1. Introduction

Recently mesoporous silica spheres include magnetic metal nanoparticles, have an attractive idea for chemistry researchers [1-3]. These nanocomposites have active surfaces area for use in various sciences. This nanostructure has the potential for use as the nanocatalyst [4-6], sensors [7, 8], nanoreactors [9], and drug delivery processes [10], gas filtration [11], and also as nano-sized quantum materials [12]. The large surface area of mesoporous silica was used in optical coatings and catalytic processes [13]. The bulk mesophase [14, 15] was managed the ratio between silica-to-surfactant and silica/surfactant self-assembly formation of cubic, hexagonal, and lamellar shape [16]. Recently, the heterogeneous nanocomposite was used in organic reaction to synthesis of different organic products [17, 18].

The chromenes compounds have notable biological attributes, [19-21] such as anticancer [22], antibacterial [23], anticonvulsant [24], antimicrobial [25], anti-influenza [26], antimalarial [27], and anti-virus activities [28]. Tetrahydro-4H-chromenes were used for the cure of counting Huntington’s disease [29] neurodegenerative illnesses [30], Alzheimer’s disease [31], Parkinson’s disease [32], and schizophre-
2. Experimental procedures

2.1. Materials and Instruments

All the solvents and starting materials that used in the reaction include benzaldehyde derivatives (97%-99%), cyclohexanone (98%), malononitrile (99%), and ethanol (99%), cetyltrimethylammonium bromide (CTAB) (100%), tetraethyl orthosilicate (TEOS) (97%), sodium hydroxide (NaOH) (99%), ferric (III) chloride (FeCl₃) (97%), nickel (II) chloride (NiCl₂) (98%), and sodium bicarbonate (95%), were obtained from Sinopharm Chemical. The organic products were recognized with ¹H NMR, FT-IR, and ¹³C NMR analyses. The ¹H NMR analysis was reported in CDCl₃ solvents using Bruker DRX-400 spectrometer, and the internal reference is tetramethylsilane. FT-IR spectra were reported with a Perkin-Elmer 550 spectrometers in the range of 400–4000 cm⁻¹. The crystal structure of nanocomposite (XRD) registered with (CuKa, radiation, λ = 0.154056 nm) that worked with a 15-kV accelerating voltage at the speed of 2° min⁻¹ starting from 10° to 80°(2θ). The solution was heated to dry the water at 85°C and production of the brown colored gel. At the end of the method, the product was dry at 800 °C for 3h.

2.2. General procedure for preparation of nano magnetic NiFe₂O₄

The nickel ferrite nanoparticles were provided during a sol-gel method [29]. To the accomplishment, the chemical formula NiFe₂O₄, 40 ml FeCl₃ 6 H₂O (4 M) was stirred with 40 ml NiCl₂ 2H₂O (2 M). Then, 1.5 g citric acid monohydrate was added (C₆H₈O₇.H₂O) to the reaction mixture. The pH of the mixture increased to 7.0 added a little ammonia-water (NH₃-H₂O) to the reactions. The solution was heated to dry the water at 85°C and production of the brown colored gel. At the end of the method, the product was dry at 800 °C to 3h.

2.3. Synthesis of NiFe₂O₄@mesopore silica

To provide an active base nanocatalyst, 5 mL NaOH 1 M, and 0.65 g of CTAB were dissolved in 100 mL deionized water and heated the mixture to 35 min at 100 °C. Then 0.1 g of NiFe₂O₄ nanocomposite was dispersed in 60 ml ethanol under sonicate irradiation. The obtained solution added to the reaction mixture. 2 ml TEOS was added to the reaction mixture two times after 15 and 40 min, the reaction mixture stirred at room temperature for 15 h at the end of the reaction the product collected by centrifuge and washed three times with water and ethanol, and dried at 70 °C for 24 h. The surfactant was removed from the nanocomposite by dispersed the product in ethanol (100 mL) and ammonium nitrate (50 mg) and stirred at 80 °C for 5 h. The product was separated by the centrifuge and dried at 100 °C for overnight.

2.4. Synthesis of NiFe₂O₄/mesopore silica anchored to guanidine nanocomposite

50.0 mg of NiFe₂O₄@mesopore silica was dispersed under ultrasonic irradiation in 10.0 mL toluene solvent for 30 min. Then 5mmol guanidinium chloride, 5 mmol 3-chloropropyltrimethoxysilane, and 2.5 mmol sodium bicarbonate in 10 mL dry toluene added to the reaction mixture then refluxed for 32 h. Then, the final product was separated by centrifuge and washed with water and ethanol. The product was dried at 80 °C under a nitrogen atmosphere (Scheme 1).

2.5. General multicomponent procedure for synthesis of 4H-chromene

4H-chromenes derivatives were synthesized in the three-component reaction. In this reaction, 1 mmol of malononitrile was reacted with 1 mmol of benzaldehyde at the presence of 10 mg of nanocatalyst. The reaction was followed under ultrasonic irradiation on the ethanol
solvent. After 5 min 1 mmol cyclohexanone was added to the reaction mixture, and the process was followed by thin-layer chromatography. The final product was separated with simple filtration and purification by recrystallization in the ethanol solvent. The final product identifies by the melting point, FT-IR, and $^1$H NMR spectra ($^1$HNMR and FT-IR data were placed in SI files).

3. Result and discussion

3.1. Preparation and characterization

The NiFe$_2$O$_4$ nanoparticles were synthesized and functionalized by mesopore silica and guanidine. At first, NiFe$_2$O$_4$ was provided by the sol-gel method [48]. The obtained NiFe$_2$O$_4$ was reacted by CTAB, NaOH, and TEOS at ambient temperature to NiFe$_2$O$_4$@mesopore silica. The obtained magnetic nanocomposites reacted by guanidine under the refluxed condition to NiFe$_2$O$_4$@mesopore silica@guanidine base nanocatalyst. The nanocomposite was distinguished by various analyses such as; SEM, EDX, XRD, FT-IR, BET, and VSM.

The XRD models were recorded of the crystal structure of NiFe$_2$O$_4$@mesopore silica@guanidine displayed in Fig. 1. The XRD pattern in Fig 1 shows the peaks (miller indices) in 30$^\circ$(220), 37$^\circ$(222), 45$^\circ$(400), 58$^\circ$(511), 62$^\circ$(440) and 73$^\circ$(533), regular XRD pattern of JCPDS card that due to the crystal structure of NiFe$_2$O$_4$ and the sharp peak in 22$^\circ$ due to amorphous mesopore silica.

Effective functionalization of the NiFe$_2$O$_4$@mesopore silica@guanidine catalyst can be explained through FT-IR spectra (Fig. 2). According to the FT-IR spectrum of the nanocomposite, the presence of a peak around 458 cm$^{-1}$ showed stretching vibration of Ni-O bonding; the peak of Fe-O looked near the 793 cm$^{-1}$; the NH$_2$ stretching bond displayed near 3391 cm$^{-1}$, and the peak of the Si-O stretching bond appeared around 1084 cm$^{-1}$.

The morphology and size of the nanocomposite were defined by the scanning electron microscopy analysis. The FE-SEM images of the NiFe$_2$O$_4$@mesopore silica@guanidine (Fig. 3) shown the extremely uniform morphology for the nanocomposite. Moreover, the average particle size of NiFe$_2$O$_4$@mesopore silica@guanidine was 77-85 nm.

The surface area and pore volume diameter of NiFe$_2$O$_4$@mesopore silica@guanidine were defined using the Brunauer–Emmett–Teller (BET) technique. According to the acquired curve, the measurement of surface area was equal to 233 m$^2$ g$^{-1}$, total pore volume 0.121 cm$^3$ g$^{-1}$ (Fig. 4).

Also, to characterize the percent of each element in the nanocomposite, it was studied elemental the energy-dispersive X-ray (EDS) spectrum. The EDS curve showed the percent of O, Si, Fe, Ni, and C were 24.1%, 32.9%, 1.8%, and 30.2%, respectively (Fig. 5).

Thermogravimetric analysis (TGA) curves (Fig. 6) of NiFe$_2$O$_4$@mesopore silica@guanidine shows that losses of 60 percent of weight under 800 °C in the models are due to the release of adsorbed water, solvent, and organic materials.

Scheme 2. Synthesis of various derivatives of 4H-chromene in the presence of NiFe$_2$O$_4$@mesopore silica@guanidine nanocatalyst.
Fig. 6. TGA curves for NiFeO$_4@$mesopore silica@ guanidine.

Fig. 7. FVSM curves for NiFeO$_4@$mesopore silica@ guanidine.

Fig. 8. The recyclability of NiFeO$_4$/mesopore silica/guanidine nanocatalyst in six runs.

Table 1. Investigation of catalyst, catalyst amount in ethanol solvents for the synthesis of 4H-chromenes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Catalyst amount (mg)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et$_3$N</td>
<td>10</td>
<td>3.5</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>MgO</td>
<td>10</td>
<td>2.5</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>Morpholine</td>
<td>10</td>
<td>0.95</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>Guanidine</td>
<td>10</td>
<td>0.75</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>NiFeO$_4$/mesopore silica/guanidine</td>
<td>10</td>
<td>0.75</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
<td>NiFeO$_4$/mesopore silica/guanidine</td>
<td>10</td>
<td>0.16</td>
<td>98</td>
</tr>
<tr>
<td>7</td>
<td>NiFeO$_4$/mesopore silica/guanidine</td>
<td>5</td>
<td>0.16</td>
<td>83</td>
</tr>
<tr>
<td>8</td>
<td>NiFeO$_4$/mesopore silica/guanidine</td>
<td>15</td>
<td>0.16</td>
<td>90</td>
</tr>
</tbody>
</table>

a Reaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), cyclohexanone (1 mmol), 5 ml solvent.

b Isolated yield

Scheme 3. Proposed reaction mechanism for the Synthesis of 4H-chromene.
The magnetic properties of NiFe$_2$O$_4$@mesopore silica@ guanidine nanocomposite were recorded by the vibrating sample magnetometry (VSM) spectra of the nanocomposite. The magnetization curve of nano-composite shown superparamagnetic properties (Fig. 7).

According to the TGA and EDX analyzed, the percent of organic materials was 60%, and mesopore silica around 30%. So, the percent of NiFe$_2$O$_4$ is around 10% in the nanocatalyst structure. Because the low percent of NiFe$_2$O$_4$ and covered with two-layer of mesopore silica and guanidine compound. The MS of the catalyst was decreased, but it has superparamagnetic properties and adsorbed with an external magnet.

The synthetic reaction of 4H-chromenes from benzaldehyde, cyclohexanone, and malononitrile was optimized by various solvents, catalysts, and temperatures.

The reaction was studied by utilizing different catalysts such as morpholine, Et$_3$N, MgO, and NiFe$_2$O$_4$/mesopore silica/guanidine in the ethanol solvents. The results of the study were exhibited in Table 1.

The results were displayed NiFe$_2$O$_4$/mesopore silica/guanidine (Table 1, Entry 5) and have the best yields of product in the short reaction time. The model reaction was tested in different solvents and the result showed in Table 2.

Ultrasound irradiation was constructed as the motive energy for the improved yield of 4H-chromenes, that due to the increased temperature correlated to the production of hot spots. While the reaction was carried out without sonic irradiation in low yield and long reaction time (Table 3, entry 1). The best power for the reaction was acquired 45 W based on product yield and reaction time (Table 3, entry 5).

After optimization of the model reaction for the synthesis of 4h-chromene (4a-g), 1 mmol of benzaldehyde (1a-g), 1 mmol of malononitrile (2), and 1 mmol of cyclohexanone (3) were mixed in ethanol solvent and 5 mg NiFe$_2$O$_4$/mesopore silica/guanidine added to the mixture as the base nanocatalyst. The reaction was done under 45 power ultrasonic irradiation (Scheme 2) (Table 4).

### Table 2.
Investigation of solvent for the synthesis of 4H-chromenes *

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>$T_{\circ}C$</th>
<th>Time (h)</th>
<th>Yield * (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetonitrile</td>
<td>25</td>
<td>0.75</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Chloroform</td>
<td>25</td>
<td>0.92</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Ethanol</td>
<td>75</td>
<td>0.16</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>Methanol</td>
<td>25</td>
<td>0.75</td>
<td>90</td>
</tr>
</tbody>
</table>

* Reaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), cyclohexanone (1 mmol), 5 ml solvent.

### Table 3.
Several Power for the ultrasonic multicomponent reaction for synthesis of bis-ortho-aminocarbonitrile tetrahydronaphthalene 4a *

<table>
<thead>
<tr>
<th>Entry</th>
<th>Power (W)</th>
<th>Time (min)</th>
<th>Yield * (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silent</td>
<td>180</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>60</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>50</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>35</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>10</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>30</td>
<td>96</td>
</tr>
</tbody>
</table>

* Reaction conditions: Benzaldehyde (1 mmol), Cyclohexanone (1 mmol), Malononitrile (1 mmol), 5 ml Solvent.

The mechanism of the reaction for the production of 4H-chromenes

<table>
<thead>
<tr>
<th>4a-l</th>
<th>Yield %</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a: X= H, Y= H, 98, 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4b: X= Br, Y= H, 95, 15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4c: X= NO$_2$, Y= H, 96, 16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4d: X= F, Y= H, 92, 17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4e: X= N,N dimethyl, Y= H, 93, 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4f: X= Cl, Y= H, 91, 18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Reaction conditions: benzaldehyde (1 mmol), cyclohexanone (1 mmol), malononitrile (1 mmol), 0.1mmol nanocatalyst (5 mg), ethanol solvent (5ml), 45 power ultrasonic irradiation.

* Isolated yield
included various steps, at the first step, benzaldehyde and malononitrile reacted under Michael addition and formation the intermediate A under the nanomagnetic base NiFe$_2$O$_4$/mesopore silica/guanidine nanocatalyst. Then the cyclohexanone under condensation reaction joins to the intermediate A and formation intermediate B. The process followed by a cyclization reaction, the 4H-chromene (4a) compounds synthesis by absorption of the hydrogen, and double bonds rearrangement (Scheme 3).

3.2. Catalytic comparisons

To display the efficiency and influence of new methods for the synthesis of 4H-chromene derivatives, the obtained results were compared with the other methods, catalysts, and conditions (Table 5). As can be seen, the present study with different methods for added the starting material, nanocatalyst, and using ultrasonic irradiation is superior in yield of pure products and short reaction times.

3.3. Reusability

The reusability and nanocomposite are important advantages for commercial utilization. The reusability of NiFe$_2$O$_4$/mesopore silica/guanidine nanocatalyst, was tested in six runs of the model reaction, and the results reported in Fig 8.

4. Conclusion

In this study, it was functionalized the NiFe$_2$O$_4$/mesopore silica with the guanidine compound. The mesopore silica has a large area for functionalization on the surface and pore. The reaction of benzaldehyde, malononitrile, and cyclohexanone as the model reaction was selected by used NiFe$_2$O$_4$/mesopore silica/guanidine as a nanocatalyst in the excellent yields and short reaction times. The nanocomposite identified by FT-IR, SEM, XRD, VSM, BET techniques, and the organic products recognized by the melting point, $^1$H NMR, and FT-IR analyses.

Supporting Information

Experimental details, copies of $^1$H and FT-IR and of products is available free of charge via the Internet here.

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Conflict of interest

The authors declare that there is no conflict of interest.

REFERENCES


