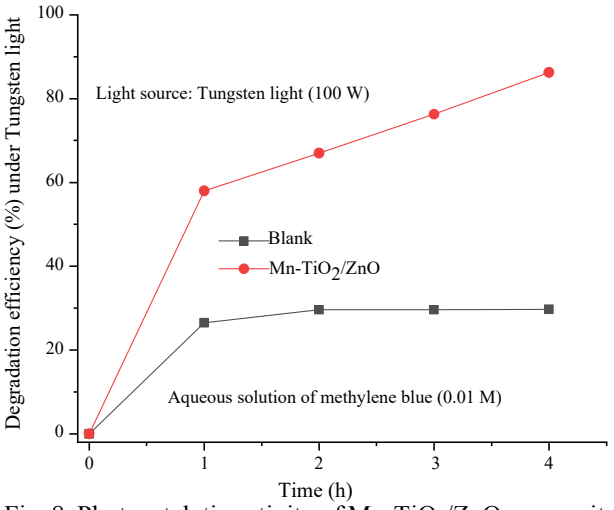

Fig. 8. Photocatalytic activity of Mn-TiO_2/ZnO composite with visible light source

Photocatalytic treatment of real-time wastewater

In the current research, the contribution of the Mn-TiO_2/ZnO nanocomposite to the photocatalytic degradation of the micro-pollutants in real-time municipal wastewater was investigated with various irradiation sources (Fig. 9).

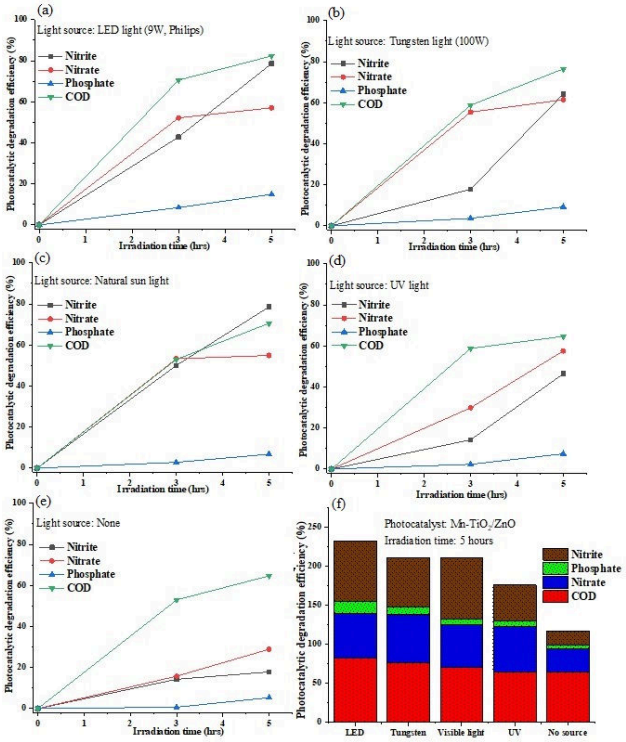

Fig. 9. Photocatalytic degradation efficacy of Mn-TiO_2/ZnO composite in degradation of micro-pollutants with various irradiation sources

In addition, the experiments were conducted in the absence of irradiation using a photocatalyst, and the obtained results clearly implied that the micro-pollutants were partially degraded in the absence of the irradiation source. This could be due to the enhanced surface area and porous structure of the composite. Moreover, the potential degradation of the pollutants was observed with the LED light source, which could be attributed to the synergistic effects of TiO_2 and ZnO in the nanocomposite with the desired properties. Therefore, it could be concluded that the co-existence of TiO_2[24] and ZnO improved the overall degradation rate of the micro-pollutants in the municipal wastewater by promoting the

oxide systems: Comprehensive characterization and tests of photocatalytic activity. Materials 2018; 11(5): 1-19.
38. Praveen P, Viruthagiri G, Mugundan S, Shanmugam N. Sol-gel synthesis and characterization of pure and Manganese doped TiO_2 nanoparticles- a new NLO active material. Spectrochim Acta A Mol. Biomol. Spectrosc 2014; 120: 548-57.
39. Wang L, Fu X, Han Y, Chang E, Wu H, Wang H, *et al.* Preparation, characterization, and photocatalytic activity of TiO_2/ZnO nanocomposites. J Nanomater 2013; 2013: 1-6
40. Abdel-Gawad SA, Mohamed SM, Abdel Aziz HM. Adsorption study for chemical oxygen demand removal from aqueous solutions using alginate beads with entrapped activated carbon. J Indian Water Resour Soc 2017; 37(4): 8-16.
41. Hassan AH, Abdel ASM. Removal of nitrate and nitrite anions from wastewater using activated carbon derived from rice straw. J Environ Anal Toxicol 2016; 6(1): 346.
42. Lida T, Amano Y, Machida M, Imazeki F. Effect of surface property of activated carbon on adsorption of nitrate ion. Chem Pharm Bull (Tokyo) 2013; 61(11): 1173-7.
43. Giles CH, MacEwan TH, Nakhawa SN, Smith A. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. J Chem Soc 1960: 3973-93.