



Facile surface-engineered polymeric absorbents for simultaneous adsorption and degradation of organic wastes



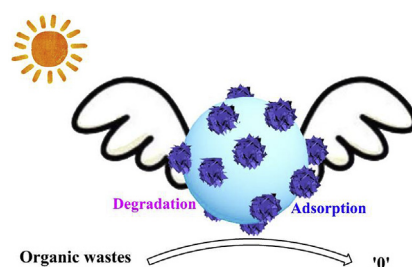
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HIGHLIGHTS

- Polymeric absorbents were surface-engineered with photocatalysts using a facile Pickering emulsion polymerization method.
- Organic wastes in water could be removed completely via simultaneous adsorption and degradation process.
- The composites could be reused without any treatments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 June 2017

Received in revised form

30 September 2017

Accepted 2 October 2017

Available online 4 October 2017

Handling Editor: Jun Huang

Keywords:

Polymeric absorbents

Photocatalytic

Organic wastes

Simultaneous adsorption and degradation

ABSTRACT

Polymeric absorbents were surface-engineered with photocatalysts for simultaneous adsorption and degradation of organic wastes in water using a facile Pickering emulsion polymerization method. This facile strategy not only overcome the low light energy utilization of traditional photocatalysts-polymer nanocomposites due to the core-shell structure, but also could convenient control the microstructure of the photocatalysts owing to the separated preparation procedure when compared to the direct growth method. Firstly, binary bismuth oxyhalide composed as $\text{BiOI}_{0.5}\text{Cl}_{0.5}$ was chosen to engineered polymeric absorbents due to its higher photodegradation efficiency especially. After the emulsification and polymerization process, $\text{BiOI}_{0.5}\text{Cl}_{0.5}$ acting as the stabilizer would be fixed on the surface of the functional polymeric absorbents to form $\text{PA@BiOI}_{0.5}\text{Cl}_{0.5}$. Batch experiments were lunched using phenol as the test substance, the results shown that $\text{PA@BiOI}_{0.5}\text{Cl}_{0.5}$ could remove phenol completely within a short time and could be reused without any treatments with a simultaneous adsorption and degradation process. Furthermore, polymeric absorbents were engineered with commercial TiO_2 to prove the generality of this strategy.

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1. Introduction

Pollution in water from organic hazardous wastes such as pharmaceutical and personal care products (PPCPs) (Bu et al.,

2013), herbicides/pesticides (Finizio et al., 2011), dyes (GuptaSuh, 2009), and aromatics/organics (He et al., 2006; Ahmaruzzaman, 2008) caused by rapid pace of industrialization and urbanization has become an urgent global environmental issue, leading a potential hazard to living systems (Zhang et al., 2013; Liu et al., 2016). As a consequence, providing clean water for people is a challenging task. So far, various technical processes are in use to deal with the organic water pollution such as biological oxidation, adsorption, chemical oxidation and incineration (Hartmann et al.,

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2010; Khin et al., 2012). Among of them, adsorption is considered an economical and effective strategy (Walcarius et al., 2010).

Compared to activated carbon, a widely used adsorbent, polymeric adsorbents such as macroporous resin amberlite XAD-4, CHA-101 and NDA-701 have attracted increasing interest for the removal of organic pollutants from wastewater due to their high capacity, satisfactory mechanical strength and feasible regeneration under complex conditions (Xu et al., 2003; Pan et al., 2007). Moreover, selectivity of the polymeric adsorbents could be achieved via the introduction of some functional monomer during the polymerization, further improving its application area (Haupt and Mosbach, 2000; Sellergren, 2000). However, widespread application of these polymeric adsorbents is still limited due to the difficulty in separating the contaminants from the adsorbents, which increases the cost and hinders reuse of the sorbents. Furthermore, the saturated adsorption of adsorbents hold back the completely removal of contaminants. Thus, it is important to develop materials that could remove organic contaminants completely and could be directly reused without separation of contaminants.

Over the past few decades, the heterogeneous photocatalytic oxidation (HPO) process using semiconductor photocatalysts (e.g., TiO_2 , ZnO) and light has attracted much attention because of its low-cost, environmental friendliness, and sustainable treatment to wastewater (Dong et al., 2014; Anandan et al., 2007; Yu and Yu, 2008). In HPO process, organic contaminants in aqueous solution could be degraded to more biologically degradable or less toxic substances without secondary pollution (Oller et al., 2006; Garcya et al., 2007). A number of new catalysts have been explored to enrich the family of photocatalysts, such as simple oxides, sulfides, complex oxides and polymers (Yan et al., 2010; Kondrakov et al., 2014; Li et al., 2012; Sprick et al., 2016; Girish Kumar and Koteswara Rao, 2015). Bismuth oxyhalides, BiOX ($X=\text{F}, \text{Cl}, \text{Br}, \text{I}$), especially the composites $\text{BiOI}_x\text{Cl}_{1-x}$, are gaining an increasing attention as a new family of promising visible light driven photocatalysts for pollutants degradation due to longer life time of charge carriers and higher redox abilities. And the composites $\text{BiOI}_x\text{Cl}_{1-x}$ can easily be modulated by changing the composition of the wide-band-gap semiconductor (BiOCl) and the narrow-band-gap semiconductor (BiOI) (Xiao et al., 2012; Chen et al., 2013). However, pure semiconductor photocatalysts cannot meet specific requirements in some environmental cases, such as high concentrations of contaminants, selective adsorption, and so on.

The combination of the inorganic photocatalysts and organic functional polymer provide a potential solution to these problems. The formed composites could not only remove contaminants completely within a relatively short time, but also the photocatalyst-polymer nanocomposites could be directly reused without further treatment under simultaneous adsorption-photodegradation process (Chen et al., 2016). For example, TiO_2 nanoparticles have been encapsulated by MIP with core-shell structure for selective adsorption and degradation of organic molecules (Shen et al., 2007, 2008), and TiO_2 was immobilized in cellulose matrix using a direct growth method for photocatalytic degradation of phenol under weak UV light irradiation (Zeng et al., 2010). However, the core-shell structure of composite restrict the photocatalytic degradation because of the difficult penetration of light when photocatalyst act as the inner core and polymer act as the outer shell. On the other hand, the structure of the photocatalyst which is directly related to the degradation performance would be inconvenient controlled during the direct growth on the surface of matrix. Hence, developing a new strategy that could attach the separately synthesized photocatalysts on the surface of the polymeric adsorbents was urgently needed.

Herein, a recyclable polymer adsorbents-photocatalyst ($\text{PA@BiI}_x\text{Cl}_{1-x}$) composite was fabricated by immobilization of

visible-light-driven binary bismuth oxyhalide semiconductor ($\text{BiOI}_{0.5}\text{Cl}_{0.5}$) on the surface of polymeric adsorbents (Scheme 1) using a Pickering emulsion polymerization method. First, $\text{BiOI}_{0.5}\text{Cl}_{0.5}$ was prepared and chosen as the semiconductor photocatalyst, and then used as the particle stabilizer to construct a stable Pickering emulsion of cross-linking monomer (the oil phase) in water. After the polymerization of the oil phase, the $\text{BiOI}_{0.5}\text{Cl}_{0.5}$ would be fixed on the surface of polymer particle. Moreover, the polymeric adsorbents could be designed to adsorb organic wastes from water by introducing functional monomer into the oil phase. Therefore, simultaneous adsorption and degradation would be achieved for efficient removal of organic wastes and this composite could be directly reused without any treatment. In this study, simultaneous adsorption and degradation was evaluated using phenol, which was considered to be harmful and difficult separated from water as the test substance. Batch experiments were carried out, and the results shown that the as prepared composites could remove phenol from the aqueous solutions efficiently and cyclically. And this strategy could also be used to prepare other kinds of polymer adsorbents-photocatalyst composite.

2. Experimental section

2.1. Materials

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were provided by Sigma-Aldrich, and other reagents including KI, KCl, styrene and *tert*-butyl acrylate were bought from the Sinopharm Chemical Reagent Co., Ltd. Titanium dioxide (TiO_2) nanoparticles was purchased from Aladdin. All the reagents mentioned above were analytical grade and used without further purification.

2.2. Instrumentation

The structure and morphology of $\text{PA@BiOI}_{0.5}\text{Cl}_{0.5}$ and $\text{BiOI}_{0.5}\text{Cl}_{0.5}$ were characterized by scanning electron microscopy (SEM, Hitachi S-4800). The phase structure of samples were determined by X-ray diffraction (XRD, X'Pert-Pro MPD) with the scanning range was $10\text{--}70^\circ$.

2.3. Preparation of $\text{BiOI}_{0.5}\text{Cl}_{0.5}$

Binary bismuth oxyhalide composites with different molar ratio of iodine and chloride ($\text{BiOI}_x\text{Cl}_{1-x}$, $x=0\text{--}1$) were synthesized according to literature for synthesis of pure bismuth oxyhalide (Hu et al., 2014). Depending on the feed molar ratio of KI to KCl (1:0, 0.75:0.25, 0.5:0.5, 0.25:0.75 and 0:1) different bismuth oxyhalide composites were obtained and labeled as BiOI , $\text{BiOI}_{0.75}\text{Cl}_{0.25}$, $\text{BiOI}_{0.5}\text{Cl}_{0.5}$, $\text{BiOI}_{0.25}\text{Cl}_{0.75}$ and BiOCl , respectively. In a typical synthesis, KI (a mol) and KCl ($0.002\text{--}a$ mol) ($a=0, 0.0005, 0.001, 0.0015$ or 0.002) were dissolved into 20 mL ethylene glycol. The solution were added into another 20 mL ethylene glycol with 0.002 mol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ under stirring. After that, the mixture was transferred into a 50 mL Teflon-lined autoclave and heated to 160°C for 12 h. The obtained solution was washed with ultrapure water and ethanol for several times. After centrifugation, the $\text{BiOI}_x\text{Cl}_{1-x}$ powder was yielded after drying at 60°C for 12 h.

2.4. Preparation of $\text{PA@BiOI}_{0.5}\text{Cl}_{0.5}$

$\text{PA@BiOI}_{0.5}\text{Cl}_{0.5}$ was prepared by Pickering emulsion polymerization according to the literature with some modification. First, 25 mg $\text{BiOI}_{0.5}\text{Cl}_{0.5}$ were dispersed in 2 mL water in a 5 mL tube. And 0.5 mL of TRIM, 0.5 mL of DVB, 0.3 mL of tertiary-Butyl Methacrylate, 6.2 mg of BPO, and 31.5 μL of DMA were added in another 5 mL

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