Preparation and characterization of magnetic zirconium oxide nanocomposite as a catalyst for reduction of methylene blue

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Abstract

In this work, magnetic zirconium oxide ($\text{ZrO}_2/\text{Fe}_3\text{O}_4$) nanocomposites were synthesized in different mass ratio as (1:1), (3:2), (5:2) and (7:2) and fairly characterized by various techniques like; X-ray diffraction, X-ray energy dispersion analysis, scanning electron microscope, transmission electron microscopy, Fourier transform infrared spectroscopy, and vibrating sample magnetometer. Characterization results showed the prepared nanocomposite had stable core/shell structure in nanometer scale, 12 nm, with magnetically property that nominate it for catalytic application in chemical reactions. The prepared nanocomposites were evaluated in the reduction reaction of methylene blue and in the presence of NaBH_4 as a catalyst. Observed results revealed that the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposites in mass ratio as 5:2 exhibited remarkable catalytic activity with excellent reusability. Obtained results are presented and discussed here.

Keywords $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite · Superparamagnetic · Core-shell · Reduction · Methylene blue

1 Introduction

The accessible magnetic materials are magnetite (Fe_3O_4), and it is one of the most studied ferrimagnetic compounds. Due to extensively application of magnetic nanomaterials in various scientific fields like ultrahigh density magnetic storage media [1–3], medicine [4, 5] biological labeling, tracking, imaging, detection, and separations [6], and ferrofluid [7] they have attracted the significant attention in recent years. Due to the negligible energy barrier in the hysteresis of the magnetization loop and noticeably small coercivity, magnetite nanoparticles with size below 26 nm exhibit superparamagnetic behavior [8, 9]. Consequently, nanoscale materials and magnetite have been intensively studied recently in diagnostic, biomedical, and removal or separation of hazardous materials [10–15]. For the end goal, the magnetite nanoparticles act as a catalyst or supporter in reduction or oxidation of dangerous many

dyes and easily separated from the solution reaction by using a magnetic field [16–18].

3,7-Bis (dimethylamino)-phenothiazin-5-ium chloride, known as methylene blue (MB), is one of the famous harmful pollutants and has detrimental effects on human health [19]. To convert this dangerous dye form to suitable products, many strategies like photochemical and biological degradation, oxidation, and reduction, have been reported in recent years. Among them, the catalytic reduction of blue color MB into colorless reduced form (leucomethylene blue, LB) is considered more preferable. LB is the counterpart of MB and has numerous applications in various industrial fields. However, this reduction reaction is the kinetically unfavorable reaction. Consequently, different catalytic systems utilized based on nanomaterials to speeding up this specific reaction [19].

Herein, magnetite (Fe_3O_4) nanoparticles were used as a supporter for the immobilizing of the ZrO_2 on them to

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synthesize magnetic zirconium oxide nanocomposites. The mass ratio of the ZrO_2 to Fe_3O_4 was changed to control the magnetization and catalytic activity. The prepared nanocomposite was characterized, and its catalytic activity in the reduction of MB was investigated. Observed results are presented and discussed.

2 Experimental and processer

2.1 Materials and instruments

Doubly distilled de-ionized water (Millipore Milli-Q, France, 18 M Ω) was used to preparation of all the solutions. Zirconyl chloride (ZrCl_4), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), methylene blue (MB), and all other chemicals were purchased from Merck[®]. An X-ray diffractometer (Bruker Advanced D8 model), that use CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$), was used for crystal structure study of the prepared powders. A Perkin Elmer Spectrum Version 10.00.00 was used for Fourier transform infrared (FTIR) spectra recording. A scanning electron microscope (SEM) equipped with EDXA (Philips XL-30) was used for morphology and elemental analysis of the samples. The transmission electron microscope, TEM (Philips-EM-208S), was used for the size measurement of the prepared nanocomposites. Vibrating sample magnetometer (VSM, Daghigh Meghnatis Kashan Co., Kashan, Iran) was used for magnetic measurements at room temperature. And finally, a double-beam UV-Vis spectrophotometer (Cintra 404) was used for monitoring the reduction reactions of MB dye.

2.2 Preparation of magnetic zirconium oxide nanocomposites

The magnetic zirconium oxide nanocomposites were synthesized via chemical co-precipitation methods. 25 mL of HCl (1 M) was deaerated with N_2 gas for 20 min, then $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in ratio as 2:1 were added to it. 250 mL of 1.5 M NaOH solution at 80 °C was prepared and then, the HCl solution was added dropwise into it under vigorous stirring. A permanent magnet was used to separate obtained magnetic nanoparticles (Fe_3O_4) from the reaction medium. Prepared Fe_3O_4 washed with 200 mL deionized water four times. For coating, the ZrO_2 on the prepared Fe_3O_4 , 1 M solution of ZrCl_4 in HClO_4 was added dropwise into the suspension of Fe_3O_4 nanoparticles. By addition of 2 M NaOH within one h, the pH was adjusted to 8.0, at 80 °C, under N_2 gas, and stirred for two h. By varying the proportion of precipitated ZrO_2 on Fe_3O_4 nanoparticles suspension, the mass ratio of ZrO_2 to Fe_3O_4 adjusted to 1:1, 3:2, 5:2, and 7:2. Finally, the prepared nanocomposites were thoroughly washed with deionized water.

2.3 Catalytic reduction of MB

For investigation of catalytic activity of prepared nanocomposites, 50 mL aqueous NaBH_4 solution ($5.3 \times 10^{-3} \text{ M}$) was added to 50 mL of MB azo dye (10 ppm) and 7 mg magnetic zirconium oxide nanocomposites were dispersed in it mixture solution. The solution mixture was stirred at room temperature, and then the concentration of MB in solution was monitored by UV-Vis spectrophotometer at λ_{max} of 665 nm.

3 Results and discussion

3.1 Characterization of magnetic nanocomposite catalyst

The XRD patterns of prepared Fe_3O_4 and $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite presented in Fig. 1. As can be seen, the planes (111), (200), (220), and (311) of ZrO_2 are observed at 2θ 30.4, 35.2, 50.6, and 60.3° in the pattern (c), respectively. Furthermore, the planes (220), (311), (400), (511), and (440) of magnetite (Fe_3O_4) are observed at 2θ 30.0, 35.5, 43.5, 57.2, and 62.7° in the pattern (b), in which demonstrated the high purity Fe_3O_4 spinel structure was synthesized. Comparison of the XRD pattern (a) with patterns (b and c) in Fig. 1, proved the existence of zirconia in the resulting composite that marked in pattern (a). Finally, by using the Scherrer's formula, the average crystallite size as $12 \pm 1 \text{ nm}$ was calculated from the broadening of XRD peaks [20].

The composition of the prepared nanocomposite was further analyzed by using the X-ray energy dispersion analysis (EDXA), Fig. 2a. Elemental analysis (Fig. 2, inset) showed the main elements in the composite were iron, oxygen and zirconium that confirmed preparation of $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite successfully. For comparison the SEM image and related EDX analysis of ZrO_2 presented in Fig. 2b. The actual size and shape of the prepared nanocomposite were analyzed by using TEM imaging (Fig. 2c, d). As can be seen, the prepared composite had spherical in form and tendency to agglomeration. The TEM image in Fig. 2c showed a core/shell structure for prepared $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite in around the crystallite size calculated by using Scherrer's formula (12 nm). The SAED image obtained from the edge and the center of one of the spherical, non-agglomerated $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite, Fig. 2e. As can be see, when traversed from the edge towards the center of the particle, a number of diffraction spots are observed in the SAED pattern of the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanoparticle. This

Fig. 1 The typical XRD patterns of the as-prepared $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite (a), Fe_3O_4 (b), and ZrO_2 (c)

indicates that a large number of nanocrystallites related to ZrO_2 , as a shell, are located at the edge of the core particle, Fe_3O_4 .

Figure 3A shows the FTIR spectrum of the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ (5:2) nanocomposite. As can be seen, the characteristic bands at $500\text{--}850\text{ cm}^{-1}$, which is due to the Zr–O bond, of zirconia were observed in the FTIR spectrum [21]. Found evidence related to surface functional groups of prepared nanocomposite proved successful synthesis of magnetic zirconium oxide.

Figure 3B shows the vibrating sample magnetometer (VSM) analysis of the prepared nanocomposites with different mass ratios of ZrO_2 to Fe_3O_4 . As can be seen, all of the nanocomposites showed the typically superparamagnetic behavior, no coercivity, remanence, and hysteresis. However, in the application of magnetic materials, the saturation magnetization is a critical factor in effective magnetic separation. ZrO_2 is a nonmagnetic material, and increasing the mass ratio of it led to decreasing the magnetic strength of resulting nanocomposite. As can be seen from Table 1, the saturation magnetization of prepared nanocomposites decreased by increasing the ZrO_2 amount. The core–shell coupling model was used to explain the observed behavior [22]. It is the assumption that each particle consists of Fe_3O_4 core that coated by a constant thickness nonmagnetic shell of ZrO_2 . According to this model, the non-magnetic coating layer (ZrO_2) make a disordering on the magnetic moment of surface and forms a magnetic dead layer on the surface of Fe_3O_4 nanoparticles, that cause to decreasing the magnitude of the magnetization via quenching the surface moment [23]. Based on the core–shell model, and also in agreement by HRTEM image (Fig. 2b inset), due to the spherical form of particles, the magnetization is given by this equation:

$$M = M_0[(D - 2t)/D]^3$$

where M_0 , D , and t are the magnetization of Fe_3O_4 , the diameter of whole core–shell particle ($\text{ZrO}_2/\text{Fe}_3\text{O}_4$), and thickness of the dead layer (ZrO_2), respectively. Based on existing relationship and XRD, TEM results ($D = 12\text{ nm}$), the depth of the non-magnetic layer t of $\text{ZrO}_2/\text{Fe}_3\text{O}_4$; (1:1), (3:2), (5:2) and (7:2) were calculated as shown at Table 1.

We found that the magnetization value for $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ (5:2) nanocomposite is enough for magnetic separation with a conventional permanent magnet (Fig. 3A inset). Also, the thickness of the sample shell is suitable for our future studies in catalytic studies.

3.2 Application of the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ for the reduction of MB dye

The reduction reaction of MB azo dye in the presence of NaBH_4 and $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite was selected to the evaluation of the catalytic activity of prepared nanocomposite. In this process, the blue color solution of MB change to a completely colorless solution. Of course, the original color of solution can return during 1.5 and 4 h in the presence of the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite. Figure 4 shows the changes in the absorption band of MB in the presence of the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite during catalytic reduction. In addition, the reduction times of MB dye in the presence of Fe_3O_4 and its nanocomposite are summarized in Table 2. The results revealed that the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite in weight ratio as 5:2 showed the best catalytic performance. This catalytic behavior is due to facilitate the electron transfer from BH_4^- to the MB dye in the reduction process on the surface of the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite.

Fig. 2 **a** The SEM image of the prepared $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite and corresponding EDX analysis results (inset). **b** The SEM image of the prepared ZrO_2 nanoparticles and corresponding EDX analysis results (inset). **c, d** The TEM images of the prepared $\text{ZrO}_2/\text{Fe}_3\text{O}_4$

nanocomposite. The scale bars are 40 nm, and 5 nm in **c, d**, respectively. **e** The SAED image obtained from the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite

As can be concluded from data in Table 2, the catalytic activity of the prepared $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite for the reduction of MB is comparable with previously reported catalysts [19, 24–26].

3.3 Catalytic mechanism

Our literature survey show, that most researchers used the typical Langmuir–Hinshelwood model for the reduction of MB in the presence of reductants at nanocatalysts surface [30, 31]. In the present work, this mechanism can be applied and schematically illustrated in Scheme 1. Based on this mechanism both MB and NaBH_4 , were adsorbed

onto the surface of $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite. Adsorption of NaBH_4 and MB molecules over the surface of $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite occur via two manners, direct absorption and hydrogen bonding-assisted absorption. These adsorptions are rapid and reversible in nature. Apart from the physical adsorption, hydrogen bonding plays an important role in attaching the MB molecules onto the surface of $\text{ZrO}_2/\text{Fe}_3\text{O}_4$. Oxygen functional groups bonded to Zr and Fe atoms in $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite are more favorable for hydrogen bonding. Adsorbed borohydride ions (BH_4^-) release hydrogen on $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ surface, which also generally helps in the adsorption of MB by forming catalyst-H complexes on its surface. After adsorption, MB

Fig. 3 **A** The FTIR spectrum of (a) Magnetite (Fe_3O_4), (b) ZrO_2 , and (c) $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ (5:2) nanocomposite. **B** The VSM magnetization curves of $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposites at room temperature. Inset is the response of the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ (5:2) nanocomposite to a permanent magnet

Table 1 Magnetization (at 7500Oe) and thicknesses of the non-magnetic layer (t) of samples

	Fe_3O_4	$\text{ZrO}_2/\text{Fe}_3\text{O}_4$ (1:1)	$\text{ZrO}_2/\text{Fe}_3\text{O}_4$ (3:2)	$\text{ZrO}_2/\text{Fe}_3\text{O}_4$ (5:2)	$\text{ZrO}_2/\text{Fe}_3\text{O}_4$ (7:2)
M (emu/g)	42.5	22.7	15.5	10.1	6.9
t (nm)	–	1.1	1.7	2.3	2.7

Table 2 The reaction time in the reduction of MB by using $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite in comparison to recent works

Type of catalyst	Reaction time/min	References
–	120	This work
Fe_3O_4	60	
ZrO_2	35	
$\text{ZrO}_2/\text{Fe}_3\text{O}_4$	5	
$\text{Fe}_3\text{O}_4\text{-Ag}$	18	[27]
$\text{Fe}_3\text{O}_4\text{@HA@Ag}$	20	[28]
$\text{Fe}_3\text{O}_4\text{@Nico-Ag}$	5	[29]

HA humic acid, Nico nicotinic acid

Fig. 4 UV-Vis spectra of MB during the catalytic reduction

molecules interact with the adsorbed molecules of NaBH_4 on the surface of $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite. $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite acts as an agent that overcomes the kinetic barrier and catalyzes the reaction by facilitating electron transference from the NaBH_4 to the MB molecules [32, 33]. The product formed, LMB, desorbs from the surface of the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite and diffuses from the surface to the bulk region [32].

3.4 Recyclability of catalyst

To explore the recyclability of the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite, it separated from the reaction solution by using a permanent magnet, washed with double distilled water and ethanol, then dried and used up to 3 times in the reduction reaction of MB. Our results showed that the $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite in one, two, three and four catalytic runs showed reaction times as 5, 6, 8, and 10 min for 100% reduction of MB, respectively (Fig. 5). Consequently, the efficiency of recovered catalysts maintains significantly

Scheme 1 Possible mechanism of MB reduction in the presence of NaBH₄ at ZrO₂/Fe₃O₄ nanocomposite

Fig. 5 The recyclability of catalyst during four catalytic runs

unchanged, indicating the high stability of the ZrO₂/Fe₃O₄ nanocomposite as a catalyst in real applications.

4 Conclusion

In this work, the ZrO₂/Fe₃O₄ nanocomposites were successfully prepared and characterized by using XRD, SEM, EDXA, TEM, FTIR, and VSM techniques. Based on the dead layer model, by increasing nonmagnetic ZrO₂ shell at Fe₃O₄ magnetic core, the magnetization of samples decreases. However, the increase of the contribution of ZrO₂ in ZrO₂/Fe₃O₄ is resulting in the increased catalytic activity of prepared composite. In the processes of filtering or separation, unhealthy materials from wastewater under the external magnetic field, high magnetization, and high catalytic activity are two key factors. According to two parameters: (1) magnetization and (2) thickness of ZrO₂, superparamagnetic ZrO₂/Fe₃O₄ (5:2) nanocomposite

was the best candidate in the catalytic reduction of MB. Prepared nanocatalyst showed good performance in catalytic reduction of MB in the presence of NaBH_4 . Therefore, this newly synthesized $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ nanocomposite can be a promising nanocatalyst for the reduction of industrial waste azo dyes like MB during the wastewater treatment.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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