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Article

Synthesis and application of magnetically recyclable nanocatalyst $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ in the reduction of azo dyes

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ABSTRACT

A novel method for synthesizing magnetically recyclable nanocatalyst $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ (Nico = nicotinic acid) was introduced. The structural, morphological, and magnetic properties of the nanocatalyst were characterized by Fourier transform infrared spectroscopy, X-ray powder diffraction, scanning electron microscopy, and vibrating sample magnetometry. Finally, $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ was examined toward the hydrogenation of azo dyes methyl orange, methylene blue, eosin Y, and rhodamine B. The nanocatalyst showed excellent reusability properties that remained unchanged after several catalytic cycles. Therefore, the current findings show the potential of the prepared $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ nanocatalyst as a candidate for application in the purification of organic aqueous pollutants for wastewater treatment.

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1. Introduction

Persistent organic pollutants, such as dyes, antibiotics, or pesticides, have complex aromatic structures and are non-biodegradable and harmful to the environment. Accordingly, the degradation of azo dye pollutants, which is challenging, has received much attention recently. Among the azo dyes, methyl orange (MO), an organic sulfosalt, methylene blue (MB), a heterocyclic aromatic dye, eosin Y (EY), a tetrabromofluorescein (or its disodium salt) dye, and rhodamine B (RhB) have been studied and considered as very harmful pollutants. These dyes can decolorize upon application of oxidation, adsorption, degradation, or catalytic reduction processes [1–4].

Various types of adsorbents have been studied toward the removal of the above-mentioned dyes from aqueous solution in the literature; however, magnetic adsorbents have gained more attention owing to their easy control and fast separation capabilities [5–7]. Accordingly, superparamagnetic iron oxide (Fe_3O_4) nanoparticles have been mainly examined owing to the

their large magnetic moment, excellent superparamagnetism, and high stability in aqueous media [8,9]. Furthermore, they have been used as a supporting material for catalysts because they can facilitate the separation of the catalyst from the reaction system using an external magnetic field. More specifically, a magnetic core in the nanocatalyst is useful for enabling separation of the suspended catalyst particles from the solution, whereas the nanocatalyst itself is effective for destroying organic azo compounds in wastewater. For example, Kurtan et al. [10–12] reported the synthesis of magnetically recyclable nanocatalyst $\text{Fe}_3\text{O}_4@\text{APTES}@\text{PAMAM}-\text{Ag}$ (APTES = (3-aminopropyl)triethoxysilane; PAMAM = poly(amido amine)) for application in the reduction of 4-nitrophenol to 4-aminophenol; the authors also reported rapid color degradation of organic dyes by $\text{Fe}_3\text{O}_4@\text{His}@\text{Ag}$ (His = histidine). Thus, combining a magnetic material with a noble metal (catalytic component), such as Ag or Cu, is important for preparing catalysts featuring both magnetic and recyclable and good catalytic activities. The preparation of such catalysts affords a bridge between homo-

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geneous and heterogeneous catalysis by providing recycling possibilities through simple magnetic separation [13–16].

Accordingly, in this study, an easy and convenient method to fabricate $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ (Nico = nicotinic acid) magnetically recyclable nanocatalyst (MRC) is demonstrated. The MRC can effectively decolorize organic azo compounds such as MO, MB, RhB, and EY during the industrial and domestic wastewater treatment. Moreover, $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC exhibits excellent catalytic activity toward the reduction of the dye pollutants and can easily be recovered by a magnet.

2. Experimental

2.1. Catalyst preparation

$\text{Fe}_3\text{O}_4@\text{Nico}$ nanocomposite was prepared by a reflux method. Analytical grade chemical reagents $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (Merck) were used as precursors. The metal salts at the required stoichiometric ratios (0.02 mol $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and 0.009 mol $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$) were dissolved in distilled water (40 mL) in a three-neck round-bottom flask under magnetic stirring to achieve a homogeneous solution. Then, nicotinic acid (0.008 mol) was added under vigorous stirring. Concentrated NH_3 solution (10 mL) was added dropwise under constant stirring to adjust the pH of the solution to 10 to induce the precipitation of ferrites. Then, the solution-containing flask was transferred to a heating mantle, where it was refluxed under argon at 80 °C for 5 h. The obtained $\text{Fe}_3\text{O}_4@\text{Nico}$ nanocomposite was separated from the reaction mixture using a permanent magnet and washed with distilled water and ethanol solution several times to remove impurities. Finally, a black powder was obtained and dried at 80 °C for 4 h.

The prepared $\text{Fe}_3\text{O}_4@\text{Nico}$ nanocomposite (150 mg) was dispersed in deionized water (50 mL) assisted by sonication for 30 min. Then, $\text{Cu}(\text{NO}_3)_2$ solution (30 mL, 0.2 mmol/L) was added and the resulting mixture was vigorously stirred for 30 min, after which NaBH_4 (0.6 g) was promptly added, and the mixture was allowed to react for 1 h under rapid stirring. The product was separated magnetically and washed several times with deionized water to eliminate impurities. The synthesis procedure is schematically shown in Scheme 1.

2.2. Catalyst characterization

Fourier transform infrared (FT-IR) spectra were recorded in transmission mode with a PerkinElmer BX FT-IR spectrometer. The powder samples were ground with KBr and compressed into pellets. FT-IR spectra in the range 4000–400 cm^{-1} were recorded to investigate the nature of the chemical bonds present in the prepared material.

The crystalline structure of the resultant nanoparticles was determined by X-ray diffraction (XRD) using a Rigaku D/Max-III C with $\text{Cu } K\alpha$ radiation in the 2θ range of 20°–70°.

The surface morphology of the composites was analyzed by scanning electron microscopy (SEM) on a JEOL JSM 7001F scanning electron microscope. The elemental composition of sample was determined by SEM-EDAX (energy-dispersive

Scheme 1. An illustration for the fabrication of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst.

X-ray analysis).

Ultraviolet-visible (UV-Vis) spectroscopy was performed in the range of 300–800 nm on a Shimadzu UV-2600 UV-Vis spectrometer.

Vibrating sample magnetometry (VSM) measurements were performed using a vibrating sample magnetometer (LDJ Electronics Inc., Model 9600). The magnetization measurements were carried out in the presence of an external field at increasing magnitudes up to 15 kOe at room temperature.

The thermal stability of sample was determined by thermogravimetric analysis (TGA) on a PerkinElmer STA 6000. The powder sample (6 mg) was heated from 30 to 800 °C at a heating rate of 10 °C/min under N_2 atmosphere.

2.3. Catalytic studies

Separate catalytic reduction experiments were performed for the different aqueous azo dyes studied herein (MO, MB, EY, and RhB). A dye solution (100 μL) concentration of 10 mmol/L was used to which freshly prepared NaBH_4 aqueous solution (1 mL, 100 mmol/L) was added in a UV-cuvette. The volume of the resulting solution was then adjusted to 3 mL with distilled water. A $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ nanocatalyst amount of 1 mg was used to catalyze the azo dye solutions of MO, MB, EY, and RhB. In all dye solution systems examined, the dye solution became colorless at the end of reduction process, which was indicative of the degradation of the dyes. The reduction was monitored with a UV-Vis absorption spectrophotometer. After degradation was complete, the $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ nanocatalyst was separated using a magnet, and the process was repeated to investigate the recyclability of the catalyst.

3. Results and discussion

3.1. Characterization

To investigate the crystallinity and crystal structure of the prepared $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$, XRD powder analysis was performed, and the results are presented in Fig. 1. It confirmed that the material prepared consists of two inorganic phases, i.e., Fe_3O_4 as indicated by the characteristic diffraction peaks that could be indexed to the planes (220), (311), (400), (422), (511), and (440) (ICDD 19-0629) [17–20] and Cu ((111) and (200),

Fig. 1. XRD powder pattern of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC.

ICDD 85-1326). The mean crystallite size of Fe_3O_4 nanoparticles (19.8 nm) was estimated from the diffraction pattern using Scherrer formula.

The FT-IR spectra of pristine nicotinic acid, $\text{Fe}_3\text{O}_4@\text{Nico}$ nanocomposite, and $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC are presented in Fig. 2. Pristine nicotinic acid displayed characteristics peaks corresponding to functional stretching of $\nu(\text{C}=\text{O})$ 1700 cm^{-1} , $\nu(\text{C}-\text{O})$ 1300 cm^{-1} , and $\nu(\text{C}-\text{N})$ 1326 cm^{-1} [21]. Upon binding with the Fe_3O_4 surface, the $\nu(\text{C}=\text{O})$ band shifted to 1634 cm^{-1} in the $\text{Fe}_3\text{O}_4@\text{Nico}$ nanocomposite because the carboxylic group in nicotinic acid is involved in the binding process to the Fe_3O_4 nanoparticles surface. The binding of nicotinic acid to the surface of Fe_3O_4 is explained in detail in our previous papers [22–24]. Furthermore, the C–N stretching absorption of the pyridine ring of free nicotinic acid ($\nu = 1321\text{ cm}^{-1}$) shifted to a higher frequency of 1340 cm^{-1} in $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC. It was believed that the Cu nanoparticles coordinated to the nitrogen atom of the pyridine ring [12,21,25,26].

The thermograms of free nicotinic acid and product ($\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$) are shown in Fig. 3. Nicotinic acid displayed a single-step degradation below 270°C that could be attributed to the release of physisorbed water and degradation of the organic backbone of nicotinic acid. No further weight losses were observed above 270°C , which confirmed complete degradation of nicotinic acid. In contrast, $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRCs showed a two-step degradation behavior. The first degradation up to 500°C was attributed to the loss of chemisorbed water and de-

Fig. 2. FT-IR spectra of Nico (1), $\text{Fe}_3\text{O}_4@\text{Nico}$ (2), and $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC (3).

Fig. 3. TGA curves of Nico (1) and $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC (2).

composition of side groups. The subsequent degradation observed upon further heating to 700°C was attributed to the degradation of the organic backbone. The percentage of the organic and inorganic content in $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRCs was accordingly estimated as $\sim 9\%$ and $\sim 91\%$, respectively.

Fig. 4 shows the room temperature magnetization curve of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$. As observed, $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ did not display remanence or coercivity at 27°C , thereby indicating that it is superparamagnetic at room temperature. The saturation magnetization of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ was $\sim 50\text{ emu/g}$.

To determine the morphology and chemical composition of the product (elements present on the surface and in the product), SEM and EDAX measurements were undertaken. As shown in Fig. 5, SEM analysis confirmed the homogeneity of the product (as indicated by the presence of tiny nanoparticles). EDAX measurements confirmed the presence of Fe, Cu, C, O, and N as the major elements in the product and absence of impurities. Because of the formation of tiny nanoparticles (with spherical morphology), accurate particle size determination could not be done. Additionally, a certain degree of particle agglomeration was observed in the product.

3.2. Catalytic studies

A previous research work showed that Cu nanoparticles played a key role in the catalytic reduction of azo dyes such as MO, MB, EY, and RhB [26]. The catalytic reduction of MO, MB, RhB, and EY was chosen as model reactions to evaluate the catalytic performance of the newly synthesized

Fig. 4. M-H curve of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC.

Fig. 5. SEM images of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC.

$\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst in the presence of NaBH_4 . The choice of the dyes was based on two factors, i.e., their harmful effect to the environment and different colors during the reduction process. Changes in the color of the dye solution can be conveniently monitored by UV-Vis absorption spectroscopy. Fig. 6(a) shows a typical evolution of the UV-Vis spectra of MO. The results showed that partial reduction of MO occurred within 2 h in the presence of NaBH_4 only. In contrast, upon addition of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst (in the presence of NaBH_4), complete reduction was achieved within 60 s of reaction as seen in Fig. 6(b).

Fig. 7(a) shows the UV-Vis absorption spectra of MB reduction in the presence of NaBH_4 only. As observed, no appreciable changes in the UV-Vis spectrum were observed, thereby suggesting that MB could not be effectively reduced in the presence of NaBH_4 only. However, upon addition of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst to the MB-based NaBH_4 aqueous solution, the characteristic band of MB at 650 nm disappeared within 50 s of reaction (Fig. 7(b)). This result implied that the reduction of MB had been successfully achieved owing to the inclusion of Cu nanoparticles in the magnetic nanocatalyst.

Fig. 6. Time dependent UV-Vis absorption spectra of MO for the reduction of MO. (a) In the presence of only NaBH_4 ; (b) In the presence of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ and NaBH_4 ; (c) Rate constant versus time in the presence of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ and NaBH_4 .

Fig. 7. Time dependent UV-Vis absorption spectra of MB for the reduction of MB. (a) In the presence of only NaBH_4 ; (b) In the presence of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ and NaBH_4 ; (c) Rate constant versus time in the presence of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ and NaBH_4 .

In the case of EY, complete reduction was not observed even after 3 h of reaction in the presence of NaBH_4 only (Fig. 8(a)). However, the addition of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC was effective in achieving complete and fast degradation of EY. The maximum absorption peak at 510 nm disappeared within 9 min of reaction (Fig. 8(b)).

Finally, as a typical example of organic pollutants, RhB was also studied to evaluate the catalytic activity of the $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst. As observed in Fig. 9(a), the main absorbance peak of RhB did not change significantly with increasing reaction time. In contrast, the catalytic reduction of RhB proceeded successfully upon addition of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ (Fig. 9(b)). This result also demonstrated that Cu nanoparticles played an important role in the catalytic reduction of RhB.

The kinetic data obtained for the reduction of MO, MB, EY, and RhB were fitted to first-order rate equations. The catalytic efficiency of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst toward the degradation of the different azo dyes studied herein is shown in Figs. 6(c), 7(c), 8(c), and 9(c), respectively. The calculated rate constants for the reduction of MO, MB, EY, and RhB were 0.05 s^{-1} , 0.04 s^{-1} , 0.22 min^{-1} , and 1.21 min^{-1} , respectively. These results showed that the reduction of MO and MB was more efficient than that of RhB and EY, as indicated by the magnitude of the reaction rates, which decrease in the order

$\text{Rate}(\text{MO}) > \text{Rate}(\text{MB}) > \text{Rate}(\text{RhB}) > \text{Rate}(\text{EY})$. Furthermore, $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ exhibits a considerably higher rate constant than those reported for other catalysts [4,11,26–28].

Additionally, the reduction of MO in the presence of NaBH_4 and Cu nanoparticles was investigated to clarify the individual catalytic effects of Cu nanoparticles and $\text{Fe}_3\text{O}_4@\text{Nico}$ nanocomposite. As shown in Fig. 10(a), in the presence of NaBH_4 and Cu nanoparticles, MO degradation was complete within 4 min. In contrast, in the absence of Cu nanoparticles and presence of NaBH_4 and $\text{Fe}_3\text{O}_4@\text{Nico}$, the reduction of MO was not effective (Fig. 10(b)).

3.3. Mechanism of catalysis

The composition of the catalyst is a decisive factor that influences the catalytic activity [29,30]. In the catalytic mechanism of reduction, Cu nanoparticles supported on $\text{Fe}_3\text{O}_4@\text{Nico}$ surface serve as an electron relay system and play a key role during electron transfer [27,31,32]. Fig. 11 schematically illustrates the possible catalytic mechanism for the reduction of azo dyes in the presence of NaBH_4^- by Cu nanoparticles. In the reaction mixture, both the dye and BH_4^- are adsorbed onto the surface of the Cu nanoparticles. Therefore, when Cu nanoparticles are used in the catalytic reduction, BH_4^- and azo dye first diffuse from the aqueous solution to the Cu nanoparticles sur-

Fig. 8. Time dependent UV-Vis absorption spectra of EY for the reduction of EY. (a) In the presence of only NaBH_4 ; (b) In the presence of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ and NaBH_4 ; (c) Rate constant versus time in the presence of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ and NaBH_4 .

Fig. 9. Time dependent UV-Vis absorption spectra of RhB for the reduction of RhB. (a) In the presence of only NaBH_4 ; (b) In the presence of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ and NaBH_4 ; (c) Rate constant versus time in the presence of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ and NaBH_4 .

Fig. 10. Time dependent UV-Vis absorption spectra of MO for the reduction of MO. (a) In the presence of NaBH_4 by Cu NPs; (b) In the presence of NaBH_4 by $\text{Fe}_3\text{O}_4@\text{Nico}$.

face. And Cu in $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ serves as a catalyst to transfer electrons from BH_4^- to the azo dye, leading to the production of leuco azo dye derivatives or *p*-phenylenediamine.

3.4. Recyclability of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC in MO reduction

To investigate the recyclability of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC in MO reduction, $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC was separated magnetically and reused in the color degradation of MO to evaluate its recycling performance. As observed in Fig. 12, only a small loss in the catalytic activity of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC was observed

Fig. 11. Proposed mechanism of dye reduction on $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst.

Fig. 12. Recycling of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst for the reduction of MO by NaBH_4 .

after successive five catalytic reactions. This observation indicated the high stability of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC. Furthermore, the conversion percentage decreased slightly after the fifth catalytic cycle. The small decrease in the catalytic performance of the catalyst may be due to the loss of catalyst during recycling. The color change of the azo dye and easy separation of the catalyst after the catalysis reaction are given in Fig. 13.

4. Conclusions

We demonstrated a facile method for the synthesis of copper nanocatalyst on functionalized Fe_3O_4 magnetic nanoparticles. The newly synthesized $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst was examined in the degradation of chemically and biologically resistant azo dyes. The findings of the current UV-Vis studies showed the good decolorization potential of the newly synthesized $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst in the degradation of azo dyes in wastewater. More specifically, the magnetic nanocatalyst could easily reduce azo compounds (MO, MB, EY, and RhB) in the presence of NaBH_4 . Moreover, this unique nanocatalyst could be easily separated from the reaction mixture by simple magnetic attraction. The synthesized nanocatalyst is characterized by its simple and facile preparation, easy and rapid separation from reaction mixture,

Fig. 13. Photos that illustrates color degradation of azo dyes after catalysis reaction and easy recyclability of $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ magnetic nanocatalyst by a magnet.

Graphical Abstract

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Synthesis and application of magnetically recyclable nanocatalyst $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ in the reduction of azo dyes

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A novel method for synthesis of recyclable Cu nanocatalyst on $\text{Fe}_3\text{O}_4@\text{Nico}$ magnetic nanoparticles (MRC) was introduced. $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Cu}$ MRC was successfully applied for hydrogenation of azo dyes, and methyl orange (MO), methylene blue (MB), eosin Y (EY), and rhodamine B (RhB) were studied.

and cost effectiveness, moisture insensitivity, and recyclability properties, which make the catalyst an excellent, superior, and sustainable catalytic system in comparison with other nanocatalysts. Thus, the synthesis method presented herein shows potential as an ideal platform for the fabrication of highly efficient magnetic catalysts for various heterogeneous catalytic reduction applications.

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