Water Research 94 (2016) 363–370

Contents lists available at ScienceDirect

Water Research

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

Highly recoverable TiO_2–GO nanocomposites for stormwater disinfection

Gen Wang [a, b], Wenjun Feng [c], Xiangkang Zeng [a], Zhouyou Wang [a], Chuanping Feng [b], David T. McCarthy [c], Ana Deletic [c], Xiwang Zhang [a, *]

[a] Department of Chemical Engineering, Faculty of Engineering, Monash University, Clayton, VIC, 3800, Australia
[b] School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing, 100083, China
[c] Environmental and Public Health Microbiology Laboratory. (EPHM Lab), Department of Civil Engineering, Faculty of Engineering, Monash University, Clayton, VIC, 3800, Australia

A R T I C L E I N F O

Article history:
Received 21 November 2015
Received in revised form
10 February 2016
Accepted 29 February 2016
Available online 3 March 2016

Keywords:
TiO_2
Graphene oxide
Accelerated sedimentation
Stormwater
Disinfection

A B S T R A C T

A highly recoverable titanium dioxide-graphene oxide (TiO_2–GO) composite was developed by a facile method of ultrasonic treatment of GO nanosheets and TiO_2 nanoparticles, which should overcome the separation problem of nanosized TiO_2 from treated water. Separability of the prepared samples was systematically investigated by gravity settling experiments. The samples' photocatalytic activity for stormwater disinfection was also studied under the irradiation of a solar simulator. The results demonstrated that TiO_2–GO showed high efficient separability due to its accelerated settling behaviour. Zeta-potential analysis showed that the accelerated sedimentation of the catalyst was attributed to the aggregation of TiO_2–GO resulting from the electrostatic attraction between TiO_2 and GO. The TiO_2–GO composite with a mass ratio of 100:2 (TiO_2-2%GO) achieved both higher separability and good photocatalytic activity for stormwater disinfection. Its suspension became clear (turbidity < 50 NTU) after 8 h of sedimentation, while 99.5% of *E.coli* were deactivated in 90 min. The TiO_2–GO composite exhibited excellent durability; no apparent change in the separability of TiO_2-2%GO was observed after 10 treatment cycles (15 h in total), while only slight decrease in the photocatalytic activity was noted. In conclusion, the developed TiO_2–GO composite showed promising results for stormwater disinfection.

1. Introduction

There is a high demand, fostered by growing world population and increasing water pollution, for non-traditional water resources such as wastewater and stormwater. In particular, stormwater, which is usually of better quality than wastewater, holds great potential as an alternative water resource due to higher level of public acceptance (Feng et al., 2012). However, the presence of pathogens in stormwater needs to be addressed as it presents risk to human health (Wong et al., 2013). In recent years, solar photocatalysis has shown a great potential as a low-cost and environmentally friendly technology for water disinfection (Chong et al., 2010; Malato et al., 2009; Spasiano et al., 2015). Among solar photocatalytic technologies, heterogeneous photocatalysis employing nanosized semiconductor catalysts (such as TiO_2, ZnO, WO_3, MoO_3, ZrO_2, SnO_2, CuO, etc.) has been demonstrated to be very effective for bacterial removal and refractory organics degradation (Augugliaro et al., 2006; Chong et al., 2010). Among these semiconductors, TiO_2 nanoparticle is the most commonly studied photocatalyst for water purification, owing to its high catalytic efficiency and safety, excellent physio-chemical stability, and low cost (Chong et al., 2010; Malato et al., 2009; Spasiano et al., 2015). In a heterogeneous photocatalytic purification process, TiO_2 nanoparticles are usually dispersed in the liquid suspension to form a photolysis slurry system, in order to improve the ratio of active catalytic surface to reaction volume to provide high photocatalytic efficiency (Augugliaro et al., 2006; Spasiano et al., 2015). However, due to the ultra-small particle size and polydispersity, separation of nanosized TiO_2 particles from treated water is extremely difficult, increasing the complexity and cost of the water treatment process.

In order to address the separation problem, insensitive efforts have been devoted to immobilizing TiO_2 nanoparticles on different kinds of substrates, such as polymer beads (Zhao et al., 2011),

* Corresponding author.
E-mail address: xiwang.zhang@monash.edu (X. Zhang).

http://dx.doi.org/10.1016/j.watres.2016.02.067
0043-1354/

membranes (Leong et al., 2014) and magnetic nanoparticles (Coronado et al., 2013; Lin et al., 2012; Liu, 2012; Makovec et al., 2011). More recently, graphene based materials (graphene oxide (GO), reduced graphene oxide (rGO) and other forms of functionalized graphene) have been explored as substrates for nanosized photocatalysts (Lambert et al., 2009; Linley et al., 2014; Szabó et al., 2013; Wang et al., 2013; Zhang et al., 2010). Due to their large specific surface areas (up to 1700 m^2/g (Szabó et al., 2006)), they are excellent platform for attaching nanoparticles (Linley et al., 2014). Meanwhile, owing to its weakly acidic character, GO is negatively charged in aqueous medium (Lambert et al., 2009). The presence of positively charged nanoparticles among the sheets of negative GO would lead to the formation of large aggregates (Lambert et al., 2009) which could be separated from water by flocculation and subsequent sedimentation or hydrocyclone (Szabó et al., 2013). For instance, Wang et al. (Wang et al., 2013). Produced recyclable TiO_2-rGO composites through 5 h hydrothermal reaction of TiO_2 and GO at 150 °C. Tamas et al. (Szabó et al., 2013). Synthesized TiO_2–GO composites through one day of magnetical stirring of exfoliated GO and TiO_2 nanoparticles at a pH of 8.5 ± 0.3. The prepared composites showed accelerated sedimentation performance as compared to pure TiO_2. Therefore, there is a great potential to separate TiO_2 nanoparticles from water by combing TiO_2 with GO. However, all the existing separation methods are very complicated and not cost-effective. Either high reaction temperatures (Wang et al., 2013) or long reaction times (Szabó et al., 2013) are needed, often resulting in very high production costs. Therefore, developing a simple method to synthesize recoverable TiO_2–GO composites is required.

In addition, the aforementioned studies only focused on the photocatalytic activity of the recoverable TiO_2–GO composites in the ultraviolet region (Szabó et al., 2013; Wang et al., 2013). Minimal attention has been paid to their activity under solar light irradiation which is the ideal light source, particular for water disinfection. Finally, TiO_2 photocatalytic disinfection methods have rarely been used for disinfection of stormwater, which has far different chemical composition and pathogen levels than more studied domestic and industrial waste water.

In this study, recoverable TiO_2–GO nanocomposites were prepared by one-step ultrasonic mixing of TiO_2 (P25, Degussa) nanoparticles with GO nanosheets. Settling behaviour of the composites in deionized (DI) water was systematically studied. Photocatalytic activity of the composites toward stormwater disinfection under solar light irradiation was investigated. Durability of TiO_2–GO toward *E.coli* deactivation was tested through successive disinfection experiments. Settling behaviours of the composites in stormwater before and after repeated disinfection experiments were also studied. The results were very encouraging, suggesting that the proposed separation method could significantly advance the practical application of photocatalytic oxidation in stormwater treatment.

2. Experimental

2.1. Synthesise of TiO_2–GO nanocomposites

Graphene oxide (GO) was prepared from graphite flakes (Sigma–Aldrich) according to the modified Hummer's method (Hummers and Offeman, 1958). TiO_2–GO nanocomposites were synthesized through a modified one-step colloidal blending method (Gao and Sun, 2013). In a typical TiO_2–GO synthesis procedure, a predetermined amount of GO was dispersed in 50 mL of deionized (DI) water by ultrasonication (Unisonics, 50 Hz, Australia) for 30 min, and then 1 g TiO_2 (P25, Degussa) was added to the as-prepared GO suspension. The mixture was then sonicated for 90 min and further stirred for 30 min at room temperature to produce homogeneous suspension. The resultant TiO_2–GO suspension was diluted with DI water to 100 mL and stored at room temperature for further use. In order to investigate the influence of GO loading on the sedimentation and photocatalytic activity of the nanocomposites, TiO_2–GO with three different mass ratios of TiO_2 to GO, 100:1, 100:2 and 100:3, were prepared by changing the mass of GO (0.01, 0.02 and 0.03 g, respectively). The resultant composites were denoted as TiO_2-1%GO, TiO_2-2%GO and TiO_2-3%GO, respectively. For comparison, TiO_2 suspension was also prepared without GO addition. pH values of the prepared GO, TiO_2 and TiO_2–GO stock suspensions were all 3.6 ± 0.1.

2.2. Characterizations of the TiO_2–GO composites

The morphology of the as-synthesized TiO_2–GO was characterized by transmission electron microscopy (TEM, FEI Tecnai G2 T20 TWIN, USA). 20 μl of GO, TiO_2 and TiO_2-2% GO stock suspensions were dispersed in 1 mL ethanol and a drop of the suspension was dropped on a Cu grid (Ted Pella, USA). UV–vis absorption spectra were recorded by a UV–visible spectrophotometer (UV–2600, SHI-MADZU, Japan). Zeta potential values of TiO_2, GO and TiO_2–GO nanocomposites at different pH values (2–11, adjusted with 0.1 M HCl or 0.1 M NaOH) were determined by a Zetasizer Nano SZ (Malvern Instrument, Worcestershire, UK). The measurement was repeated three times for each sample. A Particle Sizing System (780 APS, Accusizer, USA) was applied to determine the particle size distribution of TiO_2 and TiO_2–GO composites. Optical microscopic images of the samples were obtained with a microscope (Olympus, B × 60, Japan).

2.3. Sedimentation experiment

Settling behaviours of the TiO_2–GO composites in both DI water and stormwater were investigated in glass cylinders (100 mL, diameter 2.8 cm, height 24 cm). Settling profiles of the TiO_2–GO suspension (1.0 g/L) as a function of sedimentation time were determined in terms of turbidity variation of the suspension. In each experiment, 10 mL prepared TiO_2–GO suspension (10.0 g/L) was diluted with DI water or stormwater to 100 mL, forming a suspension with initial concentration of TSS_0 = 100 mg/L. The resultant TiO_2–GO suspension was homogenized by vigorous shaking, that was then poured into a cylinder and left to stand for 5 h (in DI water) or 8 h (in stormwater) until a TSS removal larger than 99.5% was obtained. At predetermined time intervals, a 2 mL aliquot was collected 1 cm below the surface and analysed for turbidity using a Turbidimeter (1100 IR, Merck, USA). The amount of TiO_2–GO settled in 10 min was determined as TSS removal. After 10 min of sedimentation, the supernatant was removed using a pipette and then filtered a membrane (0.45 μm), and dried and weighted the residue left on the filter until a constant weight was obtained. Then the amount of the composites settled in 10 min was determined through minus the amount of the suspended composites by the total amount (100 mg). For each composite, the sedimentation experiment was performed at least three times. To make a comparison, the settling behaviour of non-altered TiO_2 nanoparticles was also investigated under the same condition.

2.4. Solar photocatalytic disinfection

Photocatalytic disinfection was carried out under the irradiation of a solar simulator (66912, Newport, USA) equipped with an AM 1.5 filter at 300 W. *E.coli* (ATCC 11775) was used as an indicator of bacteria contamination in stormwater. The stormwater was prepared following the procedure described previously (Blecken et al.,