

RESEARCH PAPER

## Preparation and Characterization of a Molybdenum(VI) Schiff Base Complex as Magnetic Nanocatalyst for Synthesis of 2-Amino-4H-benzo[h]chromenes

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### ABSTRACT

A new recoverable molybdenum nanocatalyst was prepared by immobilization of a Schiff base ligand on the surface of silica coated magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) through condensation reaction between 3-aminopropyl triethoxysilane and 2-hydroxy-1-naphthaldehyde and succeeding reaction with dioxomolybdenum(VI) acetylacetonate (MoO<sub>2</sub>(acac)<sub>2</sub>). The synthesized catalyst was characterized by inductively coupled plasma, thermogravimetric analysis, scanning electron microscopy, vibrating sample magnetometry, Energy-dispersive X-ray, Fourier transform infrared and X-ray diffraction spectroscopy. Catalytic performance of the synthesized nanocatalyst was investigated for the preparation of 2-amino-4H-benzo[h]chromenes. The compounds were prepared high yield through one-pot, three-component reaction of 1-naphthol, various of aldehydes and malonitrile in the presence of nanocatalyst, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Mo-Schiff base, under solvent-free conditions. The benefits of this protocol are short reaction time, simple work-up procedure, high yields and use of the concept of green chemistry. The magnetic nanocatalyst could be separated easily from the reaction media using an external magnetic field and reused in subsequent catalytic runs without significant deterioration of its activity.

### How to cite this article

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### INTRODUCTION

In the recent decades, magnetic nanoparticles (MNPs) have attracted considerable attention because of particular application and properties [1]. High area to volume ratio and easy isolation by an external magnetic field are regarded as two special features of the magnetic nanoparticles. They have important applications in different fields such as magnetic resonance imaging (MRI), sensors, saving information, separation metal ion and biomedicine particularly in the fields of pharmacology [2,7]. Fe<sub>3</sub>O<sub>4</sub> nanoparticles have

been paid much attention by researches because of having various properties such as chemical stability, superparamagnetic property, high level contact, environmental sustainability, low price and low toxicity [8, 9]. It is necessary to modify the surface of these particles for especial goals such as improving the efficiency of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The surface coating of magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) has benefits like protecting against oxidation, agglomeration, conservation of crystal structure of these nanoparticles in high temperatures [10, 14]. Due to the particular properties of magnetic

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nanoparticles, they can be applied as support for homogeneous catalysts. The Schiff base complexes of transition metals which have been known as homogeneous catalysts can be immobilized on the surface of the magnetic nanoparticles. The advantages of immobilization of homogeneous catalysts on the surface of magnetic nanoparticles as support are easy isolation and recovery of catalyst from reaction media by an external magnet in order to reusability of the nanocatalyst [15-19]. In fact, the immobilized catalysts on the surface of nanoparticles are considered as a bridge between homogeneous and heterogeneous catalysts which are known as an interphase catalyst. One of the ideal supports is  $\text{Fe}_3\text{O}_4$  which can be used to heterogenize homogeneous catalysts [20-21].

Metal transition complexes of Schiff base have been studied extensively due to their potential application in catalytic systems [22-23]. One of the interested complexes in this field is Schiff base complexes of dioxomolybdenum(VI) which have been attracted remarkable attention as homogeneous catalysts in reactions such as epoxidation of alkenes and oxidation of sulfides [24-25]. Molybdenum complexes immobilized on the surface of modified magnetite nanoparticles as support have been used in many catalytic systems [26-27].

A main group of natural oxygen-including heterocyclic compounds are 2-aminochromenes. They are extensively found in edible vegetables and fruits [28-29]. They have attracted much attention in drug research due to their different pharmacological and biological activities, take for example antifungal, antibacterial, antioxidant, antidepressant, antitumor and antiallergenic activities [30-36]. 2-Aminochromenes are also broadly applied as potential biodegradable agrochemicals, pigments and cosmetics [37-39]. In synthetic chemistry for the synthesis of biologically interesting compounds, the development of economical, eco-friendly and effective methods is problematic. The chemical industry is known as one of the principal contributors to environment pollution in regard to the utilizing dangerous chemicals and especially huge amounts of volatile, flammable and toxic organic solvents. Lately organic reactions under solvent-free conditions have drawn a lot of attention from scientists [40]. In other words, multicomponent reactions (MCRs) have been known as protocol to produce active biological compounds because of easy and simple

method of synthesis. For the synthesis of 2-amino-4H-benzo[h]chromenes, different methods were reported [41-44]. Although these methods are efficient, but many of them require expensive catalyst, difficult workup and toxic organic solvents [45-48].

Therefore, considering the pharmacologically and biologically importance of chromenes, attempt to develop a green method for preparation this heterocyclic is still in demand. Herein, we report preparation, characterization Schiff base complex immobilized on nanomagnetic particles,  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{Mo-Schiff}$  base, and investigation of its catalytic activity in a three component reaction of 1-naphthol, malonitrile with aldehydes to synthesis 2-amino-4H-benzo[h]chromenes.

## MATERIALS AND METHODS

All the chemicals and solvents without any further purification were analytical reagent grade where purchased from Aldrich, Merck or Fluka.  $\text{MoO}_2(\text{acac})_2$  was prepared as described in the literature [49]. Thermogravimetric (TGA) analysis of the synthesized nanomaterials were performed on a Perkin Elmer analyzer. The TG analyzer was regulated under nitrogen atmosphere at heating rate of  $10^\circ\text{C}/\text{min}$  in a temperature ranging of  $50-900^\circ\text{C}$ . Ultrasonic generators were carried out on a SONICA-2200 Ep, input 50- 60 Hz/305w. The nanoparticles were analyzed using a Holland Philips X Pert X-ray diffraction diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5404 \text{ \AA}$ ) in the  $2\theta$  range of  $10-80^\circ$  at room temperature. The SEM image of nanostructures were recorded by means of VEGA/TESCAN KYKY-EM3200 microscope. Magnetic properties of samples were measured by Vibrating samples magnetometer (VSM, MDK, Model 7400). FT-IR spectra were recorded using a Bruker FT-IR instrument (KBr pellet,  $450-4400 \text{ cm}^{-1}$ ).

### Preparation of $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{Mo-Schiff}$ base nanocatalyst

Silica coated magnetic nanoparticles and the amino-functionalized MNPs were synthesized by the literature methods [50, 51]. The prepared nanoparticles (1 g) suspended in 50 ml ethanol and 2-hydroxy-1-naphthaldehyde (3mmol, 0.516 g) was added into the reaction mixture and refluxed for 12h. The  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{Schiff}$  base was isolated using an external magnetic field. The obtained nanomaterial was washed with ethanol

3 times and dried at 80°C for 6h. In the next step, immobilized Schiff base on the surface of magnetic nanoparticles (1 g) was dispersed in 50 ml ethanol and 3mmol of MoO<sub>2</sub>(acac)<sub>2</sub> in 50 ml ethanol was added to this reaction mixture and refluxed for 12h. The prepared nanocatalyst was separated by magnetic decantation. To remove the unreacted MoO<sub>2</sub>(acac)<sub>2</sub>, soxhlet extraction was carried out with ethanol and the resulting nanocatalyst dried at 80°C for 6h.

#### General procedure for the synthesis of 2-amino-4H-benzo[h]chromenes derivatives

A mixture of aldehyde (1 mmol), 1-naphthol (1 mmol), malononitrile (1 mmol), and nanocatalyst (0.2 g) was heated to 125 °C under solvent-free conditions. As indicated in Table 2, the reaction mixture was heated for an appropriate time. By thin-layer chromatography (TLC), the progress of the reaction was controlled until the aldehyde was disappeared. At the end of the reaction, the reaction mixture was cooled to room temperature and 3 mL of ethanol was added to the reaction mixture and stirred for 4 min. The synthesized nanocatalyst was isolated by magnetic decantation, washed with ethanol 3 times, dried and then reused in the next reaction. The obtained product was filtered and washed with cold ethanol. The synthesized 2-amino-4H-benzo[h]chromenes derivatives were crystallized from hot ethanol in order to gain pure products.

#### Selected spectral data

2-Amino-4-(4-chlorophenyl)-4H-benzo[h]chromene-3-carbonitrile (Table 2, entry 1).  $\nu_{\max}$  (KBr) 3468, 3327, 2192,1669, 1599, 1407,1374, 1101 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>): 4.82 (br s, 2H, NH<sub>2</sub>), 4.88 (s,1H, CH), 7.01-8.20 (10H, Ar).

2-Amino-4-(4-nitrophenyl)-4H-benzo[h]chromene-3-carbonitrile (Table 2, entry 4).  $\nu_{\max}$  (KBr) 3473, 3349, 2191,1650, 1624,1511,1402,1350, 1099 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>): 4.90 (br s, 2H, NH<sub>2</sub>), 5.0 (s,1H, CH), 6.96-8.22 (10H, Ar).

2-Amino-4-(3-nitrophenyl)-4H-benzo[h]chromene-3-carbonitrile (Table 2, entry 3).  $\nu_{\max}$  (KBr) 3470, 3328, 2192,1666, 1601,1525,1406,1375, 1102 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CD<sub>3</sub>CN): 5.73 (br s, 2H, NH<sub>2</sub>), 5.09 (s,1H, CH), 7.04-8.30 (10H, Ar).

## RESULTS AND DISCUSSION

### Preparation and Characterization of Immobilization Molybdenum Complex (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@ Mo-Schiff)

The preparation route synthesized nanocatalyst is shown in Fig. 1. In order to prepare nanocatalyst, initially Fe<sub>3</sub>O<sub>4</sub> MNPs were modified with silica via chemical bonds to obtain Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. In the second step, through reaction between silanol groups of (3-aminopropyl)triethoxysilane (APTES) and hydroxyl groups of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> surface were functionalized with APTES to obtain Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@NH<sub>2</sub> [51]. In the next step, Schiff base ligand was formed by condensation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@NH<sub>2</sub> amine group with carbonyl

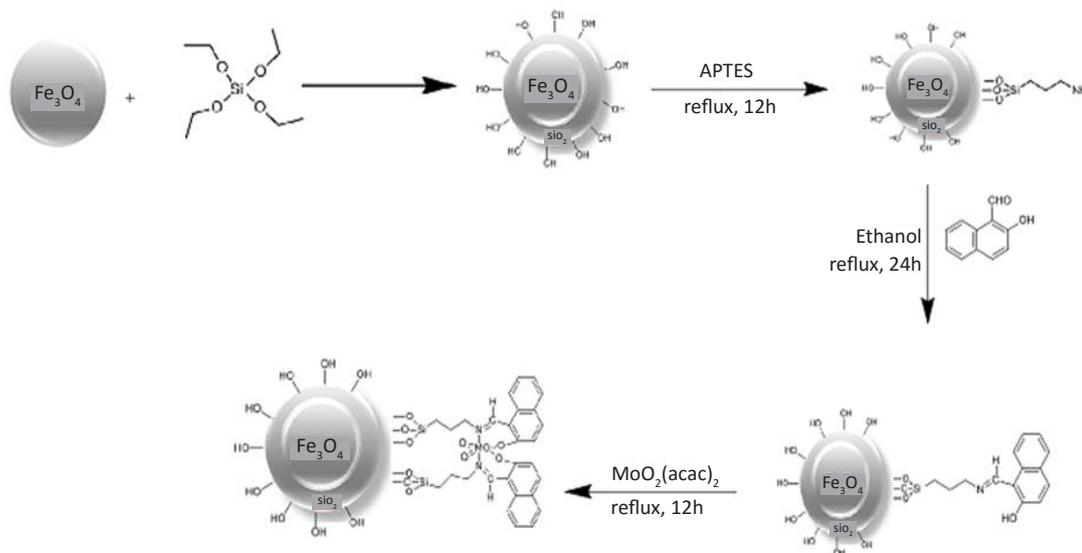


Fig. 1. Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Mo-Schiff base

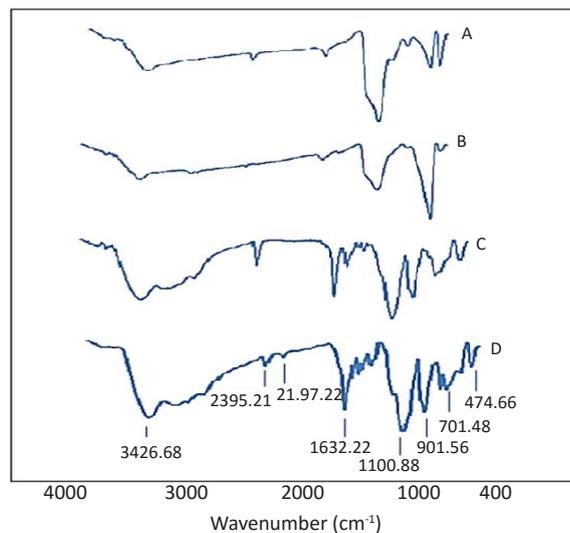


Fig. 2. FT-IR spectra of (A)  $\text{Fe}_3\text{O}_4@SiO_2$  (B)  $\text{Fe}_3\text{O}_4@SiO_2@APTES$  and (C)  $\text{Fe}_3\text{O}_4@SiO_2@Mo\text{-Schiff}$  base, (D) used  $\text{Fe}_3\text{O}_4@SiO_2@Mo\text{-Schiff}$  base.

of 2-hydroxy-1-naphthaldehyde. Then, the immobilized molybdenum Schiff base complex,  $\text{Fe}_3\text{O}_4@SiO_2@Mo\text{-Schiff}$  base, on the surface of silica was formed by the reaction between of  $\text{MoO}_2(\text{acac})_2$  with the composite  $\text{Fe}_3\text{O}_4@SiO_2@Schiff$  base. To remove unreacted species, soxhlet extraction of the nanocatalyst was carried out with ethanol and dried at  $80^\circ\text{C}$  for 6h. The prepared nanocatalyst was characterized by different methods such as XRD, SEM, EDS, VSM, TGA and FT-IR. The catalytic activity of magnetic nanocatalyst was examined for the green multicomponent synthesis of 2-amino-4H-benzo[h]chromenes.

The FT-IR spectra of all nanomaterials were shown in Fig. 2. The modified magnetite nanoparticles with silica have indicated a broad band at 798 and  $1101\text{ cm}^{-1}$  corresponding to the symmetric and asymmetric stretching vibration of Si-O-Si groups, and Fe-O vibration band appears to a new wavenumber of  $573\text{ cm}^{-1}$  (Fig. 2A). The IR spectrum of  $\text{Fe}_3\text{O}_4@SiO_2@NH_2$  demonstrates a peak at  $565\text{ cm}^{-1}$  assigned to Fe-O stretching vibration and a broad band at  $1079\text{ cm}^{-1}$  is attributed to the asymmetric vibrations of Si-O-Si. The observation of C-H vibration band at  $2925\text{ cm}^{-1}$  in the surface of the functionalized nanoparticles ( $\text{Fe}_3\text{O}_4@SiO_2@NH_2$ ) confirmed the presence of the anchored APTES group on the surface of the silica (Fig. 2B). The IR spectrum of the  $\text{Fe}_3\text{O}_4@SiO_2@Schiff$  base showed a strong peak at  $1634\text{ cm}^{-1}$  which could be attributed to the imine(C=N) stretching vibration group. This peak shifted to

new frequencies and appeared at  $1638\text{ cm}^{-1}$  due to the binding of azomethine nitrogen with the Mo. Also vibration band of O=Mo=O appeared at  $901\text{ cm}^{-1}$  in the spectrum of the nanocatalyst (Fig. 2C). The existence of  $SiO_2$  and  $Fe_3O_4$  in the nanocatalyst were indicated with the observation of vibration bands at 694, 1096 and  $3426\text{ cm}^{-1}$ , corresponding to Fe-O, Si-O-Si and OH vibrations, respectively.

By utilizing ICP chemical analysis the Mo loading of magnetic nanocatalyst was measured and found to be  $1.91\text{ mmol g}^{-1}$ .

The X-ray diffraction patterns of the prepared nanomaterials were exhibited in Fig. 3. The diffraction peaks at  $2\theta$  :  $30.1^\circ$ ,  $35.4^\circ$ ,  $43.1^\circ$ ,  $53.4^\circ$ ,  $57^\circ$  and  $62.6^\circ$  could be attributed to the (220), (311), (400), (422), (511) and (440) crystallographic faces of  $Fe_3O_4$  inverse cubic spinel. This results were confirmed with pattern of the standard  $Fe_3O_4$  (JCPDS CARD NO. 19-629). During the preparation of nanocatalyst,  $Fe_3O_4$  inverse cubic spinel structure was retained and this shown that no phase change was observed after surface modification of the magnetite nanoparticles ( $Fe_3O_4$ ). Moreover, the peak intensities in XRD pattern of the nanocatalyst (Fig.3 C) slightly decreased than uncoated magnetic nanoparticles (Fig. 3A). The decrease can be assigned to the shielding effect of silica on  $Fe_3O_4$ .

The morphology and sizes of the prepared nanostructure were studied by scanning electron microscopy. The SEM images of  $\text{Fe}_3\text{O}_4@SiO_2@Mo\text{-Schiff}$  base are presented in Fig. 4. As can be seen,

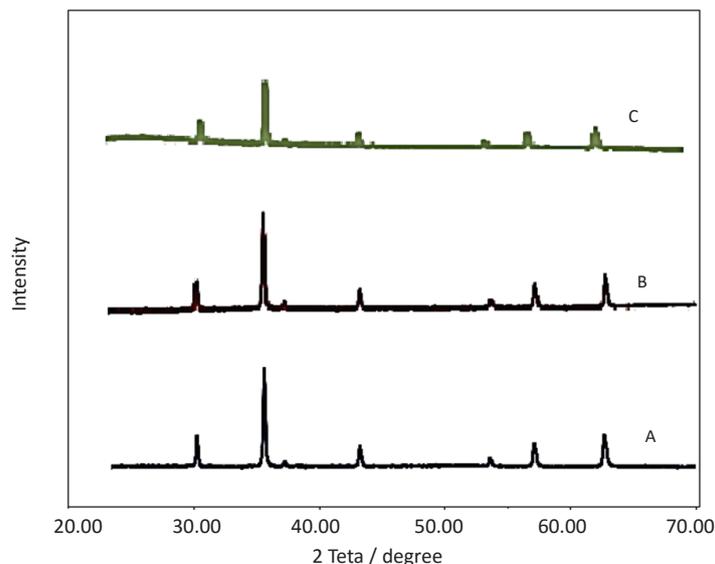


Fig. 3. XRD patterns of (A)  $\text{Fe}_3\text{O}_4$ , (B)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and (C)  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mo-Schiff}$  base.

the shape of nanoparticles is almost spherical with some aggregation and the average diameter is in the range of 50 – 90 nm. The energy dispersive spectrum (EDS) of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mo-Schiff}$  base shows that molybdenum Schiff base complex was anchored on the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and the mass percent of Fe, O, C, Si, Mo and N is 31.96%, 24.20%, 17.82%, 10.75%, 12.56% and 2.72%, respectively (Fig. 5).

The magnetic properties of all the prepared samples were investigated by vibrating sample magnetometry (VSM) at room temperature and under nitrogen atmosphere. As can be seen in Fig. 6, the saturation magnetization ( $M_s$ ) values for the magnetite nanoparticles ( $\text{Fe}_3\text{O}_4$ ), the modified magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@$

$\text{SiO}_2$ ) and the anchored molybdenum Schiff base complexes ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mo-Schiff}$  base) on the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  are 80, 52 and 22 emu/g, respectively. The decrease of magnetic saturation of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@$  Mo-Schiff base composite indicate the inert silica coating effect on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles and anchoring the Schiff base metal complex on the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ . Magnetization curves of all prepared nanomaterials approximately indicated superparamagnetic behavior because the figure shows well that hysteresis loops are narrow and remnant magnetization ( $M_r$ ) and coercivity ( $H_c$ ) values of nanomaterials are little. Decreasing of nanomaterials'  $M_s$  is probability due to reduce in crystalline order of nanomaterials [52]. Moreover, by using a permanent magnet, the prepared nanomaterials can be isolated from the reaction solution and when the external magnetic field is removed, they are enable to redisperse rapidly.

In order to confirm to immobilize molybdenum Schiff base complex on the surface of silica, TGA analyses were carried out. Fig. 7 shows TGA thermogram of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (Fig. 7A) and  $\text{Fe}_3\text{O}_4@$   $\text{SiO}_2@$  Mo-Schiff (Fig. 6B). The weight decrease around 200°C in both thermograms are assigned to adsorbed moisture on the surface of silica for  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , and for  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mo-Schiff}$ . The next weight decrease occurred above 350°C can be attributed to the loss of Schiff base ligand

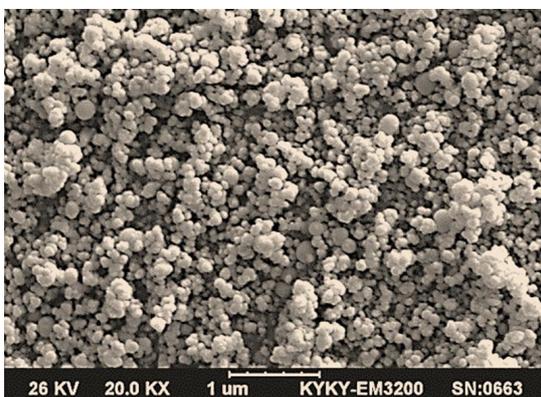


Fig. 4. SEM images of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mo-Schiff}$  base.

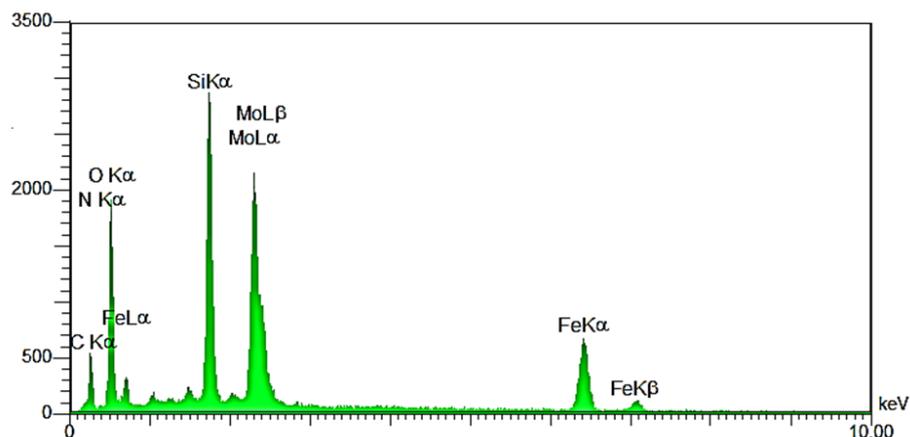


Fig. 5. EDS pattern of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mo-Schiff}$  base.

(25%) grafted on the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  surface. Therefore, the results of TGA analyses indicated the existence of grafted Schiff base ligand on the surface of functionalized magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ).

#### Catalytic Properties

After synthesis and characterization of the magnetic nanocatalyst, we have investigated its catalytic activity for the synthesis of 2-amino-4H-benzo[h]chromenes via the one-pot, three-component reaction of aldehydes, malononitrile and 1-naphthol. To find optimization of the reaction conditions, we selected the reaction of 2-chlorobenzaldehyde with malononitrile and 1-naphthol in the presence of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mo-Schiff}$  base as nanocatalyst (Fig. 8) at  $125^\circ\text{C}$  under different conditions as a model reaction. Table 2 shows the acquired results for the synthesis of

2-amino-4H-benzo[h]chromenes. As shown in table 1, the existence of nanocatalyst is necessary for this synthesis and the reaction did not proceed in the absence of catalyst after 24h.

To optimize reaction conditions factors such as effect of solvent and amount of catalyst were investigated. The model reaction was performed with the various catalyst loading under same reaction conditions. An increase in the amount of nanocatalyst from 0.07 to 0.2 g enhanced the yield from 80% to 95%. Quantities of more than 0.2 g nanocatalyst is not effective on the reaction time and yield. In the next step, the model reaction was done in different solvents and also under solvent free condition in order to investigate the effect of solvents. The results show that higher yield and shorter reaction time is observed while performing the reaction under solvent free condition. Therefore,

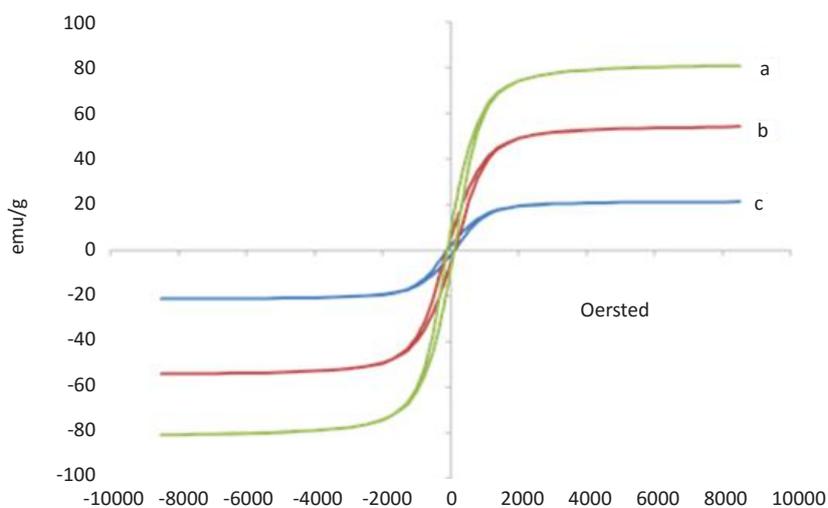


Fig. 6. VSM curves of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and (c)  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mo-Schiff}$  base.

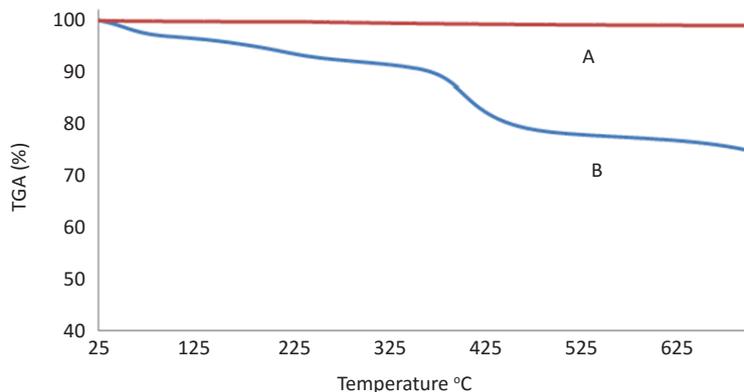


Fig. 7. TGA of (A) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and (B) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Mo-Schiff base

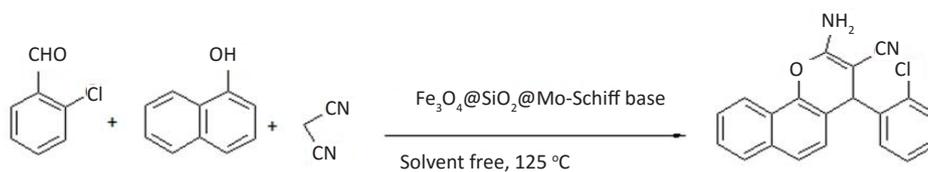


Fig. 8. Synthesis of 2-amino-4H-benzo[h]chromenes in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Mo-Schiff base.

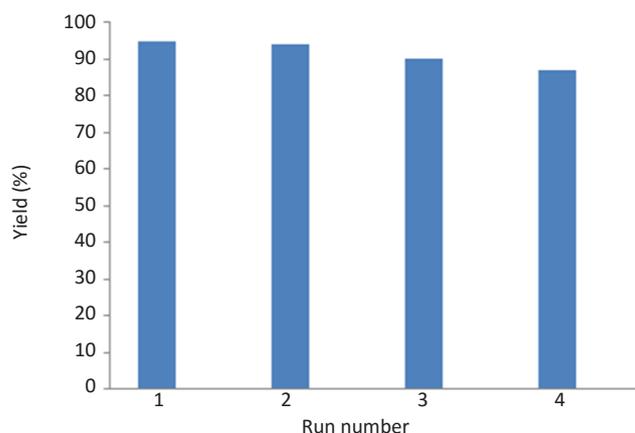


Fig. 9. Reusability of the nanocatalyst for synthesis of 2-amino-4H-benzo[h]chromenes.

the quantity 0.2 g of the nanocatalyst at 125°C under solvent free condition was selected for the optimized conditions. The model reaction in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, H<sub>2</sub>L and Mo-Schiff base complex under solvent free- conditions did not proceed well and very low yields of the product were obtained (Table 1, entry 10-12). These results indicates the rule of the immobilized catalyst in this reaction.

Finally, in order to study the efficiency of this method, we applied the optimized reaction condition to various aldehydes. As can be seen in Table 2, the satisfactory results have been obtained. All the applied aldehyde reacted with malononitrile

and 1-naphthol and it was observed good to excellent yields of products. The catalytic system in this method is comparable in some aspects such as stability, non-toxicity, easy and simple isolation and price with other systems.

To studied the reusability of the catalyst, after completion of the reaction the nanocatalyst easily isolated from the reaction media by magnetic decantation, washed with ethanol 3 times and water, dried and reused for at least 4 times. Recyclability of the catalyst without significant loss in catalytic activity shows great and practical recoverability (Fig. 9).

Table 1. Optimaization of the reaction conditions<sup>a</sup>

Entry	Catalyst(g)	Solvent	Time(h)	Yield <sup>b</sup> (%)
1	-	-	24	N.R
2	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @Mo-Schiff base	H <sub>2</sub> O	24	20
3	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @Mo-Schiff base	EtOH	24	36
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @Mo-Schiff base	MeOH	24	25
5	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @Mo-Schiff base	-	1	95
6	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @Mo-Schiff base (0.07 g)	-	1	80
7	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @Mo-Schiff base (0.1 g)	-	1	87
8	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @Mo-Schiff base (0.3 g)	-	50	95
9	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @Mo-Schiff base (0.4 g)	-	50	97
10	H <sub>2</sub> L	-	24	20
11	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	-	24	Trace
12	Mo-Schiff base	-	4	60
13	MoO <sub>2</sub> (acac) <sub>2</sub>	-	24	Trace

<sup>a</sup>Reaction conditions: 2-chlorobenzaldehyde (1 mmol) with malononitrile (1 mmol) and 1-naphthol(1 mmol) in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Mo-Schiff base as nanocatalyst (0.2 g).

<sup>b</sup>Isolated yield.

Table 2. Synthesis of 2-amino-4H-benzo[h]chromenes in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Mo-Schiff base (Fig. 8)<sup>a</sup>.

Entry	R	Time(min)	Yield(%) <sup>b</sup>	Mp(°C)(Obsd)	Mp(°C)(Ref.)
1	2-ClC <sub>6</sub> H <sub>4</sub>	60	95	162-164	161-163
2	4-ClC <sub>6</sub> H <sub>4</sub>	60	91	232-234	232-233
3	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	40	96	212-214	215-216
4	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	45	96	238-240	238-239
5	4-HOC <sub>6</sub> H <sub>4</sub>	45	90	246-249	247-249

<sup>a</sup>Reaction conditions: 2-chlorobenzaldehyde (1 mmol) with malononitrile (1 mmol) and 1-naphthol(1 mmol) in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@Mo-Schiff base as nanocatalyst (0.2 g) at 125°C under solvent-free conditions.

<sup>b</sup>Isolated yield.

## CONCLUSION

In conclusion, the covalent attachment of molybdenum Schiff base complex on the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was carried out and the structure of the prepared nanocatalyst was confirmed by FT-IR, ICP, VSM, TGA, EDS and SEM analyses. This synthesized nanocatalyst was utilized as an efficient catalyst for the synthesis of 2-amino-4H-benzo[h]chromenes. The reactions were performed under solvent free conditions. The notable advantages of the prepared nanocatalyst are easy isolation and recovery of nanocatalyst from the reaction mixture. Thus, this catalytic system was indicated green reaction conditions in the synthesis of 2-amino-4H-benzo[h]chromenes. This nanocatalyst can be reused in further catalytic runs without noticeable loss of its activity.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript

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