#### **ORIGINAL PAPER**



# Green protocol for synthesis of MgFe<sub>2</sub>O<sub>4</sub> nanoparticles and study of their activity as an efficient catalyst for the synthesis of chromene and pyran derivatives under ultrasound irradiation

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#### Abstract

In this study, the  $MgFe_2O_4$  nanoparticles were synthesized via a green and simple approach. Then an effective procedure to synthesize 2-amino-7-hydroxy-4*H*-chromene and tetrahydrobenzo[*b*]pyran derivatives was established through the chemical reaction between different aldehydes, malononitrile and resorcinol (or dimedone) in the presence of  $MgFe_2O_4$  nanoparticles as a beneficial catalyst in ethanol as solvent under ultrasound irradiation. Moreover, the synthesized  $MgFe_2O_4$  nanoparticles were easily recovered by an external magnet and reused for four times without significant loss of their catalytic activity. Simple, fast, effective and eco-friendly as well as quick purification method along with high product yields are some of the advantages of the present chemical reaction.

Keywords  $MgFe_2O_4 \cdot Chromene \cdot Pyran \cdot Ultrasound \cdot Green \cdot Nanoparticles$ 

# Introduction

Recently, spinel ferrites structures have attained great consideration due to their beneficial magnetic and electrical characteristics [1–3]. Their molecular formula is  $MFe_2O_4$ in which M is a divalent metal cation such as  $Mg^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , etc. In these inorganic compounds,  $M^{2+}$  and  $Fe^{3+}$  have been located in the tetrahedral and octahedral interstitial positions of the fcc lattice established by  $O^{2-}$  ions, respectively [4–7]. In recent years,  $MgFe_2O_4$  nanoparticles have attracted huge attention due to their vast benefits in industry such as being low magnetic materials [8, 9], gas sensors [10] semiconductors [11, 12], hyperthermia [13], lithium ion batteries [14, 15].

2-Amino-4*H*-chromenes are one of the most important family members of chromenes because of their usefulness

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Morteza Rouhani rouhani.morteza@gmail.com; morteza.rouhani@alumni.znu.ac.ir in medicinal scaffolds, particularly high spasmolytic, anticoagulant, diuretic and anti-anaphylactic properties [16–18]. Many of the current protocols for the synthesis of 2-amino-4H-chromenes [19, 20] suffer from factors such as long duration, lack of generality, use of perilous solvents and use of hazardous amine-based catalysts. Also, this problem still exists for synthesis of tetrahydrobenzo[b]pyran derivatives. The most popular approach for the synthesis of tetrahydrobenzo[b]pyrans derivatives includes the onepot reaction of aldehydes, dimedone and malononitrile under acidic or basic conditions [21]. However, most of the reported approaches have disadvantages such as harmful organic solvents, hazardous acidic condition, long reaction times, etc. [21]. On the other hand, the catalyst character is one of the most important factors which participate in the various features of a chemical reaction such as general applicability, yield, selectivity and duration. Therefore, exploring an efficient, inexpensive, reusable and easy accessible catalyst for synthesis of 2-amino-4H-chromenes is still an issue of interest.

Ultrasonic irradiation has found great applications in organic synthesis. Using ultrasound irradiation in various organic reactions has resulted in shorter reaction durations, higher yields and very milder reaction conditions [22, 23]. The collapse of cavities in the irradiated medium causes the formation of the hot spots with local temperatures and

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**Scheme 1** Synthesis of 2-amino-7-hydroxy-4*H*-chromene (5) and tetrahydrobenzo[*b*]pyran (6) derivatives with MgFe<sub>2</sub>O<sub>4</sub> nanoparticles as a catalyst in ethanol under ultrasonic irradiation

pressures to the extent of several hundred Celsius degrees and bars, respectively. This huge energy transfers to the present molecules in the reaction medium and considerably increases their inherent energy. Therefore, much more amounts of molecules can reach the minimum activation energy of the reaction. This phenomenon causes the considerable increase in the reaction rate and decreases the reaction time. Thus, using ultrasound irradiations, various organic reactions can be performed in shorter reaction time, with higher yield and under very calm conditions [24–26].

Herein, as a part of our continued interest in investigation about the effects of ultrasound irradiation on the multicomponent reactions [27–35], we wish to report an effective, simple and eco-friendly procedure for the synthesis of 2-amino-7-hydroxy-4*H*-chromenes and tetrahydrobenzo[*b*] pyrans with MgFe<sub>2</sub>O<sub>4</sub> nanoparticles as an efficient catalyst in ethanol under ultrasonic waves (Scheme 1).

# **Experimental**

#### **Chemical and apparatus**

All chemical reagents were purchased from commercial sources and utilized without further purification. All reactions were controlled by thin layer chromatography (TLC) established on pre-coated glass-backed plates Merck 60  $HF_{254}$  (0.25 mm) with UV light. Melting points were determined by Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra were recorded using a Shimadzu 8400 s FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured (CDCl<sub>3</sub> solution) with a Bruker DRX-500 Avance

spectrometer at 500 and 125 MHz, respectively. Sonication was performed in a Heisler ultrasonic bath (made in Germany) with a nominal power of 200 W. The catalyst sample was characterized using a scanning electron microscope (SEM) equipped with EDX detector (TESCAN Vega Model), at 30 kV with a gold coating. X-ray diffraction (XRD) analysis of the catalyst sample was performed with scanning range from 4° to 70° (Bruker D8 Advance, with Cu K $\alpha$  radiation,  $\lambda = 0.154060$  nm). Moreover, the ICP-AES (PerkinElmer, Optima 7300 DV), TGA (PerkinElmer, 4000), BET (Micromeritics Gemini 2375), VSM (Meghnatis Daghigh Kavir, LBKFB) and TEM (Zeiss-EM10C-100 kV) analyses were carried out for characterization of the synthesized MgFe<sub>2</sub>O<sub>4</sub> nanoparticles.

## Green procedure for the synthesis of MgFe<sub>2</sub>O<sub>4</sub> nanoparticles

For the synthesis of  $MgFe_2O_4$  nanoparticles, 0.2 g tragacanth gum was dissolved in 40 mL of double distilled water and stirred at 70 °C for 80 min. Then, 1 mmol of  $MgSO_4$ and 2 mmol Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O were added to the above-mentioned tragacanth clear solution and the resulting mixture was heated in 75 °C for 12 h to obtain a brown resin. Finally, the mixture was calcined at 600 °C in air to obtain  $MgFe_2O_4$ nanoparticles.

# General procedure for the synthesis of 2-amino-7-hydroxy-4H-chromene and tetrahydrobenzo[b]pyran derivatives under ultrasound irradiation

A mixture of aromatic aldehyde **1** (1 mmol), malononitrile **2** (1 mmol), resorcinol **3** or dimedone **4** (1 mmol) EtOH (5 ml) and MgFe<sub>2</sub>O<sub>4</sub> (0.003 g) was sonicated in a bath sonicator for the appropriate time. After the completion of the reaction (controlled by TLC), the MgFe<sub>2</sub>O<sub>4</sub> nanoparticles were separated by the external magnet and the solvent was evaporated. Finally, the remained solid product was purified with *n*-hexane/ethyl acetate in a PLC tank.

# Some spectroscopic data of the synthesized compounds

### 2-Amino-3-cyano-7-hydroxy-4-(2-fluorophenyl)-4H-chromene (5d)

M.p.: 216–218 °C; yield (85%); IR (KBr,  $v_{max}$  cm<sup>-1</sup>): 3431 (OH), 3225 (NH<sub>2</sub>), 2174 (CN), 1641 (C,C vinyl nitrile), 1556 (C,C aromatic); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ): 4.79 (s, 1H), 6.21 (d, 1H, Ar), 6.41 (dd, H), 6.62 (d, 1H, H-Ar), 6.88 (s, 2H, NH<sub>2</sub>), 7.11–7.24 (m, 4H, Ar) ppm; <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ): 55.15, 101.62, 111.14, 113.41,

114.02, 114.85, 120.10, 125.21, 128.14, 131.01, 131.54, 138.21, 149.11, 157.01, 158.85, 160.14 ppm.

# 2-Amino-3-cyano-7-hydroxy-4-(3-chlorophenyl)-4H-chrom ene (5f)

M.p.: 107–111 °C; yield (89%); IR ( $v_{max}$ , cm<sup>-1</sup>): 3423 (OH), 3342 (NH<sub>2</sub>), 2189 (CN), 1652 (C,C vinyl nitrile), 1579 (C,C aromatic); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ): 4.70 (s, 1H), 6.28 (d, 1H, Ar), 6.41 (dd, 1H, Ar), 6.59 (d, 1H, Ar), 6.89 (s, 2H, NH<sub>2</sub>), 7.01–7.32 (m, 4H, Ar), 9.71 (s, 1H, OH) ppm; <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ): 55.43, 101.56, 110.21, 114.47, 112.89, 120.85, 127.59, 130.12, 130.47, 132.16, 131.31, 132.02, 149.15, 149.22, 158.96, 160.14 ppm.

#### 2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**6a**)

M.p.: 229–231 °C; yield (86%); IR (KBr,  $\nu_{max}$ ): 1674 (C=O), 2185 (CN), 2952 (H-C<sub>sp3</sub>), 3254 (N–H), 3341 (N–H); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) 0.95 (s, 3H, CH<sub>3</sub>), 1.03 (s, 3H, CH<sub>3</sub>), 2.00 and 2.25 (2d, *J*=16.0 Hz, 2H, CH<sub>2</sub>), 2.47–2.52 (m, 2H, CH<sub>2</sub>), 4.17 (s, 1H, CH), 7.03 (s, 2H, NH<sub>2</sub>), 7.00–7.13 (m, 3H, 3CHAr), 7.28 (t, *J*=7.2 Hz, 2H, 2CHAr); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) 26.54, 27.45, 31.88, 38.87, 39.29, 50.02, 58.36, 112.78, 119.83, 126.66, 144.81, 155.55, 162.61, 195.81 ppm.

### 2-Amino-4-(3-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**6e**)

M.p.: 208–211 °C; yield (90%); IR (KBr,  $\nu$ max) 1665 (C=O), 2174 (CN), 3247 (N–H), 3365 (N–H) cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ) 0.95 (s, 3H, CH<sub>3</sub>), 1.02 (s, 3H, CH<sub>3</sub>), 2.07 and 2.23 (2d, J = 16.0 Hz, 2H, CH<sub>2</sub>), 2.43 and 2.50 (s, 2H, CH<sub>2</sub>), 3.70 (s, 3H, OCH<sub>3</sub>), 4.06 (s, 1H, CH), 6.90 (s, 2H, NH<sub>2</sub>), 6.49–6.94 (m, H, 4CHAr); <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ) 8: 26.64, 28.56, 31.79, 38.80, 39.29, 50.06, 55.58, 58.73, 113.03, 119.39, 119.93, 145.25, 158.34, 162.61, 197.21 ppm.

#### **Results and discussion**

#### Structural analysis of MgFe<sub>2</sub>O<sub>4</sub> nanocatalyst

Figure 1a shows the XRD pattern of the synthesized  $MgFe_2O_4$  nanoparticles. It can be seen that there is a high phase purity and good agreement with the existed XRD pattern for  $MgFe_2O_4$  nanoparticles (JCPDS No. 71-1232). Average crystalline size of the synthesized  $MgFe_2O_4$  nanoparticles was obtained to be 30–35 nm (determined by use

of the Scherrer equation) [35]. Furthermore, the crystallinity of the  $MgFe_2O_4$  nanoparticles has been preserved well after 4th cycle of usage (Fig. 1b).

The scanning electron microscopy (SEM) image affirmed the morphology and particle size of  $MgFe_2O_4$  nanoparticles (Fig. 2). As displayed in Fig. 2, the size of particles diameters is in the range of nanometers both in the fresh (a) and spent after 4th cycle of usage (b).

The energy-dispersive spectroscopy (EDX) revealed the elemental compositions of the MgFe<sub>2</sub>O<sub>4</sub> nanoparticles (Fig. 3). The EDX analysis affirmed the presence of O, Fe and Mg in the synthesized nanocatalyst. The quantification EDX analysis results demonstrate that the above-mentioned elements exist in expectable proportions in the synthesized MgFe<sub>2</sub>O<sub>4</sub> nanoparticles (Table 1).

The FT-IR spectrum of synthesized MgFe<sub>2</sub>O<sub>4</sub> nanoparticles demonstrates areas of the absorption between 4000-1000 and 1000-400 cm<sup>-1</sup>. The strong band of OH (3415 cm<sup>-1</sup>) shows that a vast number of OH groups are located on the surface of the MgFe<sub>2</sub>O<sub>4</sub> nanoparticles. At the range of 1000-400 cm<sup>-1</sup>, there are a high-frequency band in the ~613 cm<sup>-1</sup> and the low-frequency band in the ~434 cm<sup>-1</sup>. The high-frequency band is attributed to the stretching intrinsic vibration of unit cell of the spinel in the tetrahedral site, and the lower one is ascribed to the stretching vibration of Fe–O in octahedral site. Both of these peaks are the typical bands for spinel structure (Fig. 4).

Thermogravimetric analysis (TGA) is the evaluation of the mass change of a sample during temperature increase. This method is beneficial for studying of a decomposition reaction, specifying purity and organic content in a sample, etc. Figure 5 shows a TGA curve for dry sample of synthesized MgFe<sub>2</sub>O<sub>4</sub> nanoparticles. It can be seen that the TGA curve shows continues decline due to the weight loss by heating and decomposition of organic impurities. The net weight loss is found to be 96.90% in the temperature range studied.

The magnetic characteristics of the synthesized  $MgFe_2O_4$ were determined by a vibrating sample magnetometer (VSM). The magnetic hysteresis curve is demonstrated in Fig. 6. The recorded M–H loop shows that the synthesized sample was ferromagnetic. The saturation magnetization value was 8.56 emu/g. Also, the magnetic properties do not show considerable decline after 4th cycle of usage (Fig. 6).

Moreover, transmission electron microscopy (TEM) images show that  $MgFe_2O_4$  nanoparticles have spherical morphology and the average particles size is 36 nm (Fig. 7).

Table 2 shows the ICP-AES data both for the fresh and the used catalyst. The results show that there is no leaching of the metals happen during the reaction in the synthesized  $MgFe_2O_4$  catalyst. Also, the hot infiltration method was used and the presence of metals analyzed in the filtrate by ICP-AES analysis. The results in Table 2 show the absence of Mg



**Fig. 1** The XRD pattern of the **a** fresh and **b** spent after 4th cycle of usage  $MgFe_2O_4$  nanoparticles

and Fe in the filtrate obtained and approves the entire metal active sites during the reaction.

To confirm the catalyst efficiency of  $MgFe_2O_4$  nanoparticles, a reaction was also carried out in the absence of the catalyst and very low conversion was obtained. Furthermore, to see the effect of heterogeneous catalyst on the reaction, an experiment was done homogeneously as a reference using  $Mg^{2+}$  and Fe<sup>3+</sup> ions under the same ratio where very low and negligible reaction proceeded. All these observations confirm the catalytic role of  $MgFe_2O_4$  active sites in the catalyst.

We also studied the porous character of the MgFe<sub>2</sub>O<sub>4</sub> catalyst by evaluation of the nitrogen adsorption–desorption isotherm in Fig. 8. It shows the isotherm with a hysteresis loop between 0.8 and 1.0  $P/P_0$  which can be attributed

to the capillary type condensation of the nitrogen gas in the thin holes of the catalyst. The BET surface area and total pore volume for pores with diameter less than 145 nm at  $P/P_0 = 0.98$  of the synthesized MgFe<sub>2</sub>O<sub>4</sub> catalyst are  $10.5 \text{ m}^2 \text{ g}^{-1}$  and  $0.18 \text{ cm}^3 \text{ g}^{-1}$ , respectively, which demonstrate that synthesized catalyst has porous structure.

In order to achieve the optimum reaction conditions, the reaction of benzaldehyde, malononitrile and resorcinol under ultrasonic waves has been remarked as a model reaction.

### Study on the effects of the various solvents

In order to study the solvent effect on the reaction progress and also achieve the optimum solvent conditions for the Fig. 2 SEM images of the fresh a and spent after 4th cycle of usage  $b \text{ MgFe}_2O_4$  nanoparticles





Fig. 3 EDX graph of the **a** fresh and spent after 4th cycle of usage, **b** MgFe<sub>2</sub>O<sub>4</sub> nanoparticles

Table 1 The EDX analysis data for the synthesized  $\rm MgFe_2O_4$  nano-particles

Element	Weight percent	Atomic percent
Mg	12.14	12.85
Fe	52.36	26.48
0	35.49	66.67

reaction, the standard model reaction was carried out in the neat conditions (Table 3, entry 1) and also using various solvents, i.e., *n*-hexane,  $CH_3CN$ , THF, DMF and EtOH (Table 3, entry 2–6). Also, in order to reveal the ultrasound irradiation effects on the reaction conditions, the model reaction was performed in the classical stirring at room temperature. The best result was achieved by the reaction of benzaldehyde (1 mmol), malononitrile (1 mmol) and resorcinol (1 mmol) in EtOH by ultrasound irradiation (200 W, 10 kHz) in 30 min with 54% yield (Table 3, entry 6). The reaction did not proceed in neat conditions and in *n*-hexane as a solvent. Furthermore, applying polar aprotic solvents, i.e.,  $CH_3CN$ , THF and DMF afforded low yields of products (21%, 15% and 18%, respectively). Also, the results showed that the reaction under classical stirring conditions needs much more time for completion compared with sonic conditions (49% after 120 min). Based on the obtained results of this study, it is obvious that EtOH was the best solvent for this reaction.

### Comparison of ultrasonic irradiation frequency and reaction medium temperature

In order to investigate the effect of ultrasound irradiation frequency and reaction temperature, the standard model reaction was also carried out in 60, 70, 80, 90 and 100 kHz frequencies and at 45, 55, 65, 75 and 85 °C temperatures (Table 4). When the ultrasound frequency was 60 kHz, the yield of the product was 64% after 21 min (Table 4, entry 1). With the increase in irradiation frequency and temperature of the reaction medium from 60 to 80 kHz and from 45 to 65 °C, respectively, the reaction yields were improved from 64 to 74%. (Table 4, entries 1-3). Further increasing the ultrasound frequency and temperature caused the undesirable decrease in the product yield 68% and 52% (Table 4, entries 4 and 5). The precise assessment of the reasons of this phenomenon is to know the amounts of the activation energies. However, Safari et al. [24] have suggested that the rate of the reaction is very low at a temperature below 60 °C and at higher temperatures some sort of undesirable polymerization of the Knoevenagel condensation product might decrease the yield of the product. Therefore, the results demonstrated that the ultrasound irradiation frequency of 80 kHz, EtOH as a solvent and reaction temperature of 65 °C were the optimum conditions of the standard model reaction.

The effects of the ultrasound irradiation are due to cavitation phenomenon, the formation, growth and collapse of bubbles in an irradiated liquid [36]. Collapsing bubbles are produced, centralized "hot spots" with a temporary local high pressures and temperature are created, fastening the condensation reaction (such as Knoevenagel reaction in here). Also, sonication causes very efficient and vigorous stirring in reaction medium via improving the mass transfer and sever reaction mixture turbulence [37, 38]. All of these cases can cause the reaction to occur quickly. Now, we focus on the role of ultrasound waves in our study reaction. The proposed mechanism for the formation of products is presented in Scheme 2. On the basis of the chemistry of Knoevenagel under ultrasonic irradiation condition, it is sensible to presume that the first step may include condensation of aldehyde 1 and malononitrile 2 to produce the condensed product 3 (Knoevenagel condensation). This intermediate may be attacked by the resorcinol 4 (or dimedone 5) via a Michael addition to form 1:1:1 adduct (6 and 8). This adduct may undergo intramolecular cyclization to afford the isolated final product after a [1, 3] H-shift (7 and 9). These steps are



Fig. 4 FT-IR spectrum of the synthesized MgFe<sub>2</sub>O<sub>4</sub> nanoparticles



Fig. 5 TGA curve of the synthesized MgFe<sub>2</sub>O<sub>4</sub> nanoparticles

continuously done on the extent surface of catalyst and also in the presence of ultrasound irradiation. We believed that the passage of the ultrasonic waves through the reaction mixture plays a significant role in the Knoevenagel condensation and Michael addition steps due to the high local pressures, while one of these steps may be the rate-determining step in the reaction. Moreover,  $MgFe_2O_4$  nanoparticles as a Lewis acid probably interact with the oxygen atom in the carbonyl group of the aldehyde, and therefore, activates it for condensation with malononitrile in the Knoevenagel reaction. Furthermore,  $MgFe_2O_4$  activates cyanide group of the product (3) for attacking by resorcinol 4 (or dimedone 5) via a Michael addition and permits the reaction to be carried out effectively on its vast surface area. [27–29, 35].

# Generality of the synthesis under ultrasound irradiation

After finding more effective solvent (EtOH), temperature (65  $^{\circ}$ C) and frequency (80 kHz) for the standard model



Table 2 ICP-AES data for fresh and spent  $\rm MgFe_2O_4$  catalysts after 4th cycle

Element	Weight percent <sup>a</sup>	Weight percent <sup>b</sup>	Weight percent <sup>c</sup>
Mg	13.24	11.47	_
Fe	53.15	50.82	-

<sup>a</sup>Fresh catalyst

<sup>b</sup>Spent catalyst after 4th cycle

<sup>c</sup>After hot filtration

Fig.6 Magnetic hysteresis curve of the fresh (blue) and spent after 4th cycle of usage (red)  $MgFe_2O_4$  nanoparticles

reaction, the generality of the reaction was investigated by applying several substituted aldehydes with malononitrile and resorcinol (or dimedone) under ultrasonic irradiation (Table 5). As is mentioned earlier, the effect of ultrasound on the reaction is that it can significantly shorten the reaction time compared with classical conditions. It can be seen that the similar effects were also seen in our experiments. The obtained results in Table 5 demonstrate that ultrasound has more beneficial effects than classical stirring. Obviously, the lazy chemical reaction which was carried out under classical stirring in more longer duration (see Table 5, entry 7) was accelerated significantly along with higher yield (Table 5, entry 1). The corresponding 2-amino-7-hydroxy-4H-chromene (**5a**-**h**) and tetrahydrobenzo[*b*] pyran (**6a**-**h**) derivatives were formed in good-to-excellent yields. The results are summarized in Table 5.

# Comparison of the catalytic efficiency of MgFe<sub>2</sub>O<sub>4</sub> nanoparticles

Also, the efficiency of different catalysts in synthesis of 2-amino-7-hydroxy-4*H*-chromene and tetrahydrobenzo[*b*] pyran derivatives has been compared and summarized in Table 6. Entries 1–4 belong to 2-amino-7-hydroxy-4*H*-chromene derivatives and entries 5–8 belong to tetrahydrobenzo [*b*] pyran derivatives. The role of the MgFe<sub>2</sub>O<sub>4</sub>



Fig. 7 TEM images of the synthesized  $MgFe_2O_4$  nanoparticles



Fig. 8  $\,N_2$  adsorption–desorption isotherm of  $MgFe_2O_4$  nanoparticles

nanoparticles as catalyst was carried out by performing the model reaction (**5a** product) in the absence of it. It was observed that the **5a** product was produced in low 34% yield. It can be seen that the best yields in short reaction times can be attributed to the efficient synthetic  $MgFe_2O_4$  nanoparticles as catalyst.

 Table 3
 Optimization of the reaction solvent condition for the model reaction

Entry	Solvent	Method	Time (min)	Yield (%) <sup>a</sup>
1	_	US	30	_
2	<i>n</i> -Hexane	US	30	_
3	CH3CN	US	30	21
4	THF	US	30	15
5	DMF	US	30	18
6	EtOH	US	30	54
7	EtOH	Stirring	120	49

<sup>a</sup>Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol) and resorcinol (1 mmol); 5 mL solvent; and the ultrasonic power 200 W at room temperature in frequency of 10 kHz

#### Reusability of MgFe<sub>2</sub>O<sub>4</sub> nanoparticles

The recyclability of  $MgFe_2O_4$  nanocatalyst was studied. After completion of the reaction, the  $MgFe_2O_4$  nanoparticles were

Scheme 2 Proposed mechanism for the synthesis of 2-amino-7-hydroxy-4*H*-chromene (7) and tetrahydrobenzo[*b*]pyran (8) derivatives in the presence of MgFe<sub>2</sub>O<sub>4</sub> as a catalyst under ultrasound irradiation



 Table 4
 Optimization of the ultrasound irradiation frequency and reaction temperature for the model reaction

Entry	Temperature (°C)	Frequency (kHz)	Time (min)	Yield (%)a
1	45	60	21	64
2	55	70	16	69
3	65	80	12	74
4	75	90	10	68
5	85	100	8	52

separated with the external magnet and washed with extra acetone to remove the residual product. The nanocatalyst was reused for the new standard reaction of benzaldehyde, malon-onitrile and resorcinol under similar reaction conditions. The relation between the number of cycles of the reaction and the catalytic activity in terms of yield of the products is presented in Scheme 3. It was found that  $MgFe_2O_4$  nanocatalyst could be reused for 4 cycles with negligible loss of their activity.

Table 5Synthesis of 2-amino-7-hydroxy-4H-chromene(5a-h) and tetrahydrobenzo[b]pyran (6a-h) derivatives inthe presence of MgFe<sub>2</sub>O<sub>4</sub>nanoparticles as a catalyst underultrasound irradiation

Entry	Aldehyde	Product	Time (min)	Yield (%)	Melting point (°C, observed)	Melting point (°C, reported)
1	C <sub>6</sub> H <sub>5</sub>	5a	12	74	236–238	234–237 [24]
2	$2-MeOC_6H_4$	5b	14	79	223-226	222–224 [ <mark>24</mark> ]
3	2-MeC <sub>6</sub> H <sub>4</sub>	5c	14	76	228-231	226–229 [ <mark>24</mark> ]
4	2-F-C <sub>6</sub> H <sub>4</sub>	5d	11	85	216-218	218–221 [24]
5	$3-HOC_6H_4$	5e	15	81	215-218	215–217 [24]
6	$3-Cl-C_6H_4$	5f	11	89	107-111	106–109 [24]
7	4-MeOC <sub>6</sub> H <sub>4</sub>	5g	15	75	109–113	110–112 [24]
8	$4-MeC_6H_4$	5h	12	78	185–188	183–186 [24]
9	C <sub>6</sub> H <sub>5</sub>	6a	12	86	229-231	228–230 [39]
10	$2-ClC_6H_4$	6b	14	85	213-216	214–215 [39]
11	$2-NO_2C_6H_4$	6c	15	87	220-223	224–226 [39]
12	$3-ClC_6H_4$	6d	10	92	212-215	212–214 [39]
13	$3-MeOC_6H_4$	6e	13	90	208-211	208–210 [39]
14	$4-ClC_6H_4$	6f	11	90	212-213	210–212 [39]
15	$4-\text{MeC}_6\text{H}_4$	6g	12	89	220-224	223–225 [39]
16	$4-MeOC_6H_4$	6h	13	92	198–200	201–202 [39]

**Table 6** The comparison of<br/>catalytic activity of the synthetic<br/>MgFe2O4 nanoparticles (entry<br/>9) with some reported catalysts<br/>for synthesis of 2-amino-7-<br/>hydroxy-4H-chromene (entries<br/>1-4) and tetrahydrobenzo [b]<br/>pyran (entries 5–8) derivatives

Entry	Catalyst	Solvent	Time	Yield (%)
1	Na <sub>2</sub> SeO <sub>4</sub>	EtOH/H <sub>2</sub> O	0.75–3 h	80–98 [40]
2	TBAF	H <sub>2</sub> O	30-300 min	73–98 [41]
3	NaBr	-	10-15 min	60–95 [ <mark>42</mark> ]
4	TMAH <sup>a</sup>	H <sub>2</sub> O	0.5–2 h	79–93 [43]
5	2,2,2-Trifluoroethanol	Neat, reflux	4–5 h	81–90 [44]
6	[ADPPY][OH] <sup>b</sup>	EtOH	48 h	80-87 [45]
7	PhB(OH) <sub>2</sub>	EtOH/H <sub>2</sub> O, reflux	10–60 min	42–95 [46]
8	TTTA <sup>c</sup>	EtOH/reflux	10-30 min	57–90 [47]
9	-	EtOH,))), 65°C	12	34 (present work)
10	MgFe <sub>2</sub> O <sub>4</sub> nanoparticles	EtOH,))), 65 °C	10-15 min	74-92 (present work)

<sup>a</sup>Tetramethylammonium hydroxide

<sup>b</sup>4-Amino-1-(2,3-dihydroxypropyl) pyridinium hydroxide

<sup>c</sup>Triethylenetetraammonium trifluoro acetate



Scheme 3 Development of the yield after several recycling cycles of the catalyst

# Conclusion

In conclusion, we have introduced a novel, fast and efficient method for synthesis of a series of 2-amino-7-hydroxy-4*H*-chromene and tetrahydrobenzo[*b*] pyran derivatives in the presence of MgFe<sub>2</sub>O<sub>4</sub> nanoparticles as a catalyst under ultrasound irradiation. Moreover, MgFe<sub>2</sub>O<sub>4</sub> nanoparticles were synthesized through a green and eco-friendly approach by tragacanth gum. This sonochemical method has some benefits involving high yields, mild reactions, convenient approach and short reaction times, which turns it to an attractive synthetic approach for the synthesis of 2-amino-7-hydroxy-4*H*-chromene and tetrahydrobenzo[*b*] pyran derivatives.

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#### **Compliance with ethical statement**

Conflict of interest We have no conflicts of interest to declare.

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