Synthesis of Nano TiO_2-Fe_2O_3 Photocatalyst and photocatalytic degradation properties on oxytetracycline hydrochloride

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Abstract: Nano TiO_2-Fe_2O_3 composite photocatalyst was synthesized by solvothermal method. $Fe(NO_3)_3 \cdot 9H_2O$ and titanium isopropoxide was used as precursor. The mixture of anhydrous ethanol, 2-propanol and diethylene glycol was used as solvent. The composite photocatalyst was characterized by X-ray diffractometry, transmission electron microscopy and UV-Vis diffuse reflectance spectroscopy. The composite was composed of anatase TiO2 and α-Fe_2O_3. The average grain size of TiO_2 and Fe_2O_3 are 18nm and 16nm, respectively. The absorption spectrum of anatase TiO_2 was in ultraviolet region, while α-Fe_2O_3 exhibited high absorption in the visible light region of 400-600 nm. TiO_2-Fe_2O_3 nano particles had light absorption in the region of 200~550 nm. When the initial concentration was 60mg/L and pH was 5.5, the degradation rate reached the maximum. Moreover, the TiO_2-Fe_2O_3 nanocomposite was effective after three recycling times.

Introduction

In recent decades, the use of antibiotics brought more and more environmental problems, and the problems were attracted more and more attention. Oxytetracycline (OTC) is also called erythromycin. It is a kind of tetracyclin and is usually used. It is mainly used in the antibacterial agent for human diseases or in feed additive for animal husbandry, aquaculture and other fields [1]. However, majority of OTC was excreted in their original form after vivo metabolism by animal. Large amount of OTC entered into water. The accumulation of OTC increased the drug resistance of bacteria, which ultimately threaten the human health [2]. The usual wastewater treated technology is difficult to degrade OTC due to the good hydrophilicity and stable structure of OTC [3]. Therefore, it is urgent to find an effective water treatment technology to degrade OTC. The method of tetracycline activated sludge, biological filter or chlorination process could not effectively remove the tetracycline antibiotics in water [4]. Photocatalytic degredation is a new and promising environmental technology. TiO_2 photocatalyst has been widely used because of its stable, non-toxic, high catalytic activity and non-secondary pollution [5]. But this technology has many defects [6,7], such as the combination of electron and hole, the low photochemical catalysis efficiency, the wide band gap (about 3.2 eV), photochemical activity only in ultraviolet region and low utilization of

sunlight (< 10%). The energy gap of α-Fe_2O_3 is 2.3 eV. It could absorb the visible light and expand the photocatalyst the absorption scope, which would use the sunlight to carry on the photochemical catalysis. In this article, nano TiO_2-Fe_2O_3 composite photocatalyst was synthesized by solvothermal method. The composite photocatalyst was used to degrade OTC in water. The effects of the initial concentration of OTC solution, pH and time on the degradation efficiency of OTC were also investigated.

Experiment

A certain amount of $Fe(NO_3)_3.9H_2O$ and titanium isopropoxide (TTIP) were dispersed into the mixed alcohol solvent which containing 5mL diethylene glycol, 8 mL anhydrous ethanol and 2mL 2-Propanol. Then the mixed solution was transferred to a Teflon-lined stainless steel autoclave with a capacity of 50 mL. The autoclave was sealed and kept at 180 ^oC for 4h. After cooling down to room temperature, the products were collected and washed in turn with deionized water, anhydrous ethanol respectively and then dried in the vacuum at 80 ^oC.

The morphology and size of the samples were characterized through the transmission electron microscopy (TEM, JEOL-200cx). Crystallinity and phase analysis was performed by powder X-ray diffractometry (XRD) experiments on a Rigaku D/max 2500 with Cu Kα radiation (λ=0.154059 nm) scanning from 10 to 80 at a speed of 8^o/min. The UV-vis absorption spectra of photocatalysts were recorded by a UV-vis spectrophotometer (Techcomp ltd. U3010).

For photocatalytic degradation, 70mL aqueous OTC and 0.07g TiO_2-Fe_2O_3 powder were added to a quartz tube and stirred for 1h in the dark to equilibrate adsorption processes. A 300W iodine tungsten lamp was used as visible light source. A 300W high-pressure mercury lamp was used as a UV light source, with main wavelength of 250–400nm. Under light conditions, 5 ml of OTC solution was taken every 1 h, and the supernatant was centrifuged. The residual concentration of the OTC solution was determined by U3010 UV spectrophotometer at a wavelength of 355 nm.

Results and Discussion

The XRD patterns of TiO_2-Fe_2O_3 is shown in Fig. 1. Anatase TiO2 and α-Fe_2O_3 were observed in the profile. According to Scherrer equation, it can be calculated the average grain size of TiO_2 and Fe_2O_3 are 18nm and 16nm, respectively.

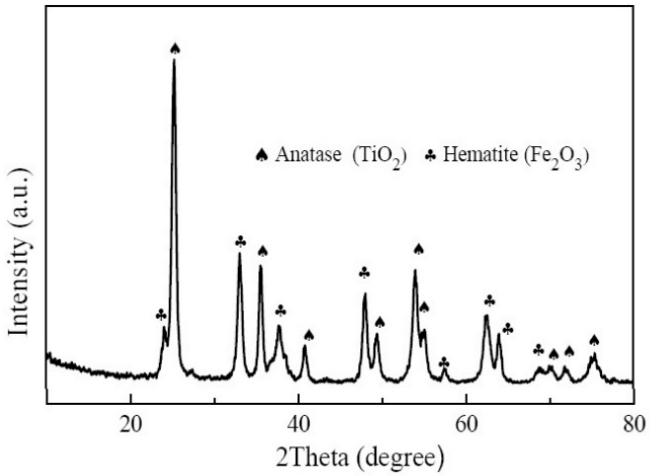

Fig.1 XRD pattern of TiO_2-Fe_2O_3 composites

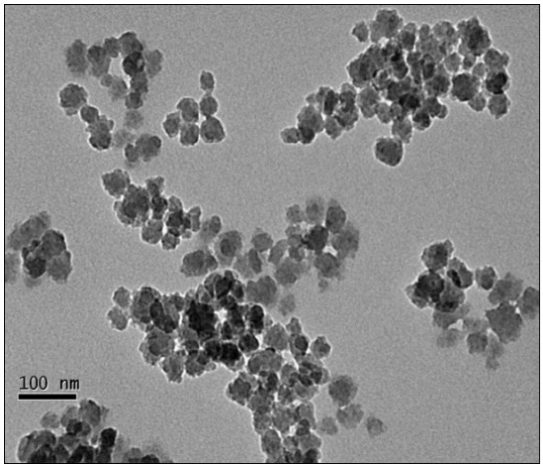

Fig.2 TEM micrograph of TiO_2-Fe_2O_3

TEM images of TiO_2-Fe_2O_3 composites is shown in Fig.2. The particles were spherical and were about 15-20 nm. This is in accordance with the XRD results.

Figure 3 shows the UV-vis absorption spectrum of anatase TiO_2, α-Fe_2O_3 and TiO_2-Fe_2O_3 composites, respectively. The absorption spectrum of anatase TiO_2 was in ultraviolet region, while α-Fe_2O_3 exhibited high absorption in the visible light region of 400-600 nm. TiO_2-Fe_2O_3 nano particles had light absorption in the region of 200~550 nm. The absorption spectrum of TiO_2-Fe_2O_3 showed an obvious red shift compared with that of anatase TiO_2.

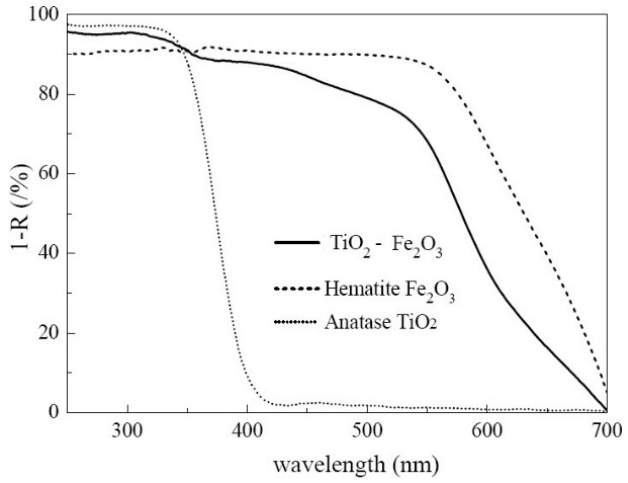

Fig.3 UV-vis absorption spectra of TiO_2-Fe_2O_3 composites, anatase TiO_2 and α-Fe_2O_3

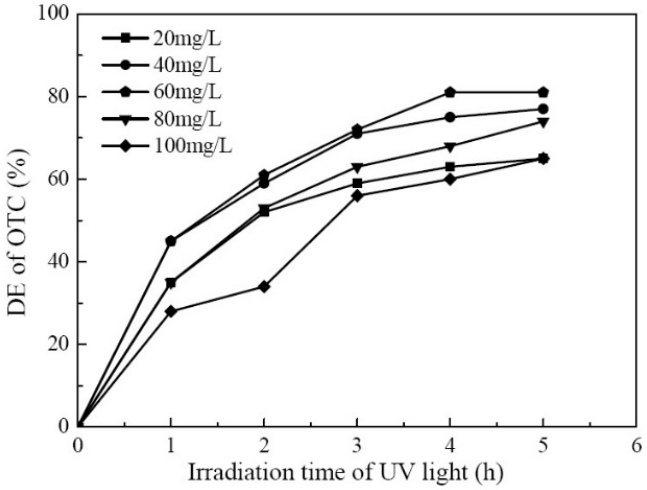

Fig.4 Degradation rate(%) of OTC on different initial concentration under UV light

The influence of OTC initial concentration on the degradation rate under the UV light irradiation (added 0.07g TiO_2-Fe_2O_3) is shown in Fig.4. When the initial concentration was lower than 60mg/L, the degradation rate increased with increase of OTC initial concentration. However, when the initial concentration is higher than 60mg/L, the OTC degradation rate decreased with increase of OTC initial concentration. Photocatalytic reactions are mainly photo-generated electrons and holes directly or indirectly redox reaction with the adsorption of OTC molecules on the surface of the catalyst. The indirect reaction is the photo-generated electrons and holes react with the water molecules or hydroxide ions on the surface of the catalyst to produce strongly oxidizing substances, such as •OH and $•O^{2-}$. Then these strongly oxidizing substances react with the OTC molecules. It is generally believed that indirect oxidation plays a major role in the degradation of OTC. When the initial concentration of OTC is low, the OTC molecules adsorbed on the surface of catalyst are less, which makes the degradation rate lower. When the initial concentration of OTC is more than 60mg / L, the surface adsorption of the catalyst is supersaturated. OTC and intermediates will accumulate on the surface of the catalyst. The adsorption capacity of the catalyst surface on water and hydroxide ions is reduced, so that the number of • OH and • O2- groups with strong oxidization is reduced, so that the degradation rate tends to decrease with the increase of OTC initial concentration. So 60mg/L is the best initial concentration and the degradation rate can reached to 85%.

The influence of initial pH of OTC on the degradation rate under the UV/vis light irradiation (initial concentration of OTC is 60mg/L) is shown in Fig.5. When the pH was lower than 5.5, the degradation rate increased with pH increasing. However, when the pH is larger than 5.5, the degradation rate decreased with pH increasing. This trend was in good agreement with photocatalytic degradation behavior, indicating that the photocatalytic process was limited by the adsorption of OTC at the surface of catalyst. When pH was equal to 5.5, the degradation rate reached the maximum at 5 h. The degradation rates under UV and vis light irradiation was 50% and 85%, respectively.

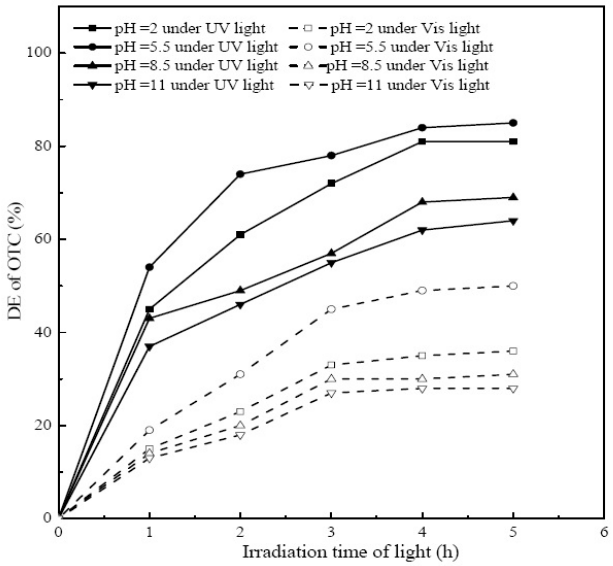

Fig.5 Effect of pH on degradation rate of OTC (60mg/L) under UV and visible light

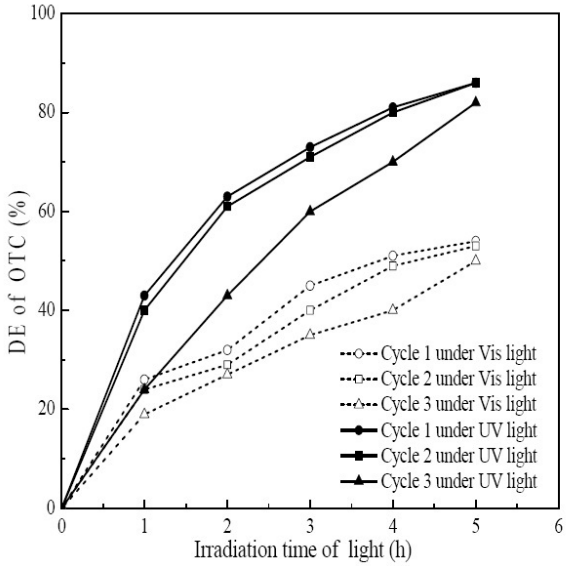

Fig.6 Photocatalytic activities for the degradation of OTC under UV-vis light for 3 cycles

The influence of TiO_2-Fe_2O_3 nanocomposite recycling on the degradation rate is shown in Fig.6. After one, two and three recycles, the degradation rates under UV irradation were 86%, 86% and 82%, respectively. And the degradation rates under vis irradation were 54%, 53% and 50%, respectively. The degradation rate declined slightly with the increasing number of cycles. So TiO_2-Fe_2O_3 nanocomposite was effective after three recycling times.

Conclusions

Nano TiO_2-Fe_2O_3 composite photocatalyst was synthesized by solvothermal method. It was characterized by XRD, TEM and UV-vis spectrum. The results showed the composite consisted of anatase TiO2 and α-Fe_2O_3 with particle size of 20nm. It exhibited strong absorption from 200 to 550 nm. The degradation rate reached maximum at proper conditions (OTC concentration was 60mg/L and pH was 5.5). The degradation rates under vis irradation and UV irradation were 50% and 85% at 5 h, respectively.

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