

RESEARCH PAPER

Biosynthesis and catalytic activity of Pd/NiFe₂O₄ nanocomposite for the reduction of wastewater pollutants

Akbar Rostami-Vartooni^{1*}, Mojtaba Bagherzadeh^{2*}, Mohaddeseh Sajjadi¹, Ahmad Reza Abbasian³

¹ Department of Chemistry, Faculty of Science, University of Qom, Iran

² Reactor and Nuclear Safety School, Nuclear Science and Technology Research Institute, Isfahan, Iran

³ Department of Materials Engineering, Faculty of Engineering, University of Sistan and Baluchestan, Zahedan, Iran

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ABSTRACT

In the present work, the preparation of nickel ferrite (NiFe₂O₄) and its surface modification by biosynthesized Pd nanoparticles (NPs) were carried out. Firstly, NiFe₂O₄ NPs were synthesized via a facile combustion approach and then Pd NPs were biosynthesized on their surface by using an aqueous *Marrubium vulgare* L leaf extract. The prepared NiFe₂O₄ NPs were characterized by FT-IR, XRD, VSM, FESEM, and EDXA techniques, which confirmed the good dispersion of spherical Pd NPs on the surface of magnetic NiFe₂O₄ nanoparticles. The catalytic activity of Pd/NiFe₂O₄ nanocomposites were evaluated in the reduction of Methylene Blue (MB), Methyl Orange (MO) and Congo Red (CR) azo dyes in the presence of sodium borohydride (NaBH₄). Observed results showed that the reduction/decolorization times in the presence of magnetically recoverable Pd/NiFe₂O₄ nanocomposites were very shorter than that of NiFe₂O₄ catalyst.

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INTRODUCTION

Dyes as water and wastewater pollutants are produced from textiles, plastics, paper, leather, food, and cosmetics industries. Different methods such as adsorption, advanced oxidation processes (AOPs), chemical reduction, biological degradation, ion exchange, membrane separation and coagulation [1-3] have been employed to remove these carcinogenic and mutagenic compounds. In the current decade, the reduction/decolorization process including NaBH₄ as a reducing agent has been reported to convert the pollutants to less toxic materials [4-6].

The usage of metal nanoparticles (MNPs) has been significantly studied in recent years due to their high specific surface area and good catalytic activity [7, 8]. Specifically, Pd NPs have been widely

used in various chemical reactions such as coupling reactions, selective oxidation of alcohols, arylation of phenols and reduction of water/wastewater pollutants [9, 10]. Immobilization of MNPs on the surface of different supports such as reduced graphene oxide, Fe₃O₄, bentonite, TiO₂, CuO, perlite, and seashell decreases the agglomeration of NPs which leads to stable catalysts with higher reactivity and good reusability [11, 12]. However, metal ferrites with inverse spinel structure, such as NiFe₂O₄, have been synthesized via different methods including co-precipitation [13], sol-gel [14], chemical reduction [15], hydrothermal [16], microwave combustion, and sonochemical methods [17].

Among several physical, chemical and biological approaches for the preparation of MNPs, biosynthetic route using plant extracts has some advantages including the elimination of toxic and

* Corresponding Author Email: a.rostami@qom.ac.ir
mjmo123@yahoo.com

expensive chemical compounds and providing gentle reaction conditions [18-25]. The phenolic compounds are present in different parts of plants, which can act as reducing and stabilizing agents for the conversion of metal ions to MNPs.

Marrubium vulgare L as a traditional plant has been used in the treatments of liver diseases, cancer and diabetes mellitus due to its antioxidant properties [26]. In addition, this medicinal plant has several pharmaceutical activities such as antibacterial, anti-inflammatory, antihypertensive, vasodilator, hypolipidemic, wound-healing and sedative potential [27, 28]. The flowers and fruits of *M. vulgare L* are good sources of tannins, amino acids and polysaccharides, whereas phenols and flavonoids are the major constituents of leaves [29, 30].

In the present study, biosynthesized Pd NPs by using the aqueous leaf extract of *M. vulgare L* were supported on the surface of magnetically recoverable NiFe₂O₄ prepared by combustion method. This biofabricated Pd/NiFe₂O₄ nanocomposite was applied for the catalytic reduction of MB, MO and CR dyes.

EXPERIMENTAL METHOD

Materials and instruments

The leaves of *Marrubium vulgare L* were collected from Isfahan province (Josheghan-Ghali city), Iran. Nickel ferrite (NiFe₂O₄) was prepared based on previously reported procedure by using Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, glycine, and KCl salt [31]. Other required materials were purchased from Merck®. The reduction reactions of water/wastewater pollutants were studied by a Lambda-35 UV-Vis spectrophotometer (PerkinElmer, United States). FT-IR spectra of the NiFe₂O₄ and its Pd nanocomposite were recorded by Cary 630 FTIR spectrometer. The XRD measurements were performed using a Philips PW 1730 X-ray diffractometer with CuKα radiation (λ=0.154 nm) to identify the phase composition of nanocomposites. The morphology and structure of Pd/NiFe₂O₄ nanocomposite was characterized by FESEM analysis (Cam scan MV2300) equipped with an energy-dispersive X-ray analysis (EDX). The magnetic property of the NiFe₂O₄ was investigated by a SQUID magnetometer (Quantum Design MPMS XL).

Preparation of NiFe₂O₄ nanocomposite

NiFe₂O₄ was synthesized via combustion

method reported by Abbasian and Afarani [32]. Firstly, the pH of 60 ml distilled water was adjusted to 4 by adding HNO₃ and then 4.44 mmol glycine solution was added to this media in a beaker (250 ml). After that, 10 mmol of Ni(NO₃)₂ was dissolved in the solution prepared in the previous section and agitated. Equal mmol of Fe(NO₃)₃ and KCl (20 mmol) were added to them under magnetic stirring for 15 min intervals at 80 °C. The resulting solution was agitated under magnetic stirring at 200 °C on the magnetic stirrer until the color of the solution changed to brown. Finally, heating was continued without stirring until the combustion reaction occurred and the dark brownish powder was produced. The obtained powders were boiled in about 400 ml of distilled water to remove unreacted KCl. The gained powders were separated by using a piece of magnet and dried at 80 °C in an electric oven. The prepared materials (NiFe₂O₄) were used as a catalyst.

Preparation of *M. vulgare L* leaf extract

The *M. vulgare L* reagent were extracted from 6 g of leaves in 80 mL of deionized water and heated at 75 °C for 20 min. Finally, the filtered extract was used in the formation of Pd NPs.

Synthesis of Pd/NiFe₂O₄ nanocomposite

A solution containing 0.2 g PdCl₂ dissolved in 0.5 M HCl was added to a mixture of 1.2 g NiFe₂O₄ and 30 mL *M. vulgare L* leaf extract. After 1.5 h, the obtained Pd/NiFe₂O₄ nanocomposite was separated using a magnet, washed with deionized water and placed in an oven at 100 °C for 30 min.

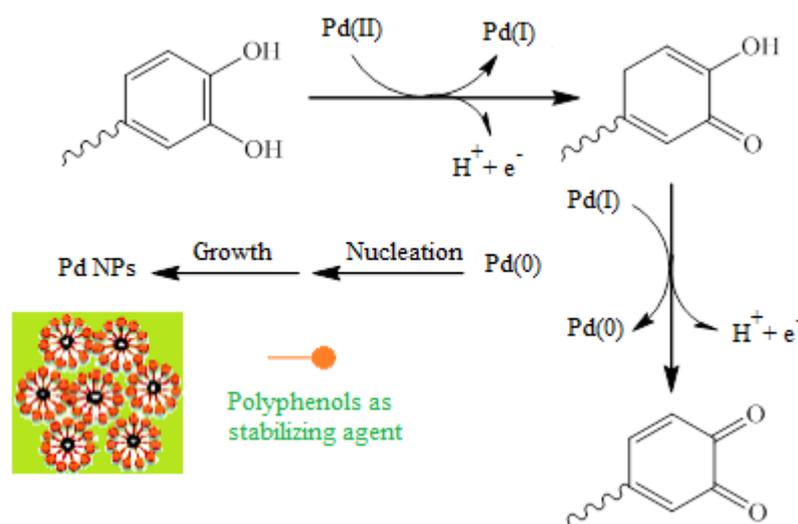
Catalytic reduction of MB, MO and CR using Pd/NiFe₂O₄ nanocomposite

4 mg of NiFe₂O₄ or its Pd nanocomposite was added to an aqueous solution of MB or MO dye (90 mL, 10 ppm) and NaBH₄ (5 mg). The mixture was then stirred at room temperature and the reduction/decolorization process was monitored by UV-Vis absorption spectrometer at λ_{max} of 664, 464 and 493 nm for measuring MB, MO and CR concentrations, respectively.

RESULTS AND DISCUSSION

Pd NPs synthesis

Scheme 1 shows that the phenolic compounds in the *M. vulgare L* leaf extract are responsible for the Pd NPs formation and stabilization [3, 33]. Immobilization of these nanoparticles on the



Scheme 1. The Pd NPs preparation by using the *M. vulgare L* leaf extract.

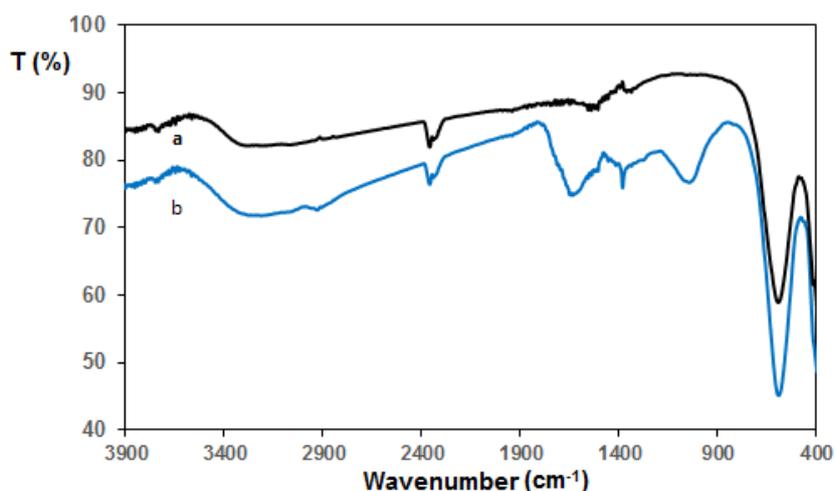


Fig. 1. FT-IR spectra of NiFe₂O₄ (a) and Pd/NiFe₂O₄ (b).

NiFe₂O₄ leads to more stable Pd NPs and high catalyst activity.

Characterization of the Ni ferrite and its Pd nanocomposite

The formation of NiFe₂O₄ support can be confirmed by the observed peaks at about 400 and 594 cm⁻¹ in its FT-IR spectrum (Fig. 1) which are attributed to the stretching vibrations of metal-oxygen bands in the octahedral and tetrahedral sites, respectively [34, 35]. The broad band in the range of 3000-3400 cm⁻¹ is assigned to the existence of surface O-H bond and absorbed H₂O by the ferrite sample. The absorption bands at 930-1645 cm⁻¹ in

the FTIR spectrum of Pd/NiFe₂O₄ nanocomposite (Fig. 1b) can be related to the C-O and C=C bonds of absorbed phenolic constituents in the aqueous extract on the nanocomposite surface by π -electron interactions [36, 37].

XRD pattern of Ni ferrite (Fig. 2) is completely compatible with the reported pattern in the literature [38-40]. The diffraction peaks at 2θ values of 30.5, 35.9, 37.4, 43.7, 53.8, 57.4, 63.0, 71.5, 74.6, 75.7 and 79.5° (Card No. 89-4927) can be easily indexed to the (220), (311), (222), (400), (422), (511), (440), (620), (533), (622) and (444) planes of cubic spinel NiFe₂O₄ (JCPDS PDF card no.10-0325), respectively. The observed peaks at 2θ values

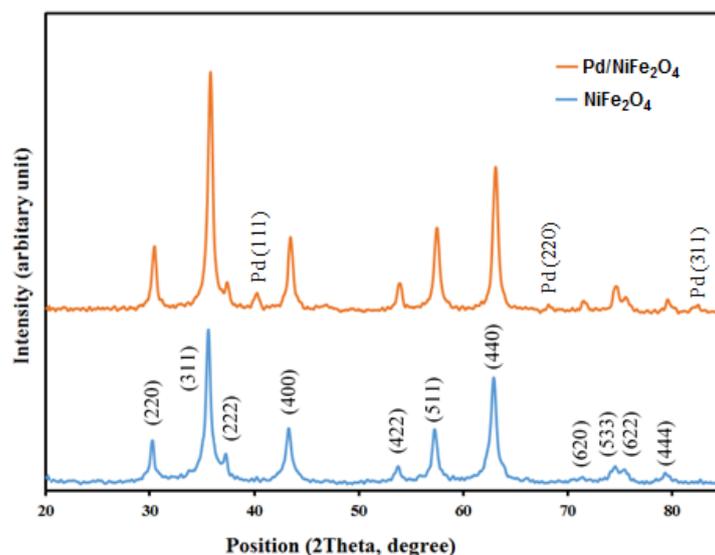


Fig. 2. XRD patterns of NiFe₂O₄ (a) and Pd/NiFe₂O₄ nanocomposite (b).

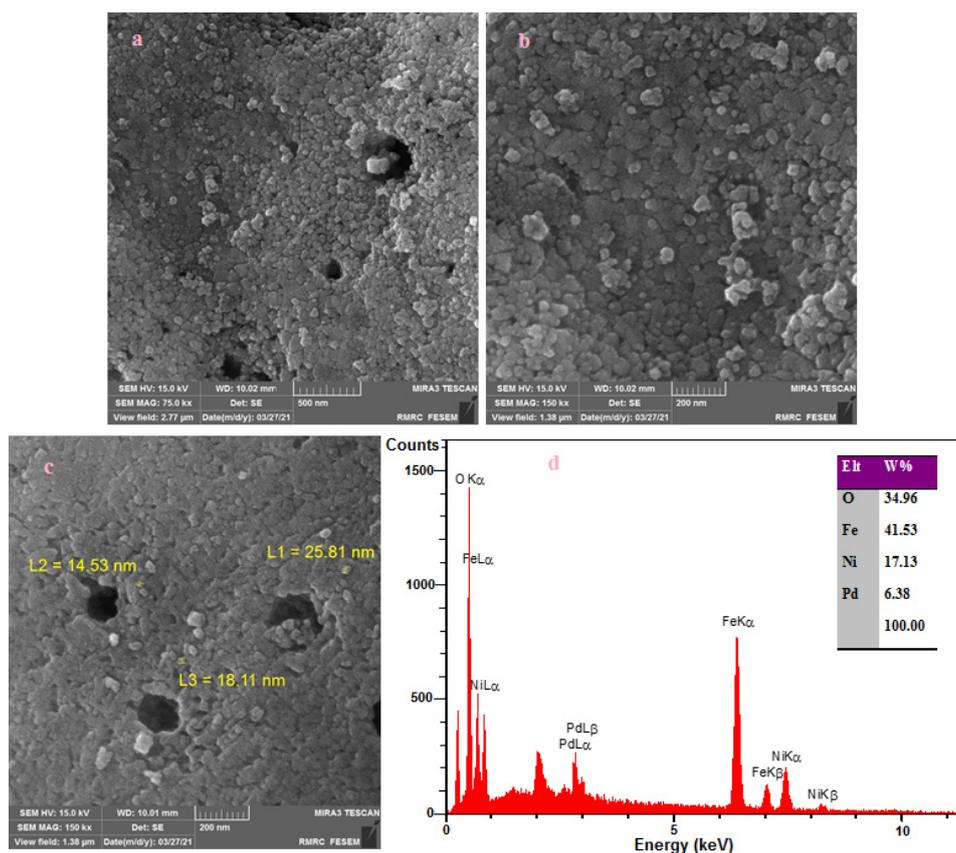


Fig. 3. The (a-c) FESEM images and (d) EDX spectrum of Pd/NiFe₂O₄ nanocomposite.

of 40.1, 68.3 and 82.5° in the XRD pattern of Pd/NiFe₂O₄ are related to the (111), (220) and (311) planes of crystalline Pd with the face-centered cubic structure [41, 42].

The FESEM images of Pd/NiFe₂O₄ nanocomposite (Fig. 3a-c) show that the produced spherical Pd NPs have dispersed well on the surface of magnetic support. EDX spectrum of Pd/NiFe₂O₄

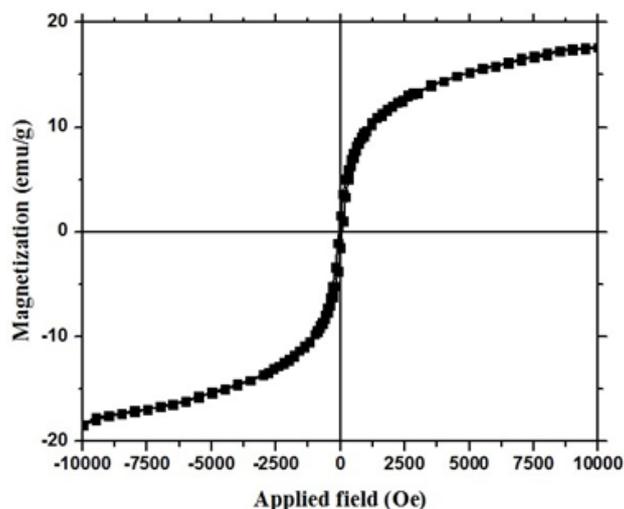
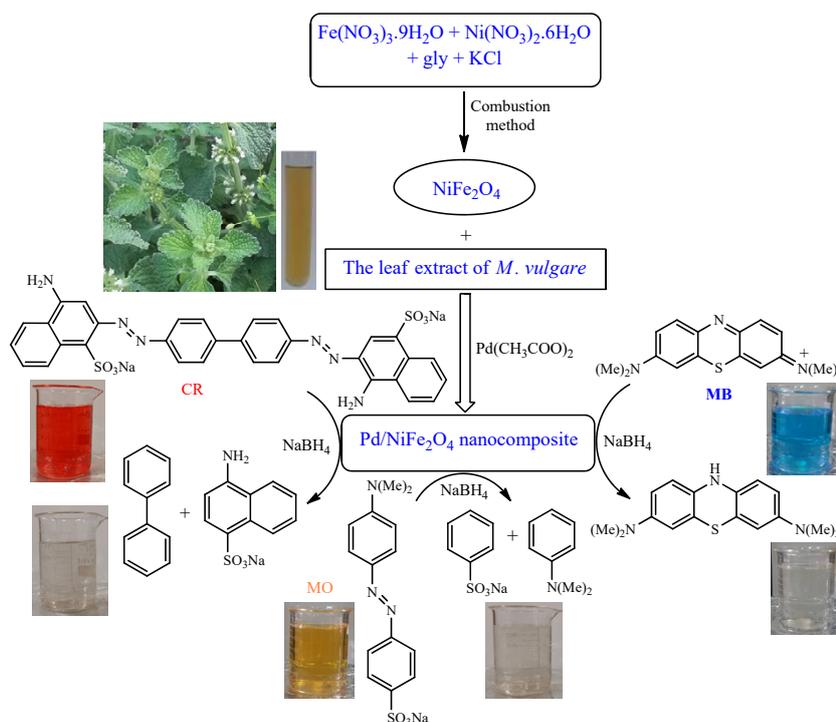


Fig. 4. Magnetization curve of the NiFe₂O₄ nanocomposite.



Scheme 2. Green synthesis of Pd/NiFe₂O₄ nanocomposite and its catalytic evaluation in the reduction of MO, MB and CR.

(Fig. 3d) confirms the presence of Pd, Ni, Fe and O elements in this nanocomposite.

Fig. 4 shows the value of saturation magnetization (Ms) for the prepared NiFe₂O₄ nanocomposite with ferromagnetic behavior is about 17.5 emu/g. This magnitude of magnetization was sufficient for the facile separation of the nanocomposite from the reactions by an external magnet.

Application of the Ni ferrite and its Pd NPs nanocomposite in the reduction of dyes

Reduction/decolorization process of azo dyes as pollutants in the presence of NaBH₄ was chosen for the investigation of catalytic activity of the Pd/NiFe₂O₄ nanocomposite (Scheme 2). In these reduction reactions, the color of MB, MO and CR solutions completely disappeared. The reduction

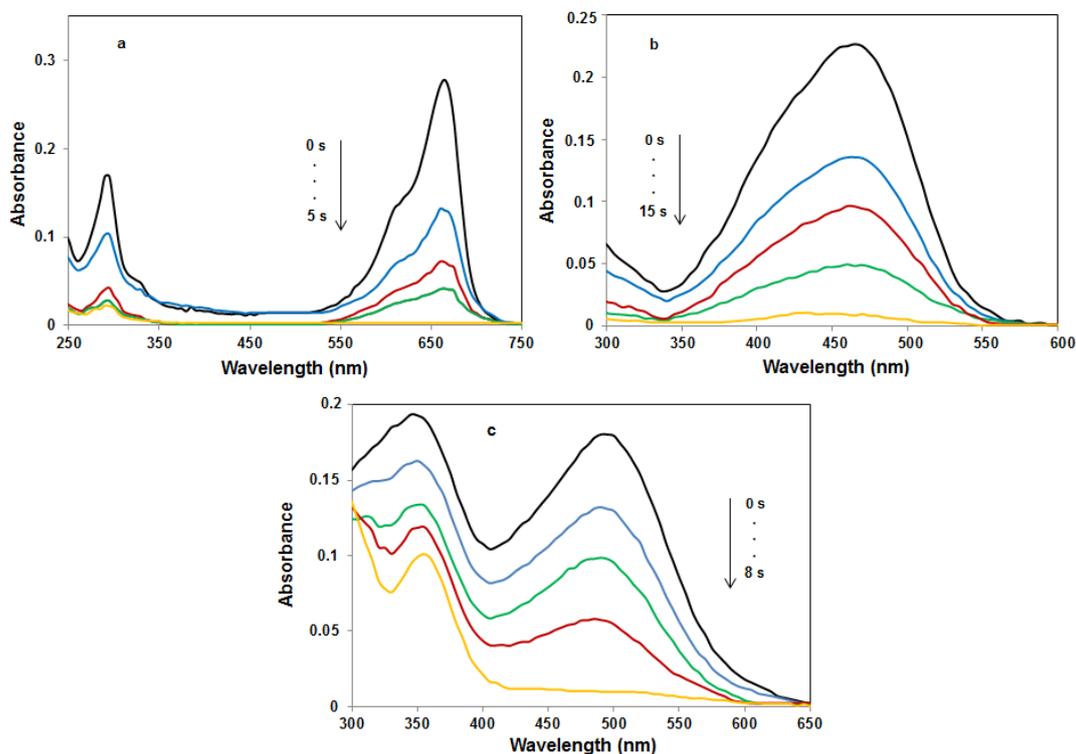


Fig. 5. Absorption intensities of MB (a), MO (b) and CR (c) solutions during the catalytic reduction.

Table 1. Reduction times of selected dyes (90 mL, 10.0 ppm) in the presence of catalyst (4 mg) using NaBH₄ (5 mg).

Catalyst	MB	MO	CR
-	90 min ^a	90 min ^a	90 min ^a
NiFe ₂ O ₄	90 min ^b	90 min ^b	90 min ^b
Pd/NiFe ₂ O ₄	120 min ^c	120 min ^c	120 min ^c
Pd/NiFe ₂ O ₄	5 s	15 s	8 s

^aNo reaction; ^bNot completed; ^cWithout NaBH₄.

products of MO and CR remained unchanged even when the reactions were continued up to 24 h. Nevertheless, the re-oxidation of the reduced form of MB occurred and the color of the solution returned to the original blue color after 3 h. Fig. 5 shows the changes of absorption intensities in UV-vis spectra of MB, MO and CR solutions at different time intervals. In addition, the reduction times of the pollutants in different conditions are summarized in Table 1. In the presence of Pd/NiFe₂O₄ catalyst, shorter reaction times were observed which indicated the electron transfer from the reducing agent (BH₄⁻) to pollutants as a rate-limiting step (rds) were facilitated on the surface of Pd NPs [43]. It could be found from the reaction times listed in Table 1, the efficiency of Pd/NiFe₂O₄ nanocomposite are comparable

to the reported catalysts in the literature for the reduction/decolorization of pollutants [6, 43-46].

Catalyst recyclability

To investigate the recyclability of the catalyst, the separated Pd/NiFe₂O₄ from MO reaction using external magnet was washed with distilled water, dried and then reused in the reduction process. The reaction times of 100% MO reduction/decolorization for 4 catalytic runs were 15, 16, 20 and 20 s, respectively. Hence, the efficiency of the recovered catalyst does not change significantly, indicating the appropriate stability of the Pd/NiFe₂O₄ catalyst.

CONCLUSIONS

In the first step of this work, Ni ferrite

nanocomposite prepared by hydrothermal process was selected as a stable and magnetically recoverable support for the biofabricated Pd NPs using *M. vulgare* L leaves extract. The formation NiFe₂O₄ and its Pd nanocomposite was confirmed by FTIR, VSM, XRD, FESEM and EDS techniques. The FESEM images and EDS spectrum showed the immobilization of well-dispersed spherical Pd NPs on the surface of the magnetic NiFe₂O₄ support. The reduction/decolorization process of MB, MO and CR dyes was fully carried out in the presence of Pd/NiFe₂O₄.

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CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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