Chemical Engineering Journal 335 (2018) 290–300

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Photocatalytic degradation of phenanthrene by graphite oxide-TiO_2-$Sr(OH)_2/SrCO_3$ nanocomposite under solar irradiation: Effects of water quality parameters and predictive modeling

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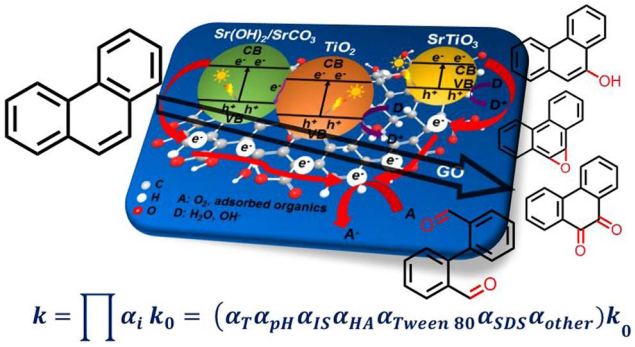
GRAPHICAL ABSTRACT



$$k = \prod \alpha_i k_0 = (\alpha_T \alpha_{pH} \alpha_{IS} \alpha_{HA} \alpha_{Tween\ 80} \alpha_{SDS} \alpha_{other}) k_0$$

ARTICLE INFO

Keywords:
Nanocomposite
Phenanthrene
Photocatalytic degradation
Water treatment
PAH

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are persistent and harmful pollutants with high priority concern in the environment. To efficiently and energy-savingly remove PAHs from water, this work prepared a novel graphite oxide-TiO_2-$Sr(OH)_2/SrCO_3$ nanocomposite and evaluated its photocatalytic activity for degradation of phenanthrene (a model PAH) under simulated solar irradiation. The presence of 50 mg/L of the photocatalyst enhanced the pseudo-first-order photodegradation rate constant of phenanthrene by 11.6 times from $0.0005 \pm 0.0000\ min^{-1}$ (control) to $0.0058 \pm 0.0004\ min^{-1}$. Superoxide radicals ($O_2^{\cdot -}$) and hydroxyl radicals ($^{\cdot}OH$) were found to be the key reactive species in the photocatalytic process. Based on analysis of intermediates and established photocatalysis chemistry, the degradation pathway was elucidated. The effects of various water quality parameters were investigated, including temperature, pH, ionic strength, humic acid and two surfactants (Tween 80 and sodium dodecyl sulfate (SDS)), and the underlying mechanisms were illustrated. Based on the effects of individual water quality parameters, two predictive models were established by addition or multiplication to predict the photocatalytic degradation rate under complex water matrices. Based on experimental results with seawater and in the presence of three model oil dispersants, the multiplicative model was shown to present a robust and accurate prediction of the phenanthrene photodegradation rate with a predicted correlation coefficient ($r^2_{pred.}$) of 0.9483. This study not only developed a new photocatalyst of high activity

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http://dx.doi.org/10.1016/j.cej.2017.10.163
Received 27 August 2017; Received in revised form 26 October 2017; Accepted 27 October 2017
Available online 28 October 2017
1385-8947/

under solar light, but also provided useful information for its practical application under various water quality conditions.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of persistent organic pollutants (POPs), and have been ubiquitously found in the environment [1]. Besides the natural sources, PAHs are often from anthropogenic sources such as incomplete combustion of fossil fuels, and accidental spillages of crude and refined oils [2,3]. Due to their persistence and potential harmful impact on the ecosystem and human health, PAHs have been classified as priority pollutants by the United States Environmental Protection Agency (USEPA) [4].

Different technologies have been studied for the removal of PAHs in contaminated water, such as adsorption, biodegradation, ultrasound irradiation, coagulation, and electrochemical oxidation [5,6]. Due to the utilization of clean solar energy and no use of any chemicals, heterogeneous photocatalytic processes under solar irradiation have attracted great interest in the last decade [7]. Titanium dioxide (TiO_2) is the most used photocatalyst due to its environment friendliness, abundant supply and cost-effectiveness [8]. However, due to the wide bandgap (~3.2 eV for anatase and ~3.0 eV for rutile) [9], TiO_2 can only be excited in the ultraviolet (UV) range, which accounts for only ~4% of the solar radiation [10]. Therefore, various efforts have been attempted to extend the utilization of TiO_2 to the visible light range (> 40% of the solar energy), such as metal/non-metal doping, noble metal deposition, semiconductors coupling, and photosensitization [11,12].

Graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional honeycomb lattice. In recent years, graphene has attracted a great deal of attentions for its potential applications in many fields, such as nano-electronics, fuel-cell technology, supercapacitors, and catalysts [13,14]. Graphite oxide (GO) is one of the most important precursors of graphene, and thus, they share similar sheet structures and properties such as high stability and semiconducting characteristics [10,15]. GO can enhance the light absorption via expanding the photoresponsive range to visible light and suppress the charge recombination by serving as a photo-generated electron transmitter, when coupled with TiO_2 [10]. To further enhance the conductivity and reduce the bandgap, noble metals (e.g., gold, palladium and platinum) are often incorporated to the GO-TiO_2 nanocomposite by surface deposition [10,16].

Compared with noble metals, strontium (Sr), as an alkaline earth metal, has much wider and richer sources, and it is the 15th most abundant element in the Earth's crust with an estimated abundance of approximately 360 ppm [17]. Sr has been widely employed as a dopant for various semiconductors (e.g., TiO_2, zinc oxide and germanium dioxide) to enhance the photocatalytic activities [18]. Moreover, the hydroxide and carbonate forms of Sr ($Sr(OH)_2$/$SrCO_3$) have been reported to have high photocatalytic activity under visible-light irradiation [19–21]. Yet, the effectiveness of coupling GO-TiO_2 with $Sr(OH)_2$/$SrCO_3$ has not been studied till now.

To address this knowledge gap, this study prepared a novel GO-TiO_2-$Sr(OH)_2$/$SrCO_3$ nanocomposite and evaluated its solar-light photocatalytic activity for degradation of phenanthrene in aqueous solution. Phenanthrene is one of the most resistant PAHs to sunlight irradiation with a photolysis half-life of 8.4 h in the near surface of water at the midday of midsummer [22]. It is known to be a human skin photosensitizer and mild allergen, and has attracted great health concerns around the world [23].

In addition, most studies on the photocatalytic degradation of pollutants by novel nanocatalysts have been focusing on the material characterization or explanation of enhanced photocatalytic mechanism [8,11], while the effects of water matrices and the applications in the real water systems (e.g., seawater) are often neglected. To bridge the gap between fundamentally developing new materials and practically applying the potential photocatalysts, this study not only provided the fundamental information on the characterization of GO-TiO_2-$Sr(OH)_2$/$SrCO_3$ nanocomposite, photocatalytic degradation mechanisms and pathway, but also investigated the effects of various water quality parameters (e.g., temperature, pH, ionic strength, and some macromolecular matrices) and constructed empirical models to predict the photocatalytic degradation rates of phenanthrene under various water chemistry conditions. Seawater samples collected from the Gulf of Mexico and oil dispersants (i.e., Corexit EC9500A, Corexit EC9527A and SPC 1000) were further employed as the water matrices to test the robustness of the photocatalyst and validate the predictive ability of the constructed models.

2. Experimental

2.1. Material synthesis

GO was synthesized according to the modified Hummers method [24], and titanium dioxide nanoparticles (Nano-TiO_2) were prepared following the approach reported in [25]. Supporting Information (SI) Text S1 provides detailed procedures for the preparation of GO and Nano-TiO_2. The GO-TiO_2 nanocomposite was then synthesized through the sono-chemical reaction of Nano-TiO_2 in the presence of the GO [15]. In brief, 3 g of the mixture of GO and Nano-TiO_2 (mass ratio = 2:1) was added to 100 mL of distilled water, and stirred for 0.5 h at room temperature (22 ± 1 °C). The suspension was then sonicated for 1 h. The resultant composite was recovered by filtration, rinsed with ethanol and then freeze-dried to yield the GO-TiO_2 composites. Subsequently, dispersing known mass of GO-TiO_2 (30 wt% of the final mass) in a 500 mL of sodium hydroxide (NaOH) solution (1 M), and a pre-determined amount of strontium chloride (SrCl, 0.5 M) was added dropwise to the dispersion at a rate of 2.0 mL/min using a Titronic Universal titrator (SCHOTT, Mainz, Germany). The resulting material, GO-TiO_2-$Sr(OH)_2$/$SrCO_3$, was then filtered, washed with distilled water until no chloride was detected in the washing water, and then freeze-dried for 48 h. For comparison, a GO-$Sr(OH)_2$/$SrCO_3$ nanocomposite was also prepared by the similar procedure with 20 wt% GO but without TiO_2.

2.2. Material characterization

The X-ray diffraction (XRD) measurements were performed on a PW1820 X-ray diffractometer (Philips, Amsterdam, Netherlands) using Cu Kα radiation. Scanning electron microscopy (SEM) images were obtained with a JSM-840A electron microscope (JEOL, Tokyo, Japan) equipped with energy dispersive X-ray (EDX) micro-analytical system (EDAX, Mahwah, NJ, USA). The EDX analysis was performed at 10 K magnification to map the distribution of Sr and Ti on the nanocomposite surface. Fourier transform-infrared (FTIR) measurements were carried out with a Nicolet 560 FTIR spectrometer on KBr wafers (Thermo Fisher Scientific Inc., MA, USA). The spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. Nitrogen adsorption-desorption isotherms were measured using AS1Win (Quantachrome Instruments, FL, USA) at the liquid N_2 temperature of 77 K, from which Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}), micropore volume (V_{mic}), total pore volume (V_t), and pore size distribution (PSD) were derived. Potentiometric titration measurements were carried out with a T50 automatic titrator (Mettler Toledo, Columbia, MD, USA) and the total surface charge (Q_{surf}, mmol/g) of the nanocomposite was then