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Research Article

One-Pot Synthesis of Bi/Fe_3O_4 and Its Catalytic Performances for 4-Nitrophenol Reduction

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Abstract

A novel approach was successfully developed for the catalyst Bi-deposited Fe_3O_4 magnetic nanoparticles, which was used in the degradation of 4-nitrophenol (4-NP). The Bi/Fe_3O_4 composite was prepared via a one-pot process from ferrous sulfate and bismuth chloride using hydrazine hydrate as a reducing agent. The catalyst was characterized by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. In the composite pure Fe_3O_4 particles were synthesized and bismuth particles were well dispersed. The catalytic performances were investigated for the reduction of 4-NP with sodium borohydride. The catalyst has higher activity when Bi/Fe molar ratio is 1:4 in the composite and the rate constant k is about 0.611 min^{-1}. The catalyst has good reusability which can be used 10 cycles without obvious deactivation. Furthermore, the catalyst can be easily separated by an external magnetic field. Copyright © 2017 BCREC GROUP. All rights reserved

Keywords: Bismuth; Bi/Fe_3O_4; 4-Nitrophenol; Reduction

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1. Introduction

4-Nitrophenol (4-NP) threatens seriously human health and natural environment due to its structural stability, difficult degradation and water solubility, which are from the production of pesticides, herbicides, insecticides and synthetic dyes cause serious pollution [1,2]. The product 4-aminophenol (4-AP) from reduction of 4-NP is an important intermediate in the preparation of several analgesic and antipyretic drugs such as acetaminophen, acetanilide, phenacetin, and so forth. It is also used as a corrosion inhibitor in paints and anticorrosion-lubricating agent in fuels. In the dye industry, 4-AP is used as a wood stain and as a dyeing agent for fur and feathers [3]. Apart from this, 4-AP is less poisonous than 4-NP. Therefore, the reduction of 4-NP to 4-AP becomes academically as well as technologically important. Indeed, a great number of studies for reduction of 4-NP with sodium borohydride to 4-AP have been performed over the past few decades, using a number of noble metal nanoparticles, such as Pt [4], Pd [5], Au [1,6] and Ag [7-10], as catalysts. To reduce the cost of catalysts, non-precious metals, such as Ni [11], Co [11,12] and Cu [11,13], were also used as catalysts in the reduction. In these studies, catalytic metal nanoparticles were mostly deposited onto silica [10], silica-coated Fe_3O_4 [7], grapheme oxide [9] or polymers [4] before conducting the reduction to prevent aggregation during the reaction. Due to their insoluble and

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superparamagnetic properties, which enable them to separate easily with an external magnetic field, Fe_3O_4 magnetic nanoparticles have recently emerged as viable alternatives to conventional materials for catalyst supports. Several strategies have been made to combine metal nanoparticles and magnetic nanoparticles coated with silica, forming nanocomposites that possess magnetic and catalytic dual functionalities. However, the materials synthesis procedures are complicated. The reduction solution of 4-NP with sodium borohydride is alkaline, and Fe_3O_4 particles are stable. So a protection layer of Fe_3O_4 particles is not necessary in the reaction.

Bi particles are cheap and easily fabricated by reduction with reducing agent such as sodium borohydride and hydrazine hydrate. More importantly, Bi is a kind of environment-friendly element. Bismuth(III) salts are considered safe and non-toxic probably due to their insolubility in neutral aqueous solutions. Therefore, bismuth and its salts appeared as suitable regents for design of “eco-friendly catalyst” [14]. Bismuth-containing photocatalysts can be used in many fields because of narrow ban gap and ability of adsorbing visible light [15], but there are few researches on bismuth-catalyzed reduction of nitrophenols. Huang et al. used the in-situ formed bismuth porous nanospheres as a catalyst for the reduction of 4-NP successfully, but the reaction rate is low [16]. Here, a facile route was developed for the preparation of catalytically active Bi/Fe_3O_4 composites via a one-pot method. Fe_3O_4 particles were prepared from ferrous sulfate using hydrazine hydrate as a precipitating and oxidizing agent [17]. Bismuth chloride solution was added to the above mixture, and then Bi/Fe_3O_4 composites were synthesized with hydrazine hydrate as a reducing agent. The Bi/Fe_3O_4 composites were characterized and their catalytic performance was investigated for the reduction of 4-NP in aqueous solution under mild conditions. These Bi/Fe_3O_4 composites are expected to be a new class of highly efficient, fully renewable and eco-friendly heterogeneous catalysts.

2. Materials and Methods

2.1. Materials

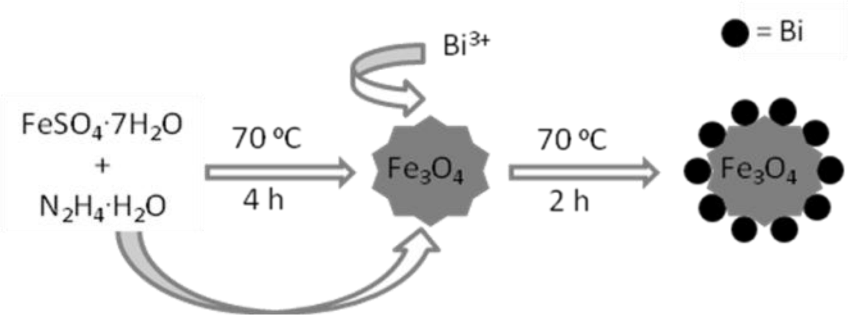
Bismuth chloride, ferrous sulfate and 4-NP were purchased from Tianjin Fuchen Reagent Co. Ltd. (China). Sodium borohydride and hydrazine hydrate (50%) were purchased from Sinopharm Chemica Reagent Co. Ltd (China). All reagents were of analytic grade and used without further purification. Ultrapure water was used throughout the whole experiment.

2.2. Catalyst preparation

Bi/Fe_3O_4 particles were synthesized by a facile one-step process. Typically, $FeSO_4{\cdot}7H_2O$ (1.39 g) was dissolved in 20 mL water. Then, the solution of NaOH (1.3 g) and hydrazine hydrate (5.0 g) in 20 mL water was added to the above solution and stirred at 70 ℃ for 4 h to yield Fe_3O_4 particles [17]. $BiCl_3$ (0.79 g) was dissolved in 20 mL HCl (0.1 M), and then the $BiCl_3$ solution was dropped into the above mixture and stirred at 70 ℃ for 2 h to obtain Bi/Fe_3O_4 composite particles. The product was recovered from the reaction mixture by a permanent magnet, washed 6 times with water and dried at 60 ℃ for 6 h. For the determination of appropriate synthesis conditions, Bi/Fe molar ratio in the reaction mixture was varied from 1:15, 1:10, 1:6, 1:4 to 1:2, and the products were denoted as Bi/Fe_3O_4-15, Bi/Fe_3O_4-10, Bi/Fe_3O_4-6, Bi/Fe_3O_4-4 and Bi/Fe_3O_4-2 respectively. The synthesis process of the Bi/Fe_3O_4 particles is presented in Scheme 1.

2.3. Catalyst characterization

XRD patterns were obtained on an X-ray diffraction (XRD) instrument (Ultima IV, Ri-

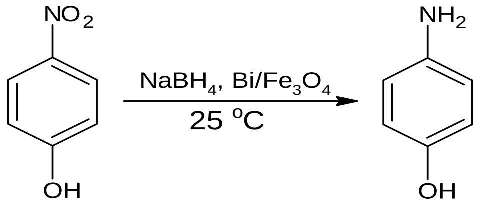


Scheme 1. Formation process of the Bi/Fe_3O_4 particles.

gaku) equipped with a Cu Kα radiation source. It was operated under the following conditions: tube voltage 40 kV, current 40 mA, and scanning range 2θ = 10-80°. The morphologies of the as-prepared samples were characterized with a JEOL JEM-2100 transmission electron microscope (TEM). Samples were dispersed in ethanol. Fourier transform infrared spectra (FTIR) were recorded between 4000 and 400 cm^{-1} with a Bruker ALPHA spectrometer.

2.4. Catalytic reduction of 4-NP

The reduction of 4-NP catalyzed by Bi/Fe_3O_4 catalyst in the presence of an excess amount of $NaBH_4$ was studied in a beaker and monitored with a UV-Vis spectrometer to examine the catalytic activity at 25 °C (Scheme 2). The reaction procedure was as follows: 10 mL of 4-NP (10 mM), 70 mL of water and 20 mL of freshly prepared $NaBH_4$ aqueous solution (0.2 M) were added into a beaker with constant stirring. In order to avoid magnetic condensation, the stirring was performed with a mechanical stirrer. Then, 0.01 g of Bi/Fe_3O_4 catalyst was added into the solution. Samples were directly withdrawn from the reaction mixture at certain time intervals followed by measuring UV-Vis absorption at 400 nm. The rate constant of the reaction was determined by measuring the change in intensity of these peaks with time. At the end of the reaction, the catalysts were separated from the mixture using a permanent magnet, washed with water and reused.



Scheme 2. Reduction of 4-NP with $NaBH_4$.

3. Results and Discussion

3.1. Characterization of Bi/Fe_3O_4

The phase structure of the sample was obtained through XRD measurement. As shown in Figure 1, the diffraction peaks at 2θ = 30.16°, 35.60°, 43.22°, and 57.14° can be indexed to (220), (311), (400), and (511) planes of inverse spinel structure Fe_3O_4 (JCPDS No.19-0629) [17]. The presence of Bi nanoparticle on the surface of Fe_3O_4 can be confirmed from the XRD patterns of Bi/Fe_3O_4-2 and Bi/Fe_3O_4-4. The peaks found at 27.18°, 37.95°, 39.62°, and 64.46° represent the planes of (012), (104),

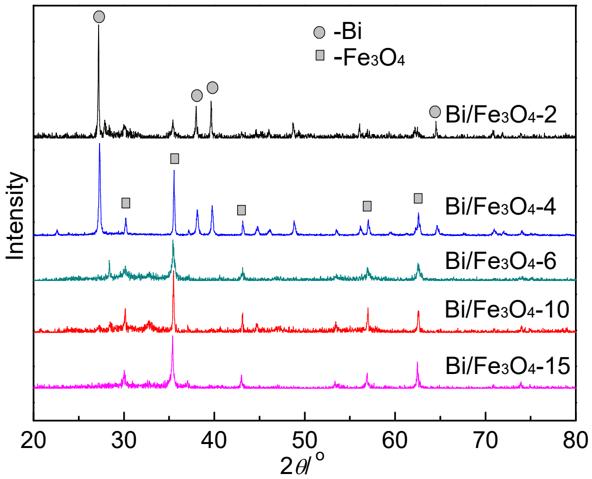


Figure 1. XRD patterns of Bi/Fe_3O_4 particles.

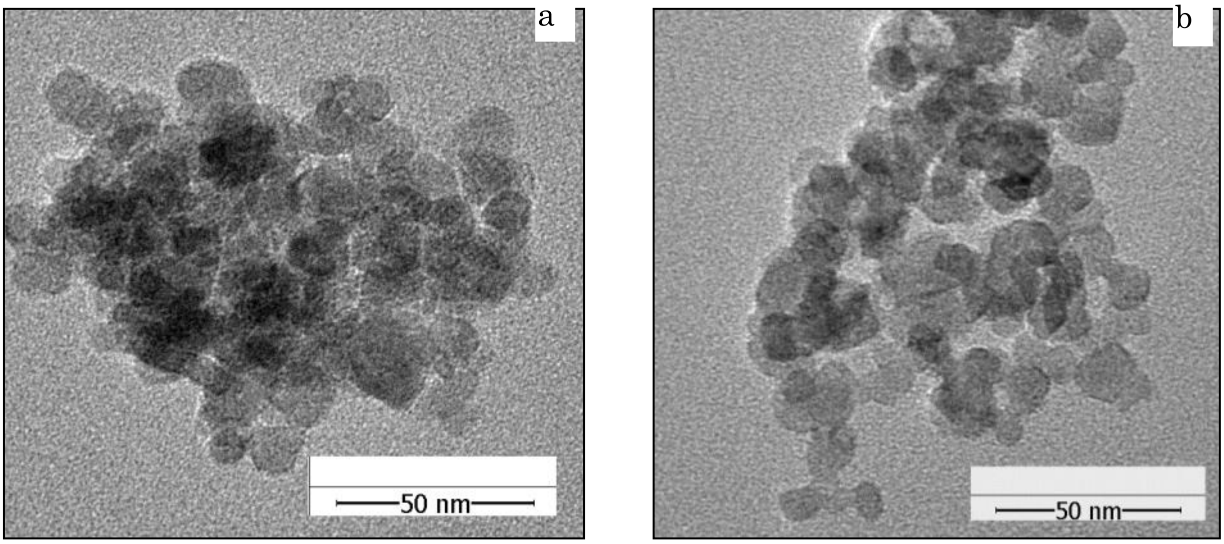


Figure 2. TEM images of Fe_3O_4 (a) and Bi/Fe_3O_4-4 (b)

(110) and (122) for bismuth crystal (JCPDS No.85-1329) [16]. No metallic Bi phase was founded from the patterns of Bi/Fe_3O_4-6、Bi/Fe_3O_4-10 and Bi/Fe_3O_4-15, indicating that Bi was evenly distributed in Fe_3O_4 particles.

Figure 2a shows the TEM image of Fe_3O_4 that exhibits mean particles sizes in the 7-18 nm ranges and acquires mainly a nano spherical-like morphology. The particle size distribution was narrow and slightly-aggregated. As seen in Figure 2b, the Bi/Fe_3O_4-4 particles turned more smother and readily identified with an average crystallite size in the 8-20 nm range, since Bi deposited on Fe_3O_4 can remedy their defects. From Figure 2, there is no obvious distinction in morphology between Fe_3O_4 and Bi/Fe_3O_4-4. The results indicate that Bi particles dispersed on the surface of Fe_3O_4 particles evenly.

From Figure 3, the absorption peaks at around 620 cm^{-1} and 480 cm^{-1} correspond to the Fe-O bond of bulk magnetite. The results indicate that Fe_3O_4 particles were successfully synthesized. The intensity of absorption peak at 620 cm^{-1} and 480 cm^{-1} increased with the increase of Fe content in the composite.

3.2. Catalytic activity

3.2.1. The effect of Bi/Fe molar ratio on the activity of the catalyst

Figure 4 shows the UV-Vis absorption spectra, representing the reduction of 4-NP to 4-AP with $NaBH_4$ in the presence of Bi/Fe_3O_4 particles. As shown in Figure 4, time-dependent UV-Vis spectra of the reaction mixture show the gradual disappearance of 400 nm peak and the gradual development of the new peak at 300 nm which confirms the formation of the 4-AP. We found that Bi/Fe molar ratio in the Bi/Fe_3O_4 composite played an important role in the catalytic activity. As shown in Figure 4, the time of complete degradation of 4-NP were 28 min (Bi/Fe_3O_4-15), 24 min (Bi/Fe_3O_4-10), 14 min (Bi/Fe_3O_4-6), 8 min (Bi/Fe_3O_4-4) and 10 min (Bi/Fe_3O_4-2) respectively. As a comparison, while bare Fe_3O_4 was used as a catalyst for the reduction, the absorption peak at 400 nm was almost unchanged. The results indicate that Fe_3O_4 has no catalytic activity, and the activity of Bi/Fe_3O_4 composite increases gradually with the increase of Bi/Fe molar ratio. Since Bi is the active component, the activity of the catalyst would increase with the increasing of Bi loading within a certain range. However, when Bi/Fe molar ratio is 1:4, the activity is highest. Further increasing of the load of Bi cannot afford significant benefits. However, when the molar ratio increases over a certain value, Bi particles would gather severely, and the greater particle size of Bi particles might decrease the activity.

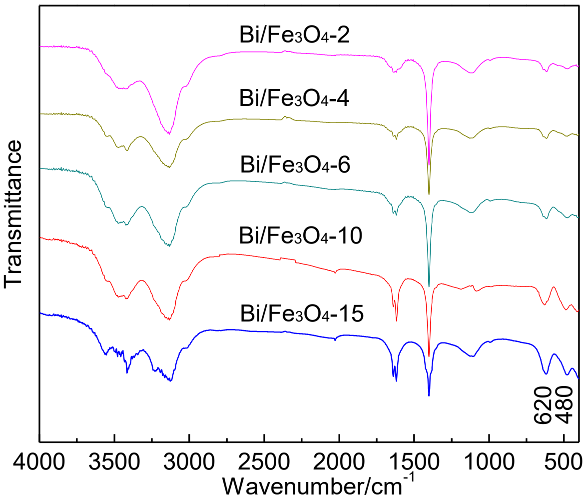


Figure 3. FTIR spectra of Bi/Fe_3O_4 particles.

3.2.2. The effect of the catalyst dosage on the reduction reaction

In this experiment, the concentration of the $NaBH_4$, used as reductant, largely exceeds (~40 times) that of 4-NP. As the initial concentration of $NaBH_4$ was very high, it remained essentially constant throughout the reaction. Therefore, for evaluation the catalytic rate pseudo-first-order kinetics with respect to 4-NP was used. The rate constants of this catalytic reaction in the presence of the Bi/Fe_3O_4-4 particles were measured from the plot of $\ln(A/A_0)$ (A = absorbance at 400 nm) versus time t.

Figure 5 shows the impact of different dosages of Bi/Fe_3O_4-4 composite on the reduction of 4-NP. When the amount of Bi/Fe_3O_4-4 was 0.01 g, 0.015 g and 0.02 g, the rate constants were 0.611 min^{-1}, 0.922 min^{-1} and 1.176 min^{-1} respectively. The reaction proceeds faster with larger amount of catalyst, which was contributed to the proportional increase in the number of active catalytic sites. That is to say, with increasing the dosage of Bi/Fe_3O_4-4 composite, more and more active sites were available to accelerate the decomposition of $NaBH_4$, thus promoting the rate of reaction. When the amounts of catalysts were same (0.01 g), the rate constant (0.611 min^{-1}) in this paper was bigger than that (0.07 min^{-1}) in literature [16], indicating that Bi/Fe_3O_4 has higher activity than porous bismuth.

3.3. Reusability

The reusability of catalyst is very important issues for practical applications. To demonstrate the reusability of the catalyst, the as-prepared Bi/Fe_3O_4 composite was easily recycled by an external magnet after the reaction, washed and recycled for the reduction. Figure 6 shows the Bi/Fe_3O_4-4 catalyst can be successfully recycled and reused for ten times with stable conversion of 97% within 8 min (0.01 g of Bi/Fe_3O_4-4 catalyst), indicating very high stability. The conversion begins to decrease after 10 cycles, probably due to gradual loss of catalyst with repeated magnetic separation.

4. Conclusions

In summary, a magnetic Bi/Fe_3O_4 composite was prepared via a facile one-pot method by using hydrazine hydrate as a reducing agent for the formation of Fe_3O_4 and Bi particles. XRD

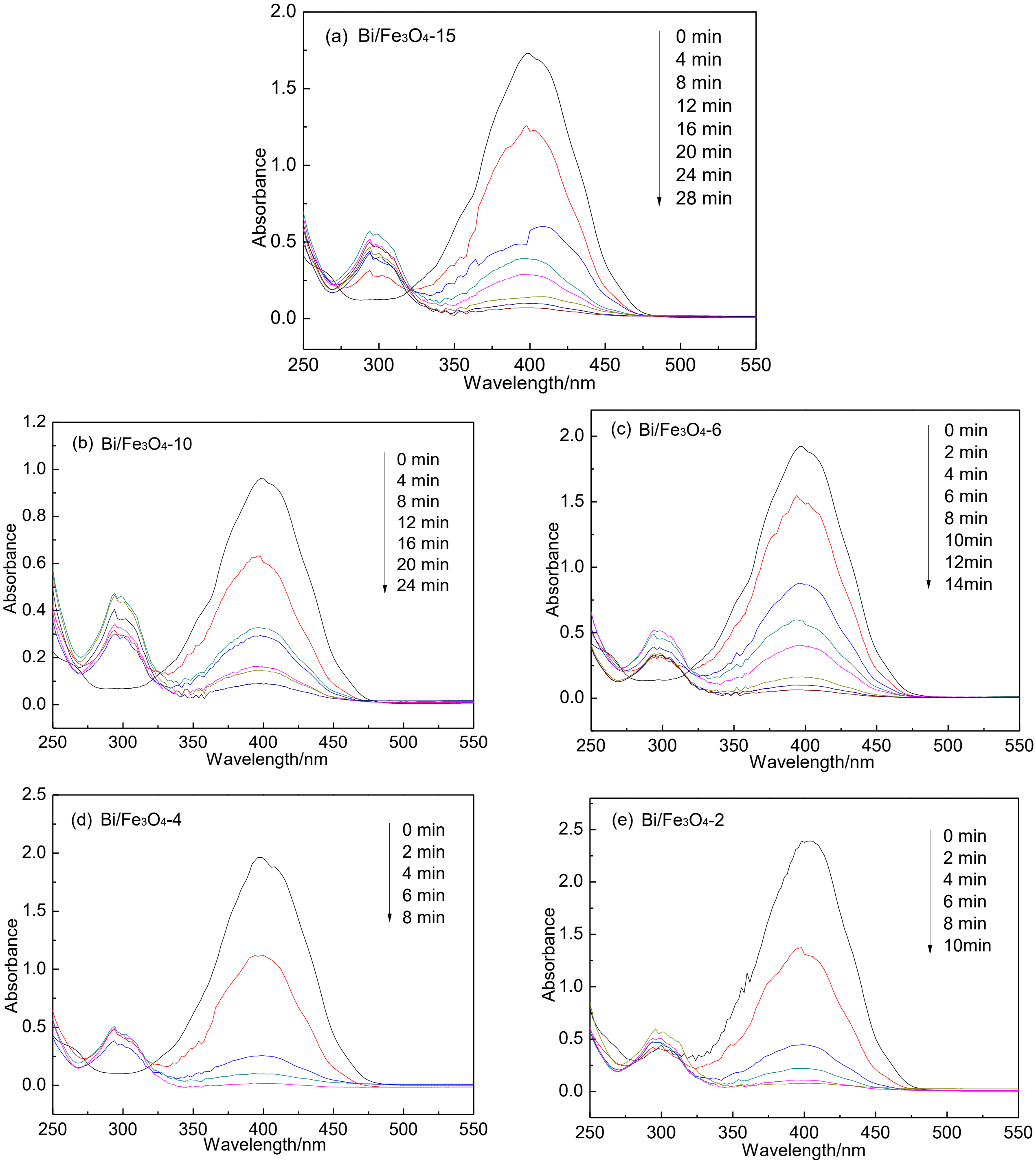


Figure 4. Effect of Bi content on the catalyst activity.

patterns indicated the catalyst was bismuth-loaded Fe_3O_4 composite particles. The catalytic activity was demonstrated by the study on the reduction of 4-NP to 4-AP with $NaBH_4$, and the Bi/Fe_3O_4 composite particles exhibited a good catalytic activity. When Bi/Fe molar ratio was 1:4, the activity of Bi/Fe_3O_4 composite was highest. Moreover, the composite exhibited well magnetic separability and excellent reusability without major loss and activity.

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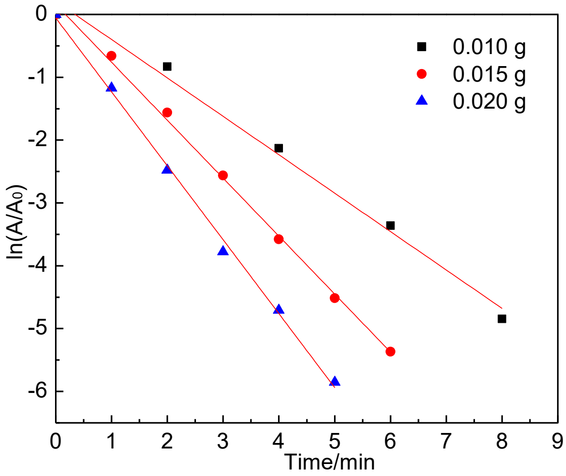

Figure 5. Effect of catalyst dosage on the reduction of 4-NP.

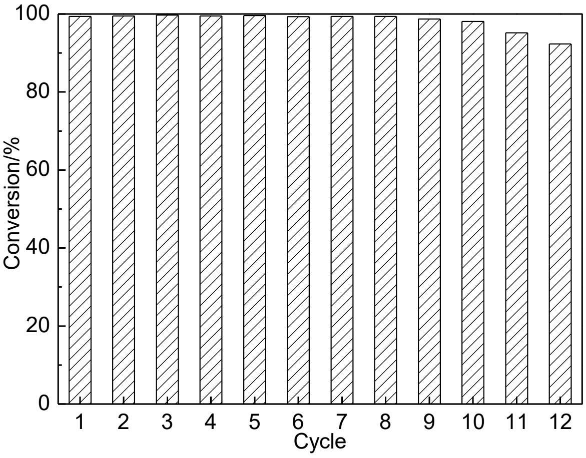

Figure 6. Reusability of Bi/Fe_3O_4-4 for the reduction of 4-NP.

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