

Heterogeneous photo-Fenton degradation of methyl orange by Fe₂O₃/TiO₂ nanoparticles under visible light



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ABSTRACT

A novel heterogeneous photo-Fenton catalyst Fe₂O₃/TiO₂ nanoparticle was successfully prepared by sol-gel method and characterized by X-ray diffraction (XRD), UV–vis absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), Photoluminescence spectra (PL) and porosimetry analysis. The characterization results showed that the nano-sized Fe₂O₃ particles appeared on the TiO₂ support and the Fe₂O₃/TiO₂ nanoparticle exhibited enhanced absorption in the broad visible-light region together with an apparent red shift in the optical absorption edge. The XPS results revealed that the presence of Ti⁴⁺ and Fe³⁺ in Fe₂O₃/TiO₂ materials. The activity of heterogeneous photo-Fenton catalyst Fe₂O₃/TiO₂ combined with the photocatalytic and photo-Fenton was assayed in the degradation of methyl orange (MO) in the presence of visible light and H₂O₂. The results showed that the heterogeneous photo-Fenton was much faster and higher removal of methyl orange than the photocatalytic degradation alone. The mineralization of the organic pollutant was investigated by total organic carbon (TOC) measurements. The Fe₂O₃/TiO₂ + H₂O₂ showed the highest TOC mineralization of MO. All these results indicate the possibility of the practical application of this photocatalyst for water treatment.

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1. Introduction

Synthetic dyes have been widely used in the paper, plastic and pharmaceutical industries leading to the mass production of synthetic dyes and mass discharge of synthetic dye-containing wastewater [1]. Unluckily, stability of these dyes is so high, and resistant to biodegradation, the presence of these pollutants in water has highly influences the quality of water because most of them are considered to be toxic or even carcinogenic, and has a serious hazard to living organisms, effective treatment of dye-containing wastewater has been actively studied for several decades [2,3]. Conventional biological and chemical processes methods are not efficient for the degradation of dyes as their molecular structure contains complex aromatic amide groups with alkyl, halogen, nitro, hydroxyl, sulfonic acid, substituent, and inorganic sodium salts [4,5]. Adsorption using activated carbon is simple and efficient for the removal of dyes but needs high cost in regeneration [6–8].

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Advanced Oxidation processes (AOPs) are promising substitute technologies for efficient elimination of organic pollutants from wastewater with high chemical stability and low biodegradability. These AOPs work at near-ambient temperature and pressure and can produce powerfully oxidizing radical species such as •OH for complete decomposition of organic contaminants into non-toxic products like CO₂, H₂O and inorganic salts [9]. Homogeneous Fenton process, which generate •OH in the presence of Fe²⁺ and H₂O₂, is one of the most common homogeneous systems proposed for treatment of organic pollutants [10,11]. However, some of its defects include the sludge production due to the post-treatment process, limited reaction of pH range 2.5–3.5, H₂O₂ scavenger, high iron loss to environment, difficulty of the iron ions recovery the limit of its application [12,13]. An alternative method can be the use of heterogeneous Fenton catalysts. Many heterogeneous Fenton catalysts have recently reported, such as iron oxides [14,15], and iron-immobilized materials [16]. However, the heterogeneous Fenton reaction can oxidize aqueous contaminants at broader pH and reduce release of iron in water after treatment, it has low reaction rate and treatment efficiency due to the low reactivity of the initial reaction between iron oxide and H₂O₂ to produce •OH [17].

This limitation of heterogeneous Fenton oxidation can be overcome by taking advantage of heterogeneous photo-Fenton oxidation of UV light irradiation ($\lambda < 360$ nm) that quickly

converts Fe^{3+} to Fe^{2+} , which reacted with H_2O_2 producing $\cdot\text{OH}$ for efficient oxidation of organic contaminants [17,18]. However, UV light-based photo-Fenton oxidation also has practical limitations; that is inability to utilize sunlight as an irradiation source since UV light only consists of approximately 5% of sunlight [19,20]. Consequently, significant efforts to develop various photo-Fenton catalysts have been made to utilize visible light as the major proportion of the solar light source [21]. Recent studies reported visible light mediated photo-Fenton oxidation by employing TiO_2 , CdS , WO_3 coated with iron oxides. Heterogeneous photo-Fenton oxidation using the modified TiO_2 , Fe^{3+} and H_2O_2 under visible lights led to significant enhancement of $\cdot\text{OH}$ production and degradation of synthetic dyes, phenol and pesticides due to synergistic effects of photocatalysis and Fenton oxidation [22,23].

For the present study, the heterogeneous photo-Fenton catalyst $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanoparticle was synthesized by sol-gel method and characterized them by a number of physico-chemical methods (XRD, DRS, XPS, and PL). The activity of heterogeneous photo-Fenton catalyst $\text{Fe}_2\text{O}_3/\text{TiO}_2$ with the photocatalytic and photo-Fenton was assayed in the degradation of methyl orange in the presence of visible light and H_2O_2 . The major mechanism associated with the photo-Fenton oxidation was suggested.

2. Experimental section

2.1. Chemicals

Isopropyl alcohol (i-PrOH, 99.8%, Guoyao Chemical Co.), titanium tetraisopropoxide (TTIP, 97%, Sigma-Aldrich), acetic acid (AcOH, Guoyao Chemical Co.), iron nitrate nonahydrate (Sinopharm Chemical Reagent Co., Ltd.), nitric acid (Sinopharm Chemical Reagent Co.), and methyl orange (Sinopharm Chemical Reagent Co.) were used without purification.

2.2. Sample preparation

The sol-gel method was used to prepare $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanoparticles catalyst. At the room temperature and under magnetic stirring condition, 3 mL titanium tetraisopropoxide was added to 20 mL isopropanol, and then 6 mL acetic acid was added into the solution. Then 0.0697 g iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was added to the solution. The solution was stirred for 24 h at room temperature; the mixture was aged at 60°C for 3 h. The sol was calcined at 500°C for different calcination times 3 h to synthesize particles. For comparison, pure titania was prepared through the same method, without adding $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

2.3. Characterization

XRD diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation was used to study the Phase formation and crystallinity of the samples. A Tristar 300 (Micromeritics) porosimeter analyzer was used to determine the Brunauer–Emmett–Teller (BET) surface area, pore volume, porosity, Barret–Joyner–Halenda (BJH) pore size and distribution (based on nitrogen adsorption and desorption isotherms). Before analysis, the samples were prepared by heating at 150°C , while injecting nitrogen gas for 2 h using a Flow prep 060 (Micromeritics). The UV–vis diffuse reflectance spectra of the prepared powders was obtained by the UV–vis spectrophotometer (Shimadzu 2450 PC) mounted with an integrating sphere accessory (ISR1200), and using BaSO_4 as reference standard. The X-ray photoelectron spectra (XPS) of the samples were recorded with MS Omicron nanotechnology using PerkinElmer Model 5300 with $\text{AlK}\alpha$ as the radiation source operated at 200 W and hemispherical electron energy analyzer. The conditions of the equipment include a

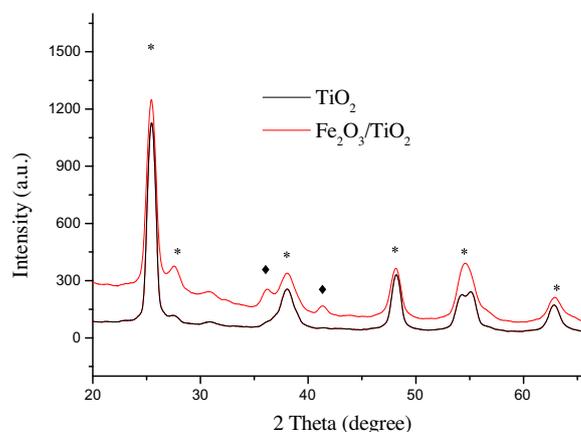


Fig. 1. XRD patterns of the TiO_2 and $\text{TiO}_2/\text{Fe}_2\text{O}_3$ samples. (* TiO_2 , ◆ Fe_2O_3).

takeoff angle of 45° and vacuum pressure of 10^{-8} to 10^{-9} Torr. The binding energies were referenced to the $\text{C}1\text{s}$ peak at 284.6 eV. Photoluminescence spectra (PL) was measured at room temperature on a SHIMADZU RF-5301 PC spectrometer using (excitation light $\text{EX} = 240 \text{ nm}$. Emission spectrometry range $\text{EM} = 350\text{--}400 \text{ nm}$).

2.4. Activity test

The photocatalytic activity of our samples was studied by degradation of methyl orange (MO) in water under visible light irradiation. Firstly, a particle suspension of the catalyst (0.5 g/L) solution was prepared and dispersed by a stirrer for 24 h. Secondly, 400 μL methyl orange solution (250 mg/L) was transferred to 50 mL particle suspension. Finally, 50 μL HNO_3 (0.05 mol L^{-1}) was added into the solution to ensure the acidity of the degradation system. The solution was placed under xenon light source, (xenon lamp current value was adjusted at 15 A, plus UV filters to remove UV light to ensure all the light is visible irradiations). To study its effect on photodegradation, 50 μL hydrogen peroxide (H_2O_2) was added into the solution. A 5 mL sample was withdrawn at time 0, 30, 60, 90, 120, 150, and 180 min. The photocatalyst was immediately removed from the samples after centrifugation with 5000 rpm for 10 min. The progress of photocatalytic degradation was monitored through the measurement of the characteristic absorbance of the solution samples by a UV–vis spectrophotometer (Shimadzu 2450 PC). Also, the measurement of the total organic carbon (TOC) by a Shimadzu $\text{TOC-V}_{\text{CSH}}$ analyzer was carried out.

3. Results and discussion

3.1. Structure characterization

Fig. 1 depicts the XRD patterns of the TiO_2 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples. Crystalline planes corresponding to the peaks for TiO_2 and Fe_2O_3 have been indexed in this figure. Several crystalline peaks are detected for pure TiO_2 sample at $2\theta = 25.3^\circ$, 38.5° , 48° , 53.8° , 55.1° and 62.6° indicating the existence of predominant anatase phase³. However, small peaks are detected at $2\theta = 27.4^\circ$ owing to the existence of small proportion of rutile phase³. Compared to the XRD patterns of TiO_2 , major peaks at 2θ values of 35.4° and 40.7° could be assigned to Fe_2O_3 (110) and (113), crystal planes (JCPDS File Card No.03-0800.52). These results were similar with Ahmed's work.³ Thus; powder XRD results revealed that there were Fe_2O_3 nanoparticles on the TiO_2 support.

The N_2 isothermal adsorption technique was employed to investigate the pore size variability of TiO_2 after the Fe_2O_3 coated. As shown in Fig. 2a, both $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and reference TiO_2

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