

Microwave Synthesis of Fe₂O₃ Nanoparticles and Its Catalyst Investigation in One-pot Synthesis of Naphthoxazinone Derivatives

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Abstract

In this work firstly Fe₂O₃ nanoparticles were synthesized via a simple chemical method. Properties of the product were examined by X-ray diffraction pattern (XRD), Scanning electron microscope (SEM) and Fourier transform infrared (FT-IR) spectroscopy. Vibrating sample magnetometer (VSM) shows nanoparticles exhibit ferromagnetic behavior. To continue some of the 2-naphthol condensed 1,3-oxazinone derivatives employing one-pot condensation reaction in the presence of Fe₂O₃ nanoparticles as an acid catalyst were described. The present methodology offers several advantages, viz. high yields, clean reaction, short reaction times, recyclability of the catalyst and simple workup procedure.

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1. Introduction

Fe₂O₃ has exhibited unique magnetic properties because of its low toxicity, good biocompatibility and tunable magnetic properties. Magnetic materials have received considerable attention in various areas such as catalysis, magnetic refrigeration systems, drug delivery and targeting, heat transfer applications, cancer therapy, enzyme immobilization and magnetic cell separation [1]. Multi-component reactions (MCRs) have attracted considerable attention since an increasing number of organic chemical

compounds are formed by multi-component reactions (MCRs) that convert more than two educts directly into their products by one-pot reactions. Further, they are performed without need to isolate any intermediate during their processes; this reduces time and saves both energy and raw material. They have merits over two-component reactions in several aspects including the simplicity of a one-pot procedure, possible structural variations and building up complex molecules. They showed various applications in organic, medicinal chemistry and in drug discovery as

well as 'green chemistry' [2-3]. One of the MCRs is the preparation of benzoxazinones. These components have received considerable attention because of the attractive pharmacological properties associated with their heterocyclic scaffold [4]. Molecules bearing these skeletons have been reported to exhibit a variety of biological properties, including anti-inflammatory, antiulcer, antipyretic, antihypertensive, and antifungal activities [5]. Some of these compounds also exhibit several important biological activities such as DP receptor antagonism [6], integrin antagonism [7], platelet fibrinogen receptor antagonism [8], calmodulin antagonism [9], and inhibition of the transforming growth factor β (TGF- β) signaling pathway [10], soybean lipoxygenase [11], and other protein kinase. Because of the importance of these compounds, several synthetic methods for 1,2-dihydro-1-arylnaphtho [1,2-e] [1,3]oxazine-3-ones have been developed [12-16]. The reported methods mainly include one-pot three-component reactions of 2-naphthol, aromatic aldehydes, and urea (Scheme1). These reactions for the synthesis of 2-dihydro-1-aryl-naphtho [1,2-e][1,3]oxazine-3-ones have been studied with the use of several catalysts and reagents such as Cu-nano-particles/PEG-400 [12], TMSCl [13], $\text{HClO}_4/\text{SiO}_2$ [14], $\text{H}_3\text{Mo}_{12}\text{O}_{40}\text{P}$ [15], montmorillonite K10 clay [16] and iodine [17-20]. Although several methods for the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-ones and 1,2-dihydro-1-arylnaphtho[1,2][1,3]oxazine-3-thiones have been reported, there is still demand for simpler, less toxic, more effective, and milder catalysts. In this article, there is growing interest in development of clean processes

involving green solvent and recycle catalyst.

There is an increasing interest in magnetic ferrite nanoparticles because of their broad applications in several technological fields including permanent magnets, magnetic fluids, drug delivery, microwave devices, and high density information storage. Ferrite has been widely studied because it possesses excellent chemical stability and suitable mechanical hardness. In addition to the precise control on the composition and structure of Fe_2O_3 different chemical and physical synthesis methods, such as precipitation, sol-gel, hydrothermal are used to produce ferrite. Among the reported methods, the microwave method is an efficient way to production of ultrafine and mono-dispersed magnetic powder. A variety of synthesis strategies for ferrites nanostructure materials have been described. Microwave method as a simple, effective and novel route has been developed to prepare nanostructures [21-24].

In the present work, Fe_2O_3 nanoparticles were synthesized by a surfactant-free microwave method without using inert atmosphere. The obtained samples were characterized by scanning electron microscopy and X-ray diffraction pattern. The magnetic properties were investigated using a vibrating sample magnetometer. Magnetic photo-catalysts have gained much attention because those can easily be separated from polluted waters by applying a simple magnetic field.

2 Experimental

2.1. Materials and Instruments

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaOH and NH_3 were purchased from Merck Company. All of the

chemicals were used as received without further purifications. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered Cu K α radiation. For SEM images the samples were coated by a very thin layer of Au to make the sample surface conductor and prevent charge accumulation, and obtaining a better contrast. Room temperature magnetic properties were investigated using a vibrating sample magnetometer (VSM, made by Meghnatis Daghigh Kavir Company) in an applied magnetic field sweeping between ± 10000 Oe.

A multiwave ultrasonic generator (Sonicator 3000; Bandeline, MS 73, Germany), equipped with a converter/transducer and titanium oscillator (horn), 1.25×10^{-2} m in diameter, surface area of ultrasound irradiating face: 1.23×10^{-4} m 2 , operating at 20 kHz, was used for the ultrasonic irradiation and the horn was operated at 50% amplitude. All ultrasonication experiments were carried out at ultrasonic power between 84–125 mW measured by calorimeter.

2.2. Synthesis of nanoparticles and nanocomposites

FeSO $_4 \cdot 6H_2O$ and Fe(NO $_3$) $_3 \cdot 9H_2O$ were taken in 2:1 molar ratio and dissolved separately in 2M HCl. This solution was mixed together and 2 mL of octanoic acid was added to the solution as a surfactant. Then, NaOH solution (1.5 M) was slowly added into the solution under microwave irradiation 900W until the pH of the mixture was 10. After complete precipitation, the resulting products were centrifuged for 15 min at 3,000 rpm, washed with distilled water and ethanol several times to remove the excess surfactant from the solution. Then, precipitation was dried in an oven at 100 °C for 3 h. The

resulting red-brown powder was calcinated at 800 °C for 2 h to remove any organic residue.

2.3. General procedure for the Fe $_2O_3$ -nanoparticles catalyzed 1,3-oxazin-3-ones derivatives

To a mixture of benzaldehyde (2 mmol), urea (3 mmol) and K $_2CO_3$ (0.3 mmol) in PEG-400 (3 mL) Fe $_2O_3$ -nanoparticles (0.001 g) were added, finely mixed together and allowed to stir for 5 min at room temperature and then β -naphthol (2 mmol) was added. The resulting reaction mixture was stirred at room temperature for a specified period (Table 1, Fig. 1). The progress of the reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, as indicated by TLC the reaction mixture was centrifuged (3000 rpm, 10 min) to pellet out the Fe $_2O_3$ nanoparticles. The particles were then washed with absolute PEG to remove all the organic impurities. These particles were reused for evaluating the performance in the next reaction. The organic PEG layer containing reaction mixture was extracted with dry diethyl ether as PEG is insoluble in ether. The ethereal layer was decanted, dried, concentrated under reduced pressure and then the product so obtained was recrystallized from hexane-EtOAc (3:1) to afford the pure product in >90% yields (Table 1). The recovered PEG and Fe $_2O_3$ nanoparticles were reused for consecutive runs to evaluate the scope of recyclability of the reaction. Structural assignments of the products are based on their FT-IR, 1H NMR, and ^{13}C NMR. The analysis of complete spectral and compositional data revealed the formation of Naphthaoxazinone products with excellent purity.

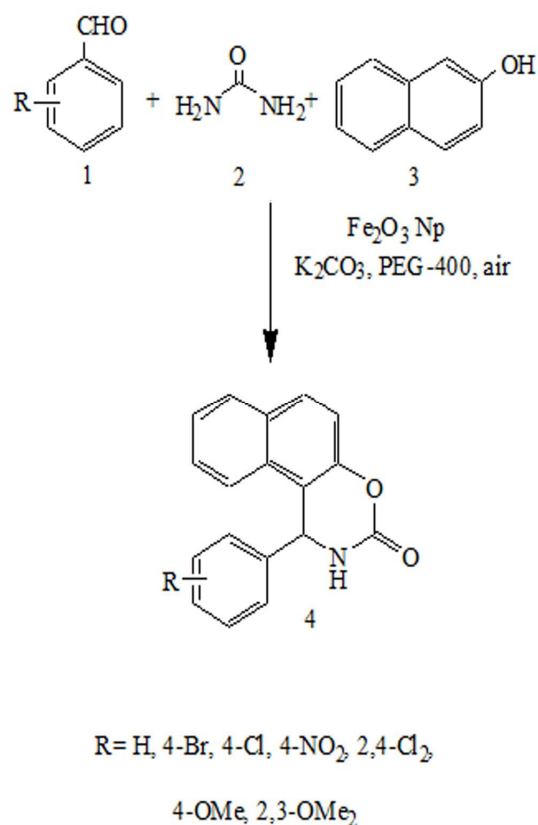


Fig. 1. Schematic of preparation at presence of Fe₂O₃ nanoparticles

3. Results and discussion

Characterization data of some important Compounds

1-Phenyl-1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3-one (4a):

Yield 91% as a white solid; mp. 216-218°C. IR (KBr, cm⁻¹): 3300 (N-H Str.); 3037 (C-H_{arom} Str.); 1670 (C=O Str.). ¹HNMR (400 MHz, CDCl₃, δ, ppm): 6.19 (1H, d, CH); 8.29 (1H, s, 1NH); 7.28-7.90 (11H_{arom}, m, 11CH_{arom}).

1-(4-Bromophenyl)-1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3-one (4b):

Yield 93% as a white solid; mp. 217-219°C; (KBr, cm⁻¹): 3214(N-H Str.); 3024(C-H_{arom} Str.); 1730(C=O Str.). ¹HNMR (400 MHz, CDCl₃, δ, ppm): 6.09(1H, d, 1CH); 6.91(1H, s, 1NH); 7.20-7.30(4H_{arom}, m, 4CH); 7.35(1H_{arom}, d, 3J=8.6 Hz, 1CH); 7.43-7.86 (4H_{arom}, m, 4CH); 7.90(1H_{arom}, d, 3J=8.6 Hz, 1CH).

1-(4-Chlorophenyl)-1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3-one (Entry 1):

Yield 92% as a white solid; mp. 205-208°C. IR (KBr, cm⁻¹): 3293 (N-H Str.); 3070 (C-H_{arom} Str.); 1650(C=O Str.). ¹HNMR (400 MHz, CDCl₃, δ, ppm): 8.91(1H, s, 1NH); 6.21(1H, d, 1CH); 7.01-7.70 (10H_{arom}, m, 8CH).

1-(2,4-Dichlorophenyl)-1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3-one (Entry 1):

Yield 94% as a white solid; mp. 208-211°C. IR (KBr, cm⁻¹): 3208(N-H Str.); 3066 (C-H_{arom} Str.); 1743(C=O Str.). ¹HNMR (400 MHz, CDCl₃, δ, ppm): 6.79(1H, s, 1NH); 6.92(1H, dd, 1CH); 7.27-7.66(6H_{arom}, m, 6CH); 7.84(2H_{arom}, t, 2CH); 8.68(1H_{arom}, d, 1CH).

The XRD pattern of Fe₂O₃ nanoparticles is shown in Fig. 2. The pattern of as-prepared Fe₂O₃ nanoparticles is indexed as a Rhombohedral cubic phase which is very close to the literature values (JCPDS No. 72-0469). The narrow sharp peaks indicate that the Fe₂O₃ nanoparticles are well crystallized.

The crystallite size measurements were also carried out using the Scherrer equation,

$$D_c = K\lambda / \beta \cos\theta$$

Where β is the width of the observed diffraction peak at its half maximum intensity (FWHM), K is

the shape factor, which takes a value of about 0.9, and λ is the X-ray wavelength (CuK α radiation, equals to 0.154 nm). The estimated crystallite size was about 20 nm.

Table 1. Various prepared Naphthoxazinone Derivatives

Aryl aldehyde	Time	Yeild	M.P
Bnza	60	91	216
4-Bromo Bnza	45	93	217
4-Nitro Bnza	40	95	204
4-Chloro Bnza	45	92	205
4-Methoxy Bnza	56	93	187
2,4-Dichloro Bnza	60	94	208
2,3-Di Methoxy Bnza	55	92	213

The XRD pattern of synthesized Fe₂O₃ nanoparticles and standards peaks are illustrated in Fig. 3. The pattern of Fe₂O₃ nanoparticles confirms a pure Rhombohedral phase which is very close to the literature values (JCPDS No. 72-0469).

Fig. 4 illustrates SEM images of synthesized Fe₂O₃ nanoparticles that obtained at calcinations temperature of 500 °C that confirm average diameter size of product is less than 40 nm.

SEM image of Fe₂O₃ that obtained at calcinations temperature of 800 °C was studied and illustrated in Fig.5. According to images agglomerated particles with average diameter about 100nm were synthesized.

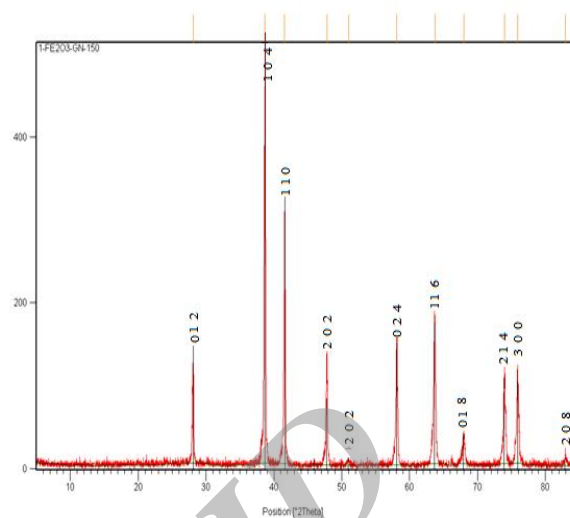


Fig. 2. XRD pattern of the Fe₂O₃ nanoparticles

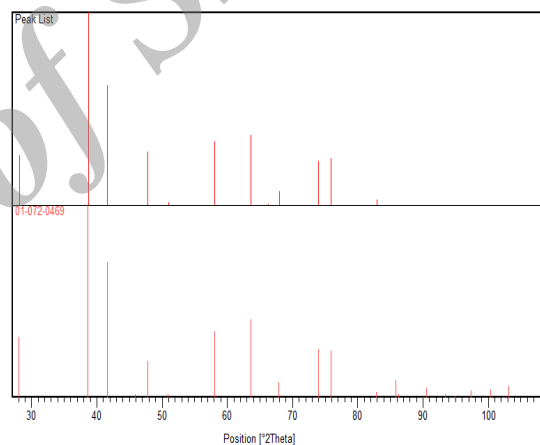


Fig. 3. XRD pattern of the prepared Fe₂O₃ versus standards peaks

Fig. 5 confirms some agglomeration compare to 500. It seems with increasing calcinations temperature from 500°C to 800°C growth stage is predominant compare to nucleation stage.

The image shows that the sample consists of larger particles compare to pure ferrite nanoparticles [21-24].

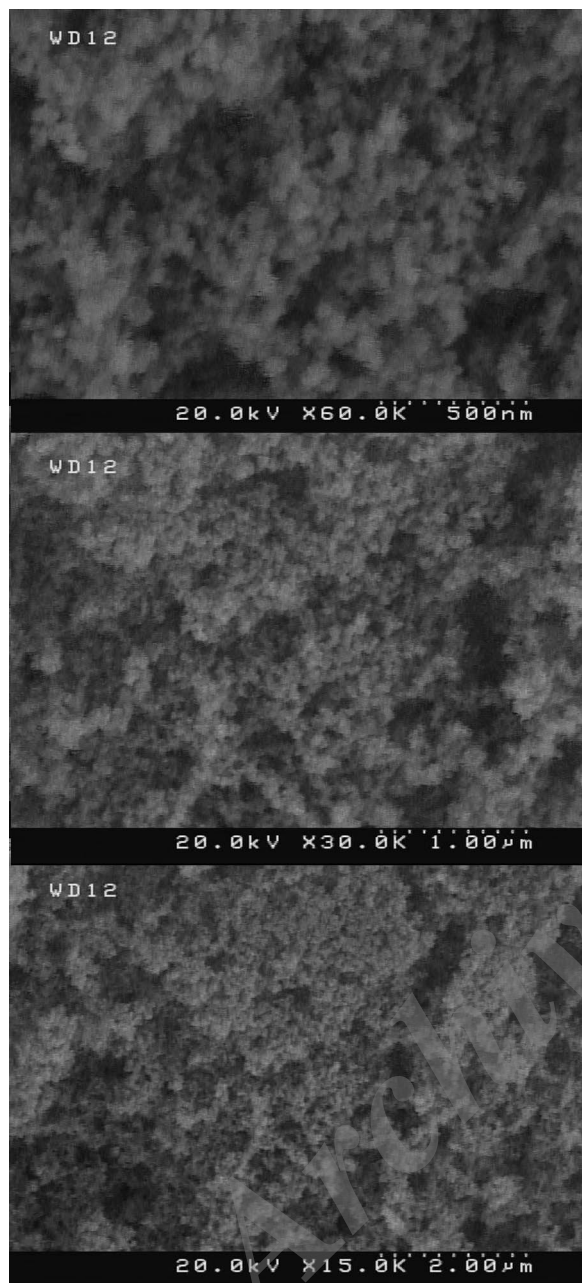


Fig. 4. SEM images of Fe_2O_3 nanoparticles prepared at 500 °C

Fourier transform infra-red (FT-IR) spectrum of synthesized nanoparticles was recorded in the range of 400–4000 cm^{-1} and spectra without and with calcination are shown in Fig. 6 and 7 respectively. Absorption peaks around 438 and 618 cm^{-1} are related to metal-oxygen Fe-O bonds. The spectrum exhibits broad absorption

peaks between 3500–3600 cm^{-1} , corresponding to the stretching mode of O-H group of –Fe-O and also hydroxyl group that are adsorbed on the surface of nanoparticles.

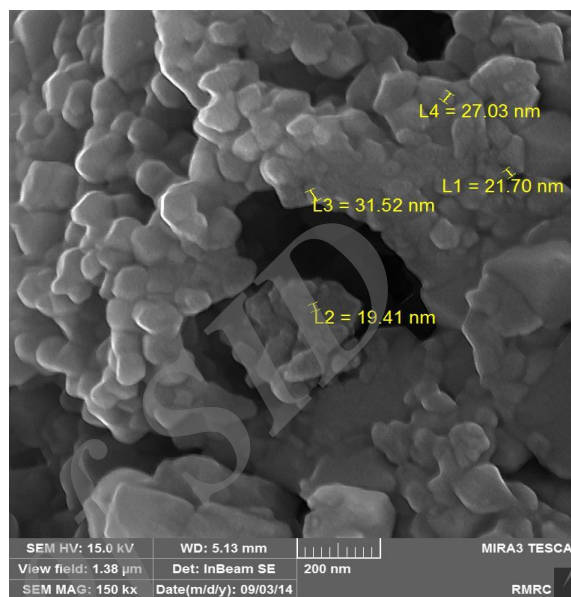


Fig. 5. SEM images of Fe_2O_3 nanoparticles prepared at 800 °C

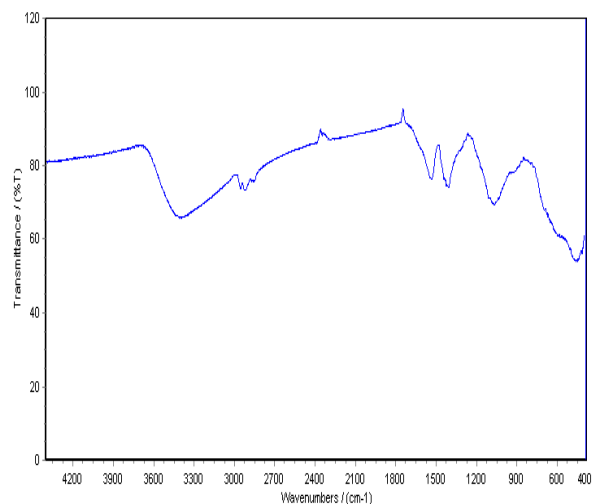


Fig. 6. FT-IR spectrum of product without calcination

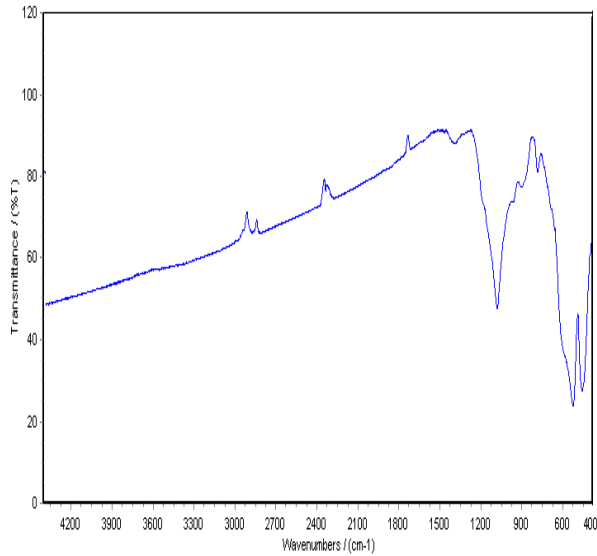


Fig. 7. FT-IR spectrum of Fe₂O₃ nanoparticles calcined at 500 °C

Microwave methods propose easy manipulation in particle size and so magnetic properties by a simple change in power of pulsation and time of irradiation.

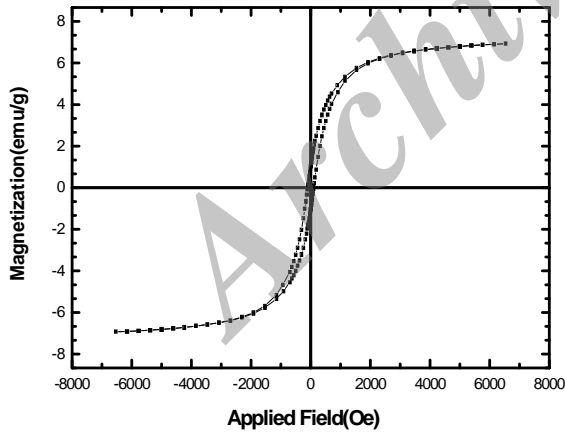


Fig. 8. Hysteresis curve of Fe₂O₃ nanoparticles prepared at 500 °C

Fig. 8 shows magnetization curve of Fe₂O₃ nanocomposites that also exhibits ferromagnetic behavior with a coercivity around 95 Oe and a saturation magnetization of 6.4 emu/g.

As-synthesized Fe₂O₃ nanoparticles obtained at 800°C also show ferromagnetic behavior and have a saturation magnetization of 4.8 emu/g and coercivity about 145 Oe (**Fig . 9**). As expected due to increasing temperature its magnetization is lower than Fe₂O₃ nanoparticles calcined at 500°C [25-28].

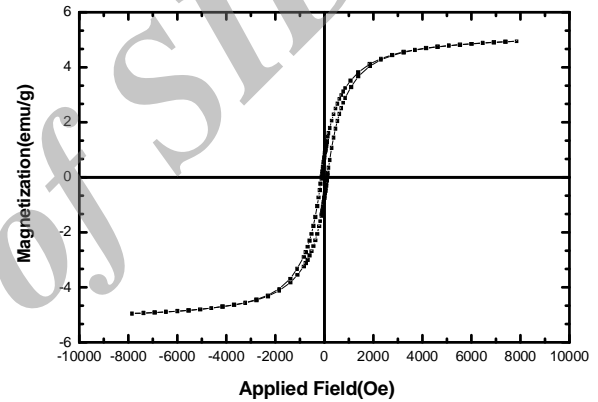


Figure 9. Hysteresis curve of Fe₂O₃ nanoparticles prepared at 800 °C

Percent and time of Fe₂O₃ recovery versus of number of cycles are shown in **Fig 10** that confirm recycling of the catalyst.

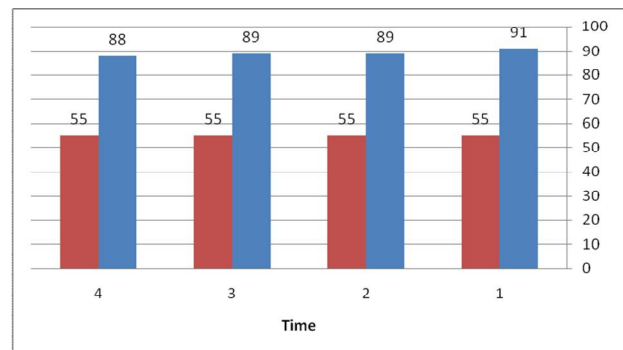


Fig. 10. Percent and time of Fe₂O₃ recovery versus of number of cycles

In view of the green chemistry, and recyclability of the catalyst, the Fe_2O_3 nanoparticles were used as catalyst for the same reaction repeatedly and the change in their catalytic activity was studied. The relation between the number of cycles of the reaction and the catalytic activity in terms of yield of the products is presented in the Fig 10. It was found that Fe_2O_3 nanoparticles could be reused for four cycles with negligible loss of their activity. It should be noted that the yields in second to fourth run are comparable to that of the first run. Hence, this procedure is advantageous over conventional reaction media.

4. Conclusion

Hematite nanoparticles were synthesized via a microwave-assisted method. For synthesis In conclusion, we have demonstrated that Fe_2O_3 nanoparticles are a novel, an efficient and environmentally friendly for the synthesis of one-pot three-component condensation of aryl naphthoxazine-3-one derivatives. The advantages of this method are shorter reaction times, simple work-up, environmentally benign, high yield, and reusability of catalyst in comparison with the other reported methods.

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