FACILE IN-SITU FABRICATION α-Fe_2O_3 NANOPARTICLES USING ZnO AS A NANOTEMPLATE FOR DYE TREATMENT

Received 15-05-2024

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TÓM TẮT

PHƯƠNG PHÁP MỚI CHẾ TẠO HẠT α-Fe_2O_3 KÍCH THƯỚC NANO ỨNG DỤNG TRONG XỬ LÝ CHẤT MÀU

Hạt nanowires ZnO có thể dùng để điều chế các loại oxit kim loại có hình dạng nanotube bằng phương pháp khuôn mẫu hi sinh (sacrificial template synthesis-STAH). Đây là một phương pháp mới, có thể điều chế được rất nhiều loại oxit kim loại mà những phương pháp thông thường không thể điều chế được. Trong nghiên cứu này, chúng tôi sử dụng phương pháp STAH để chế tạo hạt nano α-Fe_2O_3 với diện tích bề mặt riêng lớn trên 270 m^2g^{-1}, cao hơn so với cách ché tạo hạt nano α-Fe_2O_3 thông thường. Chúng tôi đã dùng hạt nano ZnO có kích thước bề mặt riêng lớn, cấu tạo hạt vẩy để thu được hạt α-Fe_2O_3 sử dụng phương pháp STAH. Hạt α-Fe_2O_3 điều chế được ứng dụng trong việc xử lý Methylene Blue bằng phản ứng Fenton. Kết quả cho thấy hạt α-Fe_2O_3 thu được có kết quả xúc tác Fenton cao hơn so với các hạt α-Fe_2O_3 điều chế bằng phương pháp thông thường.

Keywords: *Khuôn mẫu hi sinh, Fenton, methylene blue, nano ZnO, Fe_2O_3*

1. INTRODUCTION

The recent development of nanotechnology has prompted scientists to investigate new nanostructure properties of both traditional and innovative materials. The most essential aspect of metal oxide nanostructures is their huge interface area, which plays an important role in many processes, including electrochemical processes [1] and heterogeneous catalytic reactions [2-4] . In this regard, the development of synthesis for metal oxide nanostructures with large interface areas is an important focus of current research [5-6].. These materials are widely synthesized as unsupported nanoparticles using a variety of synthesis techniques, as documented in recent scientific literature [7-9].

The development of simple synthesis processes for creating metal oxide nanostructures remains an essential challenge. The STAH method (Sacrificial Template Accelerated Hydrolysis) provides a new accessible resource for material synthesis under ambient environments. This approach uses ZnO as a hard template and allows for the creation of a new generation of metal oxide nanomaterials while concurrently removing the ZnO template [10]. The procedure is straightforward and does not involve any complicated machinery (such as vessels with pressure, extreme temperature treatments, CVD approaches, etc.). It could be a notable improvement over traditional hard template procedures because it significantly makes easier the synthesis process and eliminates the template removal phase.

This study aims to investigate the production of Fe_2O_3 nanomaterials utilizing the STAH method. The mechanism and methods of synthesis are described. Also, the structural, morphological, and textural of the synthesized material, as well as it applicability in dye treatment in Fenton catalyst, are investigated.

2. METHOD

2.1. Fabrication method

2.1.1. The fabrication of the template: ZnO nanoparticles

Tan Vu et al.[11] described a method for synthesizing ZnO nanoparticles. 100 mL mixture of 0.05M zinc acetate and 1.0M urea was made. The prepared mixture was placed in a Teflon container (150 mL), and the synthesis of ZnO nanoparticles was carried out under a constant temperature 90°C for 24 hours. After that, the obtained white powder was thoroughly washed using deionized water and dried at 80°C for 5 hours. Finally, the dried powder was calcined at 215°C during 1 hour in air to obtained ZnO nanoparticles.

2.1.2. The fabrication of α-Fe_2O_3 nanoparticles using ZnO nanoparticles template

Due to the acidic of iron ion, the iron oxides were synthesized by using the dropwise method, A solution (50 mL) of iron (III) nitrate were slowly pumped into flasks containing 100 mL of water and the ZnO nanoparticles template, while the flasks were magnetically agitated at room temperature. The obtained samples were rinsed with water, and vacuum-dried at 60ºC for 90 minutes. After that, the obtained powder was calcined in air at 270°C for 2 hours to obtain iron oxides.

2.2. Material characterization

The X-ray diffraction (XRD) patterns of the synthesized zinc oxide and iron oxide were recorded on a Bruker D8 Advance instrument working at 40 kv and 40 mA using Cu Kα radiation (λ = 0.15406 nm). The crystal size of the nanoparticles were calculated from the XRD pattern by Scherrer's equation (dXRD). The morphological and size of the sample was examined by scanning electron microscopy (SEM, FEI Quanta FEG 650 model) and transition electron microscopy (TEM, Cryo thermofisher) . The specific surface area BET of the both samples was examined by N_2 adsorption isotherms (-196ºC) using Micromeritics ASAP 2020 analyser. Thermogravimetric analysis (TGA) was performed under air using TGA Q500 system (TA, US).

2.3. Fenton tests

In batch operation, Fe_2O_3 catalysts were used to degrade methylene blue (MB) solutions, similar to Fenton reaction. To prevent the influence of light, all responses took place in the dark. We compare the catalytic activity of our Fe_2O_3 powder to that of Cui et al.'s Fe_2O_3@mesoporous SiO_2 particles. The reaction was done in a mechanically agitated reactor at room temperature, using exactly the same conditions employed by Cui et al.. (0.5 g/L of Fe_2O_3, 50 mg/L of MB, and 18 g/L of H_2O_2). The liquid MB samples were gathered at determine reaction times and eliminating α-Fe_2O_3 particles by centrifuging. The absorption peaks of all the collected MB samples were measured in the range of 400-800 nm using a UV-Vis spectrometer. The MB concentration was calculated at 664 nm of the MB spectrum.

III. RESULT AND DISCUSSION

3.1. Sacrificial templated-accelerated hydrolysis

Among the many techniques for synthesis documented in the academic and patent writings, primarily for manufacturing metal oxides, hard templating approach are recognized to be amongst the best in manufacturing high surface areas of metal oxides in the form of powder[12][13]. However, these approaches need multiple synthesis stages, involving the elimination of the hard template through or dissolution or oxidation. Sacrificial template-accelerated hydrolysis (STAH) is a unique hard exotemplating approach [14] that involves the creation of nanotubes of metal oxide through the hydrolysis of metal ions near ZnO. Hydrolysis is aided by the elimination of H^+ caused by the simultaneously dissolution of the ZnO structure, which is a unique characteristic of STAH method. Thus, the main advance over traditional hard templating processes is the self-removal process of the template.

In our work, the iron oxide nanoparticle is synthesized by STAH approach. The synthesis of α-Fe_2O_3 is described as the following:

$$[Fe(H_2O)_6]^{3+} \rightarrow [Fe(OH)(H_2O)_5]^{2+} + H^+ \quad (1)$$

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \quad (2)$$

$$[Fe(OH)(H_2O)_5]^{2+} \rightarrow Fe(OH)_3 + 2H^+ + 3H_2O \quad (3)$$

Chemical and structural characterization of ZnO and Fe_2O_3 nanoparticles

Figure 1 illustrates the X-ray diffraction peaks for ZnO nanoparticles and iron oxide nanoparticles. Following the STAH reaction, the diffraction peaks of ZnO at 32º-36 º disappeared. This indicates that ZnO has been totally consumed. Iron oxides exhibit patterns of amorphous materials that are challenging to attribute to any recognized crystal structures.

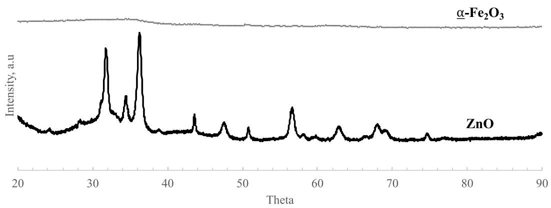

Figure 1. XRD pattern of ZnO and α-Fe_2O_3 nanoparticles

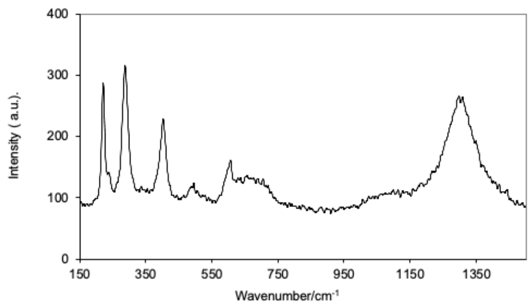

Figure 2. Raman patterns of the α-Fe_2O_3 particles.

To help with classification in the condition, we used Raman spectroscopy in Figure 2. The spectrum match with the one from hematite α-Fe_2O_3 [10].

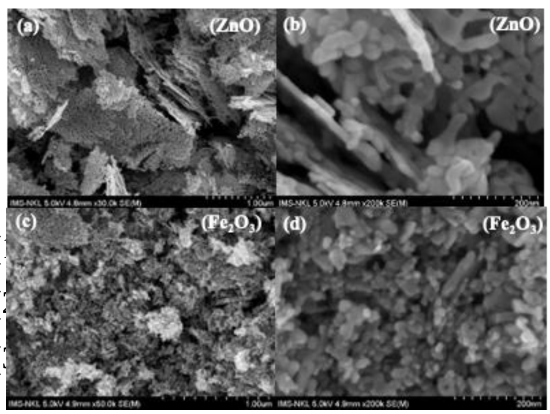

Figure 3. Low-magnification and high-magnification SEM images of ZnO and Fe_2O_3

Figure 3 displays the morphologies of the iron oxides and ZnO nanoparticles. It is evident that following the substitution process, the ZnO template's macroscopic appearance (Figure 3 a,b) remained largely unchanged. The iron oxides have been structured into arrays of uniformly sized thin nanosheets with length distributions between 1-2 μm. The particle size of the obtained Fe_2O_3 is smaller to the size of ZnO nanoparticles.

The Fenton catalyst efficiency can be calculated by examining the specific surface area, total pore volume, and average pore width of the Fenton catalyst. Table 1 shows the BET specific surface area and total volume of ZnO and Fe_2O_3 nanoparticles, which were determined using nitrogen gas adsorption. The findings indicate that Fe_2O_3 nanoparticles have a greater specific surface area (270 m^2/g), but ZnO has a lower surface area. Furthermore, Fe_2O_3 nanoparticles have a greater total pore volume of 0.74 cm^3/g compared to 0.21 cm^3/g ZnO. As a result, Fe_2O_3 may provide the best Fenton catalyst activity.

Table 1. Parameters of S_{BET} specific surface area and total pore volume Vp

Adsorbent	S_{BET} (m^2/g)	Vp, cm^3/g
ZnO	82	0.26
Fe_2O_3	270	0.74

3.2. Fenton catalytic activity of the iron oxide catalyst

To assess the potential of the current development, we test the catalytic activity in heterogeneous Fenton-like degradation of Methylene Blue (MB). This advanced oxidation method uses iron-based catalysts to stimulate an interaction between hydrogen peroxide and ferrous ions, resulting in the production of reactive hydroxyl radicals. It is a well-established and successful method for destroying a wide range of hazardous and organic contaminants [16][17].

Figure 4 illustrates the catalytic activity of the obtained iron oxide. After 210 minutes of reaction time, the MB is almost degraded.

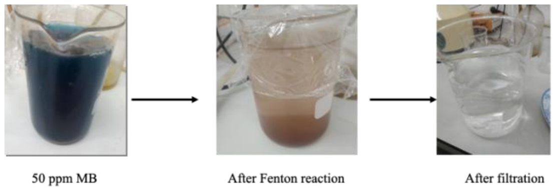

Figure 4. Fenton catalytic activity of Fe_2O_3

To evaluate the Fenton catalyst activity of Fe_2O_3 nanoparticles, samples treated with only H_2O_2 and Fe_2O_3 produced in this study using the Cui technique [18] were subjected to the same Fenton test conditions. The results demonstrate that the sample treated with simply H_2O_2 and the produced Fe_2O_3 in Cui work [18] degraded approximately 27 and 73% of the MB in 210 minutes, respectively (Figure 5). And the produced Fe_2O_3 nanoparticles completely degraded the MB solution in the same Fenton reaction period. This study displays remarkable Fenton activity when compared to the materials synthesized in the literature.

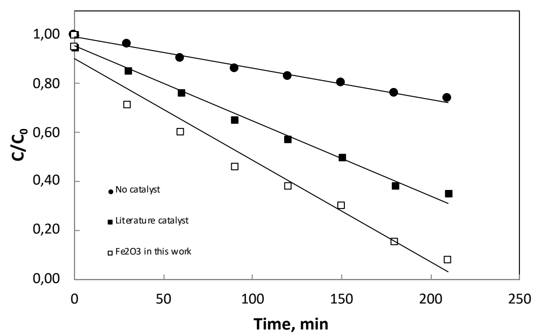

Figure 5. The figure of C_0/C versus reaction time during the degradation of MB in the presence of literature catalyst and synthesized catalyst.

To assess the catalytic stability of the synthesized material, a stability test of Fe_2O_3 was performed. The catalytic stability test of Fe_2O_3 was done five times with the recovered Fe_2O_3 after each cycle. Figure 6 depicts the acquired data, which reveal a small decline in Fe_2O_3 catalytic activity during 5 stages of reaction. Thus, it can be assumed that Fe_2O_3 is quite stable and can be reused for a variety of Fenton reaction stages. As a result, Fe_2O_3 has the potential to be an excellent Fenton catalytic material for dye treatment.

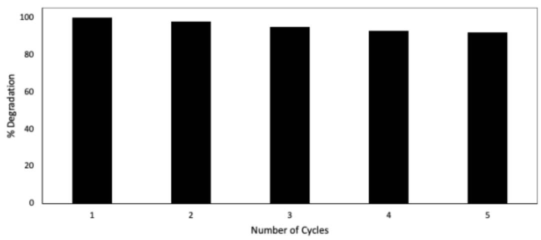

Figure 6. The stability test of the Fenton catalyst synthesized in this work

4. CONCLUSIONS

A new approach for producing iron oxide nanoparticles is presented. The method is based on the STAH mechanism in an aqueous solution. The hard template is a high surface area ZnO nanomaterial which is self-removal during the hydrolysis of iron ion. The nanosized metal oxides α-Fe_2O_3 is obtained in high specific surface area $270 m^2 g^{-1}$. The obtained material is used in Fenton-like degradation of aqueous Methylene Blue. The obtained result shows that α-Fe_2O_3 fabricated by STAH method can be an outstanding Fention catalyst for the dye degradation.

ACKNOWLEDGEMENTS

The work was supported by Hanoi University of Science and Technology through the grant number T2023-PC-102.

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