



Adsorption–photodegradation of humic acid in water by using ZnO coupled TiO₂/bamboo charcoal under visible light irradiation



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HIGHLIGHTS

- ZnO coupled TiO₂/bamboo charcoal is prepared using a microwave-assisted sol–gel method.
- HA degradation is achieved through synergistic BC adsorption and ZnO–TiO₂ photocatalysis.
- ZnO–TiO₂/BC has high photodegradation efficiency for HA under visible-light irradiation.
- ZnO–TiO₂/BC is an effective photocatalyst for the removal of organic pollutants from water.

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ABSTRACT

ZnO coupled TiO₂/bamboo charcoal (ZnO–TiO₂/BC) was prepared using the sol–gel method combined with microwave irradiation. The ZnO–TiO₂/BC and TiO₂/BC were characterized by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), N₂ adsorption (BET), and UV–vis diffuse reflectance spectroscopy (UV–vis–DRS). The ZnO dopant promoted the transformation of anatase TiO₂ to rutile phase, and a significant red shift of absorption edge was brought out due to the interfacial coupling effect between ZnO and TiO₂ particles. The BET specific surface area and total pore volume decreased with ZnO doping, indicating that some micropores were blocked. SEM studies indicated that ZnO was almost uniformly deposited on the surface of the ZnO–TiO₂/BC. The adsorption and photocatalytic degradation experiments showed that the photo-degrade efficiency for ZnO–TiO₂/BC was higher than that of TiO₂/BC, and for both composites, the removal efficiency of HA increased as pH decreased from 10.0 to 2.0. The degradation of HA by ZnO–TiO₂/BC and TiO₂/BC fitted well with the Langmuir–Hinshelwood kinetics model, and HA degradation was achieved through a synergistic mechanism of adsorption and photocatalysis. ZnO–TiO₂/BC could be used as an effective and alternative photocatalyst for the treatment of water contaminated by organic pollutants.

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1. Introduction

Humic acids (HAs) are macromolecular yellow-to-black colored natural organic matter derived from the degradation of plant, algal, and microbial material [1]. They consist of carbon, oxygen, hydrogen and sometimes small amounts of nitrogen and occasionally phosphorous and sulphur. The major functional groups in humic acid are carboxyl, phenolic, carbonyl and hydroxyl groups connected with the aliphatic or aromatic carbons in the macromolecules [2,3]. As a major fraction of natural organic matter (NOM) presents in freshwater sources, humic substances

are a primary target of water treatment processes even though themselves are not considered pollutants. Negative effects of humic substances in potable water include undesirable color and taste, absorption and concentration of organic pollutants, and biochemical decomposition in the water distribution systems [4,5]. Moreover, humic acid can react with chlorine during water treatment producing trihalomethanes, substances that are carcinogenic [6–8]. It is therefore imperative that the concentration of humic substances should be drastically reduced in raw drinking waters before chlorination begins.

Conventional methods, such as coagulation precipitation [9,10], ion exchange [11], membrane filtration [12], biofiltration [13], advanced oxidation [14] and activated carbon adsorption [15,16], have been widely applied for humic acid removal. Among the advanced oxidation processes, heterogeneous photocatalysis

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particularly with titanium dioxide (TiO_2) as photocatalyst has a widely demonstrated efficiency for degrading a broad range of organics [17–19]. Even if the famous TiO_2 semiconductor is the most used, because of its photocatalytic activity, high stability, non-toxicity and inexpensiveness, the interest is much more focused nowadays on the synthesis of photocatalyst materials to overcome its limitations. Some of the important limitations are (1) TiO_2 powder is difficult to recycle, easy to agglomerate, and causes a problem of separation from the solution; (2) TiO_2 is a wide band-gap semiconductor (3.20 eV for anatase TiO_2 and 3.02 eV for rutile TiO_2) which makes the photocatalytic activity quite limited in the visible light, solar and fluorescent light [20–22]. To overcome the first limitation, much attention has been paid to the development of supported TiO_2 catalysts. In this respect, different types of supports for TiO_2 have been tested including silica [23], perlite [24], activated carbon [25], clay [26] and zeolite et al. [27]. As the photocatalytic process is surface orientated, the efficient oxidation of organics requires adsorption onto the surface of TiO_2 [25]. Therefore, activated carbon has been extensively studied as a supporter for TiO_2 photocatalyst because of its high surface area, high adsorption capacity, suitable pore structure, and inert nature in certain rigorous circumstances [28]. To overcome the limitation of the large band gap of TiO_2 , numerous studies have been recently performed. Among these, ZnO/ TiO_2 coupling has been reported to produce an enhancement of the photocatalytic activity in comparison to pure ZnO and TiO_2 both for polycrystalline systems and films used to decompose organic pollutants in aqueous medium [29,30]. The modification of the electronic properties of the coupled materials with respect to the single ones is invoked to explain this behavior: the electron transfer from the conduction band of ZnO to the conduction band of TiO_2 under illumination and, conversely, the hole transfer from the valence band of TiO_2 to the valence band of ZnO give rise to a decrease of the pairs recombination rate, i.e., to an increase of their lifetime. This phenomenon increases the availability of the pairs on the surface of the photocatalyst and consequently an improvement of the occurrence of redox processes can be expected [31].

Bamboo is an abundant and inexpensive natural resource in China. It can be carbonized in a furnace at high temperature in the absence of oxygen to produce carbon chars. It is estimated that the throughput of bamboo charcoal (BC) in China has been approximately 40,000 tons a year. However, its utilization has not been fully explored. Therefore, BC used as a potential support to prepare ZnO/ TiO_2 coupling material for carrying out the adsorption–photooxidation of HA will enlarge its application and help to deal with the emergent wastewater treatment challenge in China. In our previous studies [32,33], a series of adsorbents based on the modification of bamboo charcoal (BC) with the microwave-assisted heating have been developed for wastewater treatment. The approach is based on hypotheses that BC is a good microwave absorber, which receives microwave energy directly through dipole rotation and ionic conduction. As a consequence, bulk temperature of the BC rises rapidly and uniformly under microwave irradiation. Therefore, microwave heating has been recently gaining attention as a novel method of activated carbon preparation due to its heating rapidly and uniformly [34].

In this work, ZnO coupled TiO_2 /BC with high adsorption–photocatalytic activity under visible light irradiation were synthesized by a microwave-assisted sol–gel method. The produced composite was characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, UV–vis–NIR scanning spectrophotometer, nitrogen adsorption analyses for Brunauer–Emmett–Teller (BET) specific surface area and mesoporous size distribution. The synergistic relationship between surface adsorption characteristics and photocatalytic potential was examined by the comparisons

of typical reaction systems during the degradation of humic acid solutions.

2. Experimental

2.1. Materials

The humic acid (GR) was obtained from Sigma–Aldrich Co. LLC. (USA). All other reagents (AR) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (China) and used as received without further purification. Stock HA solution (100 mg/L) was prepared by dissolving HA in 0.01 M NaOH solution, then ultrasonicated for 1 h for thorough dissolving and filtrated by 0.45 μm membrane. The desired solutions were prepared by dilution of the stock solution. The deionized water was used in all experiments.

The BC, provided by Suichang Mingkang Charcoal Enterprise Co. Ltd. (Zhejiang, China) with a particle size of 1–2 mm, was used to prepare the composites. Before usage, the original charcoal was activated by nitric acid and thoroughly washed in boiling de-ionized water until circum-neutral pH of the supernatant, then ultrasonicated for 0.5 h, oven dried in thin layers at 105 °C for 24 h and kept in desiccator for use.

2.2. Preparation of ZnO coupled TiO_2 /BC composite

The ZnO– TiO_2 /BC composite was prepared by a novel sol–gel route via microwave-assisted method. The tetra-n-butyl titanate was used as the precursor. During the preparation, 1.2 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 40 mL ethyl alcohol, and was stirred for 10 min with a magnetic stirrer. Whilst still stirring, a solution containing 1 mL HCl (12 mol/L) and 12 mL $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was added drop by drop over 30 min. Following this, 3 mL de-ionized water was added dropwise for hydrolysis. A desired amount of BC was then added to the Zn– TiO_2 sol at a certain viscosity during ultrasonic treatment. When Zn– TiO_2 sol coated the support was changed into Zn– TiO_2 gel, the support was dried for 30 min at 480 K in an oven. The obtained particles were set on a quartz boat which was then inserted into a modified microwave heating apparatus, and heated with continuous output 640 W power and a frequency of 2.45 GHz for 15 min. After cooling, the solid product was washed with de-ionized water and dried in oven. In addition, TiO_2 /BC composite was prepared under same procedure for comparison. It is important to remark that the manufacturing conditions used here were optimized according to the resultant material's characteristics.

2.3. Characterization of the composites

For crystal structure analysis of the prepared samples, X-ray powder diffraction (XRD) analysis was carried out on a Bruker D8 ADVANCE (German) X-ray diffractometer with Cu $K\alpha$ radiation (40 kV, 40 mA) with a 0.01° step and 2.5 s step time over the range 10° < 2 θ < 90°.

Nitrogen adsorption–desorption isotherms were used to determine BET surface area and pore size distribution (Micromeritics, ASAP 2020).

The morphology of the synthesized bifunctional carbonaceous materials were observed initially using scanning electron microscopy (SEM, Hitachi S4700) with the working distance of 5–12 mm and an accelerating voltage of 20 KeV.

The IR spectrum was recorded as KBr pellets at room temperature on a Fourier transform infrared (FTIR) spectroscopy (Nicolet Instrument Corporation, USA).

For the characterization of the light absorption features and band-gap determinations, diffuse reflectance spectra (DRS) of the

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