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Performance and mechanism into TiO_2/Zeolite composites for sulfadiazine adsorption and photodegradation

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HIGHLIGHTS

- TiO_2/ZEO (20%) composite degraded efficiently in aqueous solutions of sulfadiazine.
- Anatase nano titanium species bound to the framework through TisbndOsbndSi bond is also observed by FT-IR analysis.
- The photodegradation reaction of TiO_2/ZEO to SDZ is controlled by the surface adsorption of SDZ.
- The photodegradation processes of SDZ are firstly analyzed by 3-D fluorescence spectra.
- Photocatalytic mechanisms and degradation pathways of SDZ under UV irradiation by TiO_2/ZEO were identified.

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ABSTRACT

The composite material based on natural Zeolite coated with TiO_2 (TiO_2/ZEO) synthesized by sol-gel method was used as a photocatalyst to rapidly degrade Sulfadiazine (SDZ). The adsorption-degradation behavior and mechanism of SDZ on TiO_2/ZEO were investigated for revealing the role of adsorption and degradation under UV light. TiO_2/ZEO was easier to be separated than the bare TiO_2 powders in aqueous media. Compared with bare Zeolite, TiO_2/ZEO markedly improved the efficiency in photocatalytic degradation of SDZ: more than 90% of SDZ could be removed within 120 min of both adsorption and degradation by TiO_2/ZEO dosage of 1 $g{\cdot}L^{-1}$ at neutral pH, whereas less than 15% was removed by Zeolite alone. The Langmuir-Hinshelwood first-order linear transform with $k = 0.0212\,min^{-1}$ was observed for the photocatalytic degradation reaction of SDZ. The parameters such as loaded amount of TiO_2, initial SDZ concentration, solution pH value, humic acid (HA) concentration, and recycle numbers on removal efficiency were also studied. The enhancement in removal efficiency was not attributed to the simple adsorption of SDZ on zeolite but also the synergistic effect obtained through the combined use of TiO_2 photocatalyst and zeolite adsorbent in the composite material, which can accelerate the SDZ photodegradation in water. The photocatalytic mechanism, as characterized using ESR and trapping experiments of reactive species, indicates that the synergism effect between ^{rad}OH, h^+, $^{rad}O_2{}^-$ and $^1O_2$ all play a role in photocatalytic oxidation of SDZ.

1. Introduction

As an important photocatalyst, TiO_2 has attracted extensive attention due to higher stability, cheapness and activity in wastewater treatment [1]. However, the difficult separation and recycle of TiO_2 limit its application in water treatment [2]. To this end, the immobilization of TiO_2 on solid surface has received tremendous interest. In addition to the photocatalyst support required to have the stability, high strength, low cost, and large specific surface area, it is even more important that the catalyst attached to the support can be activated by irradiation with light as much as possible to play a catalytic role.

Activated carbon [3–5], silica [6,7], clay [8,9] and zeolite [10–12], have been regarded as a class of promising photocatalytic carrier to attempt to improve their separation from water treatment. Zeolites, in particular, have been shown to be promising due to their unique porous structures, uniform pores and channels, high surface area, excellent

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adsorption capacity and catalytic performance for pollutants [13–15], whereas it can provide the unique nanoscale reaction field, containing irregular inner surface layout and particle exchange performance. There is a special photocatalytic performance that is generally difficult to be achieved with a commonly photocatalytic system in such a reaction space. In previous studies, researchers are more concerned about the removal efficiency of pollutant [16–18]. The lack of conformity between many experiments and observations suggests that researches on the reaction mechanism still remain in the imagination and assumption stage. Many studies have reported that the photocatalytic degradation mechanism of organic pollutants in AOPs, but the reports of photocatalytic degradation combined with the analysis of intermediate products and the identification of active species are limited in recent researches [19]. Nevertheless, this missing knowledge is critical for developing TiO_2-based materials and their environmental application.

Antibiotics, a class of pharmaceuticals that are extensively and widely used in humans and animals [20], have attracted significant concerns in recent decades. They are often partially metabolized in organisms and may be excreted as the parent compounds or metabolites into environment via urine and feces [21]. The residues of antibiotics in the hospital and sewage effluents can range from few to tens of ppm [22]. The overuse and misuse of antibiotics can induce rapid emergence of antibiotic-resistant bacteria (ARB) and antibiotic resistant genes (ARGs) [23], posing a serious threat to the ecosystem and human health. SAs exhibit high solubility and chemical stability in water resulting in high residue [24]. Sulfadiazine (SDZ) has been widely reported in different environmental compartments, such as WWTPs [25], hospitals [26], livestock farms [27], river water [28] and ground water [29]. The usage of Sulfadiazine (1260 tons) is the second largest in 13 common sulfonamides in China [30]. Exposure to low concentration of Sulfadiazine can poses serious threats to the ecosystem and human health [31,32]. However, conventional approaches including absorption and biodegradation cannot achieve satisfactory results and suffer from the Low degradation efficiency and drawback of time-consuming [33]. TiO_2 photocatalysis using ultraviolet (UV) light has been extensively studied and shown to degrade a wide range of pharmaceuticals [34,35]. For instance, Cui et al. (2016) investigated the degradation characteristics of SDZ at initial concentrations of 0.2, 1.0, and 2.0 $\mu g \cdot L^{-1}$ by UV photolysis systems [36]. The result36s showed that SDZ were completely photodegraded after UV exposure of 5–30 min. Therefore, photocatalytic degradation of SDZ has a high application - prospect.

In this work, the composite material based on natural Zeolite coated with TiO_2 (TiO_2/ZEO) was be synthesized by sol-gel method, and were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), BET analyzer, Fourier transmission infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis DRS) and Thermogravimetric analyzer (TGA/DTA). The adsorption and photocatalytic performance of TiO_2/ZEO composite materials was investigated under UV light irradiation for the adsorption and photo-degradation of SDZ. In order to clarify the photocatalytic degradation mechanism, we also explored the effectiveness of SDZ under different experimental variables such as loaded amount of TiO_2, initial SDZ concentration, solution pH value, humic acid (HA) concentration. ESR and trapping experiments of reactive species were conducted to explore the oxidation mechanism of SDZ onto TiO_2/ZEO, and the SDZ degradation pathway was proposed. Based on the results, the purpose of this work was to evaluate the adsorption and photocatalysis potential of TiO_2/ZEO for SDZ, which can provide a scientific basis for environmental application in water/wastewater treatment.

2. Materials and methods

2.1. Materials

All the chemicals were used as received without further purification. Sulfadiazine ($C_{10}H_{10}N_4O_2S$, SDZ, 99%) was purchased from Dr. Ehrenstorfer, Germany. Titanium butoxide ($C_{16}H_{36}O_4Ti$, 99%), 5,5-dimethyl-1-pyrroline-*N*-oxide ($C_6H_{11}NO$, DMPO, 97%), Triethanolamine ($C_6H_{15}NO_3$, TEOA, 99.0%, GC), p-Benzoquinone ($C_6H_4O_2$, BQ, 99.5%, HPLC) and Isopropyl Alcohol (C_3H_8O, IPA, 99.9%, GC) were purchased from Sigma-Aldrich (St. Louis, US). Sodium azide (NaN_3, ≥99.7%), Ethanol (C_2H_5OH, ≥99.7%), nitric acid (HNO_3, 68%), hydrochloric acid (HCl, 38%), and sodium hydroxide (NaOH, ≥96.0%) were of analytical grade and were all purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ultrapure water used in the study was purchased from Hangzhou Wahaha Group Co. Ltd. Natural zeolite was purchased from a packing factory in Henan.

2.2. Synthesis of TiO_2/ZEO composites

The synthesis of TiO_2/ZEO composites was carried out via a sol-gel method [37]. 4 mL of Titanium butoxide was added dropwise into 2 mL C_2H_5OH. With magnetic stirring at room temperature for about 30 min., the solution was labeled A. 0.4 mL of HNO_3 and 2 mL of H_2O were added into 17 mL C_2H_5OH, and the solution was labeled B. Then, solution B was added dropwise at approximately 3 $mL \cdot min^{-1}$ with stirring. The transparent sol was obtained continued after stirring for 1 h at room temperature. An appropriate amount of Zeolite screened through a 100-mesh sieve was added into transparent sol with stirring for 30 min and ageing for 24 h at room temperature. The final products were dried at 80 °C for several hours in a vacuum oven and calcined at 300 °C for 3 h in a close roaster.

2.3. Characterization

SEM images of the samples were characterized using a scanning electron microscope (JSM-6700, Japan). The crystal morphology of samples was examined using a transmission electron microscope (JEM-2100, Japan). The specific surface area measurement of materials was determined by an automatic BET surface area analyzer (JW-BK122W, Beijing) with a nitrogen adsorption measurement at 77 K. The functional groups samples were analyzed using Fourier transmission infrared spectroscopy (Vertex 70, Germany) in a range from 4000 to 400 cm^{-1}. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation to characterize the crystal structure. Ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis DRS) was performed using a UV-2550PC ultraviolet and visible spectrophotometer from 200 to 800 nm with $BaSO_4$ as the background. Thermogravimetric and differential thermal analysis of Zeolite and TiO_2/ZEO were performed with a TGA/DTA thermal analysis instrument (7300, Japan). The samples were heated from 100 to 1000 °C at a rate of 10 $°C \cdot min^{-1}$ in air.

2.4. Adsorption and photodegradation experiments

Both of adsorption and photocatalytic experiments were carried out in a BL-GHX-V photoreactor. The activities of samples were evaluated based on the adsorption and degradation of SDZ in an aqueous solution under a 20 W UV lamp at 265 nm. The distance between the light source and the reaction device was 7 cm. An appropriate amount of TiO_2/ZEO was added to a quartz tube with aqueous suspensions of SDZ (10 $mg \cdot L^{-1}$, 50 mL). Prior to irradiation, the suspensions were magnetically stirred in the dark for approximately 1 h to reach equilibrium adsorption at 25 °C. During the reaction, suspensions were collected with a syringe at timed intervals and filtered through a 0.22 μm membrane filter for the analysis of SDZ concentration.