

A Novel Biopolymer-based Nanomagnetic Catalyst for the Synthesis of 4*H*-pyran and Tetrahydro-4*H*-chromene Derivatives

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ABSTRACT

In the present study, we have designed and synthesized a new magnetically recoverable, nanocatalyst of Ag/Fe₃O₄@starch. The successful synthesis and the structure of the nanocatalyst were confirmed and evaluated with several analytical techniques including XRD, EDX, VSM, FT-IR, TEM and TGA. The impact and efficiency of Ag/Fe₃O₄@starch were successfully investigated in the one-pot synthesis of desired 4*H*-pyrans and tetrahydro-4*H*-chromenes using three-component condensation of various aldehydes, malononitrile, and 1,3-diketesters or cyclic 1,3-diketones. The magnetic nanocatalyst was easily recovered and reused with high catalytic activity even after up to five runs.

KEYWORDS

Green synthesis, nanomagnetic, reusable nanocatalyst, starch, 4*H*-pyrans, tetrahydro-4*H*-chromenes.

1. Introduction

Green chemistry is a developing field of sustainable sciences and technologies that aids in the use of renewable feedstock as sustainable resources. Biopolymers such as starch, chitosan and cellulose, are extracted from biomass and have recyclability and reusability comparable with traditional synthetic polymers.¹ Among these green polymers, starch is well known because of its abundance and low cost when extracted from agricultural products.² One of the applications of native starch is as a sizing agent; however, further modifications can change its properties to be used as a film-forming agent owing to its outstanding coating property.³ Starch may be commercially obtained from numerous vegetal feedstock (seeds, roots and tubers) such as cornstarch, arrowroot, tapioca, wheat, rice and potato. In recent years, starch has achieved great attention as green and inexpensive support, stabilizer and reducing agent in the synthesis of metal nanoparticles.⁴ It is excellent in forming metal complexes due to the numerous hydroxyl groups present within the starch structure, allowing for control of size, shape, and dispersivity of metal nanoparticles in starch. Various reports have been made in the literature regarding the starch-stabilized synthesis of nanoparticles, such as silver,⁵ gold⁶ and palladium.⁷

The use of magnetic nanoparticles (MNPs) has recently become important because of their potential use in medicinal fields, catalysis, microfluidics, biomedicine, magnetic resonance imaging, and data storage.⁸ Fe₃O₄ MNPs have been employed as an outstanding solid catalyst in organic processes,⁹ due to their high surface area, easy synthesis and handling, simple recoverability, oxidative stability and nontoxicity. Fe₃O₄ MNPs can be synthesized by several methods, although co-precipitation is the most common technique.¹⁰ In this technique, MNPs are prepared using Fe(II) and Fe(III) ions in basic solution under an inert atmosphere.

The polyfunctionalized 4*H*-pyran and tetrahydro-4*H*-chro-

me moieties are among significant heterocyclic compounds that contain oxygen atoms, that exhibit the broad range of biological activities such as antimicrobial, anticarcinogen, a blood thinner, anti-anaphylactic anti-Parkinson, and anti-Alzheimer properties.¹¹

4*H*-pyran and tetrahydro-4*H*-chromene derivatives can be synthesized with a three-component process of aldehydes, malononitrile and a compound with an active methylene group, 1,3-diketesters or cyclic 1,3-diketones, under several conditions in the presence of a wide range of catalysts.¹²

As part of our ongoing attempts at using biopolymer-based catalysts,¹³ in this work, it was shown that silver supported on Fe₃O₄/starch nanocomposite (Ag/Fe₃O₄@starch), significantly improves the catalytic performance in a three-component reaction of cyclic 1,3-diketones/1,3-diketesters, aldehydes, and malononitrile in respect of synthesizing tetrahydro-4*H*-chromene derivatives. The prepared catalysts were investigated with X-ray diffraction (XRD), energy-dispersive X-ray spectrometry (EDX), vibrating sample magnetometry (VSM), Fourier-transform infrared (FT-IR) spectrometry, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) techniques. The successful nanocatalyst preparation was confirmed. Furthermore, different starting materials were used to evaluate the efficiency of the synthesized nanocatalysts and high yields were obtained. The reusability, as a substantial factor in catalyst design, was investigated for the prepared nanocatalyst. The nanocatalysts were reused in five cycles with no significant activity loss observed.

2. Experimental

2.1. Materials and Methods

All chemical materials needed were purchased from Acros, Fluka and Merck companies and no further purification processes were carried out on any of the chemicals. Thin-layer chromatography (TLC) silica gel on an aluminium plate was used to monitor the progress of the reactions. A Philip Harris

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C4954718 apparatus was applied for melting point measurements with no data correction. Infrared, ^1H NMR and ^{13}C NMR spectra of the synthesized materials were obtained with Thermo Nicolet Nexus 670 FT-IR spectrophotometer and Bruker Avance AQS 300 MHz spectrometer, respectively. DMSO- d_6 and TMS were used as a solvent and internal standard in NMR spectra recording respectively. XRD patterns were achieved with a JEOL JDX-8030 (30 kV, 20 mA). TGA and DTA thermograms were obtained with STA504 instrument. Magnetic properties of the nanocomposites were evaluated using a Lake Shore VSM 7410. Isolation and identification of the products were accomplished by comparing the obtained spectral data with reliable samples. TEM analysis was provided with an instrument CM30, Philips.

2.2. Cross-linking of Starch

2 g of Starch was dissolved in water (50 mL). Citric acid (0.4 g) and sodium hypophosphite (0.2 g) were added. The obtained dispersion was heated up to 90 °C under reflux conditions for 2 h. The mixture was cooled down to room temperature, and the precipitate was filtered and dried for one day in the oven at 40–50 °C. Finally, the product was crushed and powdered followed by washing with cold water several times. The resultant cross-linked starch was dried in an oven at 40–50 °C.

2.3. Preparation of Magnetic Ag/Fe₃O₄@starch Nano Biocomposites

The cross-linked starch (1 g) and 50 mL of water were mixed and the resultant mixture was warmed up to 80 °C until the starch had gelatinized. The heated starch solution was cooled down to room temperature. Then, 2.3 g of FeCl₃·6H₂O and 0.75 g of FeSO₄·7H₂O were dissolved in 25 mL water under vigorous agitation at room temperature. Thereafter, the solution was mixed drop by drop with the prepared gelatin starch for 10 min and the mixture was stirred at 80 °C. Then, NH₃ (25 %, 10 mL) was slowly added to the prepared solution and the resultant Fe₃O₄@starch was obtained by filtration after 20 min, following by rinsing with distilled water. The resultant product was dried and powdered. 1 g of powder was mixed in 35 mL water and 10 mL of 0.05 M AgNO₃ (aq.) was added. The resultant mixture was stirred at 90 °C for 30 min. Finally, the magnetic Ag/Fe₃O₄@starch nanocatalyst was rinsed several times using water and dried at 80 °C in an oven.

2.4. General Procedure for the Synthesis of 4H-pyran and Tetrahydro-4H-chromene Derivatives 4a–t

A mixture of aldehydes (1 mmol), malononitrile (1 mmol) and cyclic 1,3-diketones/1,3-diketoesters (1 mmol), and Ag/Fe₃O₄@starch (15 mg) in EtOH (5 mL) was warmed up to 50 °C over an appropriate time. The progress of the reaction was followed by TLC. The obtained mixture was cooled to room temperature and the solid material was filtered off and dissolved in hot EtOH. The catalyst was removed using a bar magnet and the precipitate was separated and crystallized from EtOH to give the desired products 4a–t in 84–95 % yield.

Spectral Data for Selected Compounds

2-Amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4k): white solid; 87 % (229 mg); M.p. 238–240 °C; IR ν_{max} : 3349, 3201 (NH₂), 2955, 2194 (CN), 1685 (C=O) cm⁻¹; δ_{H} (300 MHz, DMSO- d_6): 1.91–2.12 (2H, m, CH₂), 2.25–2.43 (2H, m, CH₂), 2.51–2.74 (2H, m, CH₂), 4.21 (1H, s, CH), 6.85 (2H, s, NH₂), 7.01–7.49 (5H, m, ArH) ppm; δ_{C} (75.5 MHz, DMSO- d_6): 20.66, 27.59, 36.49, 37.35, 58.93, 113.99, 120.46, 127.19, 127.69, 128.74, 145.46, 159.27, 165.50, 196.75.

2-Amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4H-chromene-3-carbonitrile (4p): light yellow solid; 92 % (270 mg); M.p. 229–231 °C; IR ν_{max} : 3394, 3323 (NH₂), 2963, 2882, 2198 (CN), 1661 (C=O) cm⁻¹; δ_{H} (300 MHz, DMSO- d_6): 0.94 (3H, s, CH₃), 1.02 (3H, s, CH₃), 2.05–2.21 (2H, m, CH₂), 2.57 (2H, s, CH₂), 4.16 (1H, s, CH), 6.87 (2H, s, NH₂), 6.75–6.97 (3H, m, ArH), 6.98–7.26 (2H, m, ArH) ppm; δ_{C} (75.5 MHz, DMSO- d_6): 27.51, 31.81, 34.78, 38.96, 49.67, 58.28, 112.70, 119.71, 127.29, 128.16, 129.32, 144.78, 158.51, 162.46, 195.63 ppm.

3. Results and Discussion

3.1. FT-IR Spectroscopy

The FT-IR spectroscopy was used to study and confirm the successful preparation of the cross-linked starch and nanoparticle loaded magnetic nanocatalysts. In this respect, cross-linked and non-cross-linked starch are presented in Fig. 1a, and Fig. 1b, respectively.

The two spectra have similar FT-IR pattern, except the peak in the cross-linked starch at 1736 cm⁻¹, which is related to the carboxyl and ester carbonyl bands. Fig. 1c, shows the FT-IR spectrum of Fe₃O₄@starch. The appearance of a peak at 576 cm⁻¹ corresponds to O-Fe bond vibration. Addition of AgNO₃ to a hot aqueous mixture of magnetic nanocomposite resulted in Fe₃O₄@starch stabilized silver, Ag/Fe₃O₄@starch via reduction of silver ions by hydroxyl groups in starch. The structural changes because of the interaction between Fe₃O₄@starch and silver species were studied by using FT-IR spectra (Fig. 1d). The shift at 3415 and 1635 cm⁻¹ bands (Fig. 1c) to a lower wavelength at 3393 and 1631 cm⁻¹ in the presence of Ag (Fig. 1d) was possibly due to the coordination of Ag with the hydroxyl groups in Fe₃O₄@starch.

3.2. XRD Spectroscopy

To investigate the structure of synthesized nanocatalyst, XRD was used. Fig. 2, shows the XRD pattern of Ag/Fe₃O₄@starch.

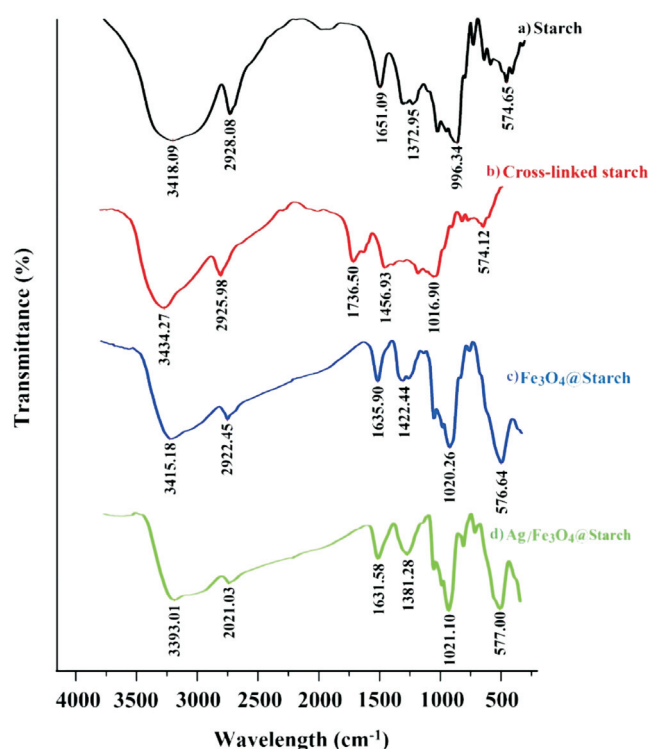


Figure 1 Near FT-IR spectra of potato starch (a), cross-linked starch (b), Fe₃O₄@starch (c) and Ag/Fe₃O₄@starch (d).

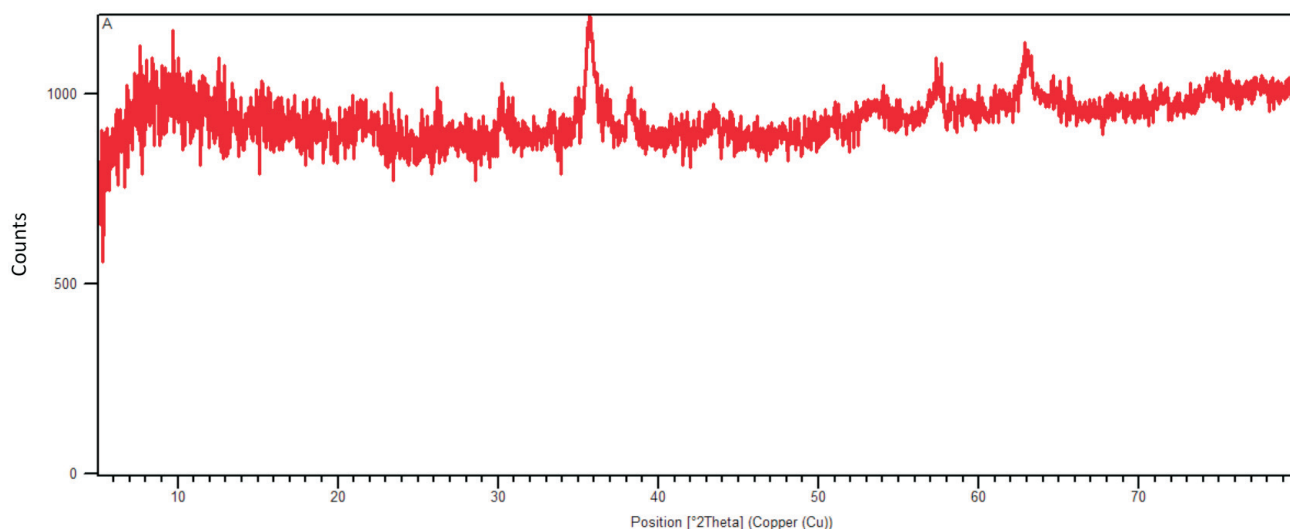


Figure 2 XRD pattern of Ag/Fe₃O₄@starch nanocomposite.

The peaks at $2\theta = 35.7^\circ$ and 62.9° were assigned to the Fe₃O₄ nanoparticles and the peaks at $2\theta = 38.2^\circ$ and 43° were attributed to highly crystalline silver nanoparticles.

3.3. TEM Analysis

TEM analysis was used to study the existence and dispersion of nanoparticle within the structure of the nanocatalyst. The TEM image of Ag/Fe₃O₄@starch confirmed the existence of the nanoparticles in the starch with a diameter below 10 nm (Fig. 3). Also, good dispersity and monodispersity of nanoparticles in the starch matrix are shown in this TEM image.

3.4. TGA Analysis

The thermal stability of Ag/Fe₃O₄@starch was examined *via* TGA. TGA analysis of the Ag/Fe₃O₄@starch nanocomposite is shown in Fig. 4. Minor weight loss 30–130 °C was assigned to the loss of adsorbed water (4.7 %). The large weight loss between 250 and 600 °C was owing to the decomposition of starch (52.3 %). The TGA/DTA curve of the Ag/Fe₃O₄@starch as shown in Fig. 4; indicates the removal of adsorbed water and organic solvents.

3.5. EDX Analysis

EDX analysis was performed for the elemental analysis of Ag/Fe₃O₄@starch. The patterns (Fig. 5) showed that the nano-

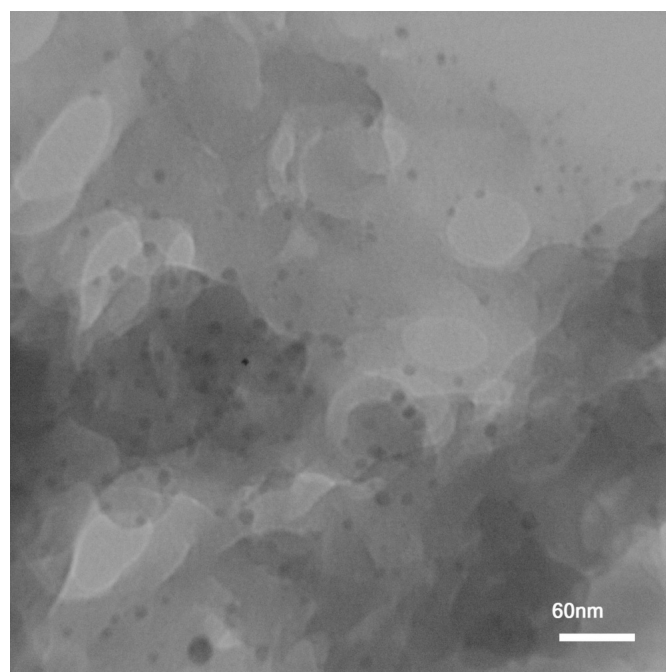


Figure 3 TEM image of Ag/Fe₃O₄@starch.

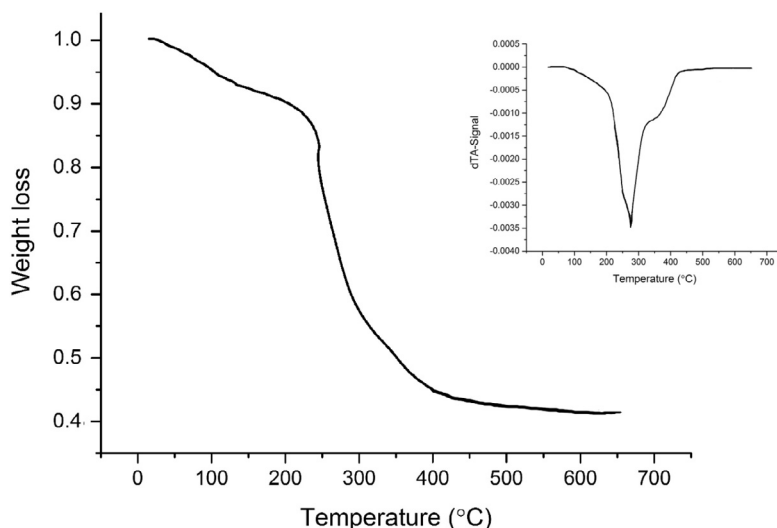


Figure 4 TGA of Ag/Fe₃O₄@starch.

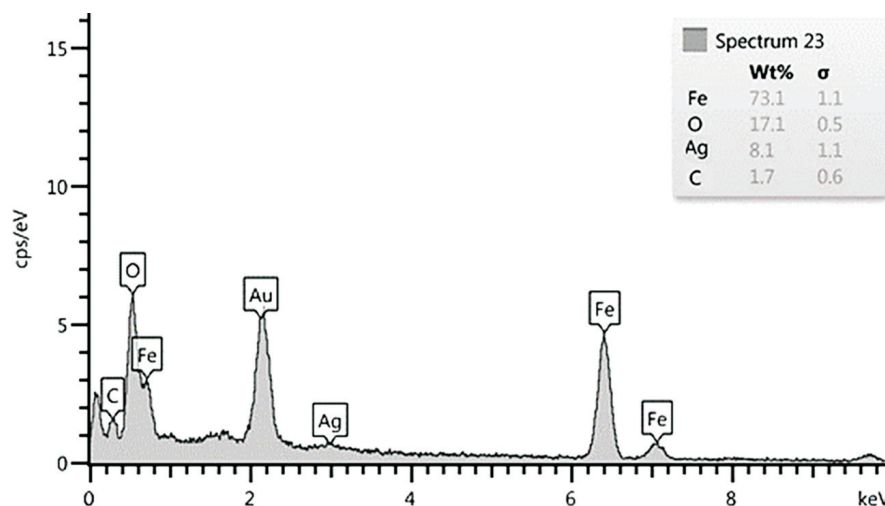


Figure 5 EDX spectrum of Ag/Fe₃O₄@starch nanocomposite.

composite contains Fe, Ag, O and C, which was well-matched with elements of the precursors. The loading of silver supported on the starch was found to be 5.2 wt. % based on the results gained from the atomic absorption spectroscopy.

3.6. VSM Analysis

Ag/Fe₃O₄@starch were simply attracted to an external magnet which showed the formation of magnetic NPs. In addition to the aforementioned simple test, the magnetic property of the Ag/Fe₃O₄@starch was measured by a VSM at room temperature (Fig. 6). The saturation magnetization (M_s) and the coercivity (H_c) of Ag/Fe₃O₄@starch were about 22.37 emu g⁻¹ and 6.3 Oe, respectively. The ease in separation and recycling of Ag/Fe₃O₄@starch used as a catalyst in the reaction was owing to the obtained high magnetic saturation.

3.7. Using of the Nanocatalyst in the 4H-pyrans and Tetrahydro-4H-chromenes Synthesis

The catalytic activity of Ag/Fe₃O₄@starch for the formation of 4H-pyrans and tetrahydro-4H-chromenes was evaluated. In a preliminary investigation, the one-pot, three-component reaction of benzaldehyde (1a), malononitrile (2) and dimedone (3d) in a molar ratio (1:1:1) in absence of any catalyst did not lead to

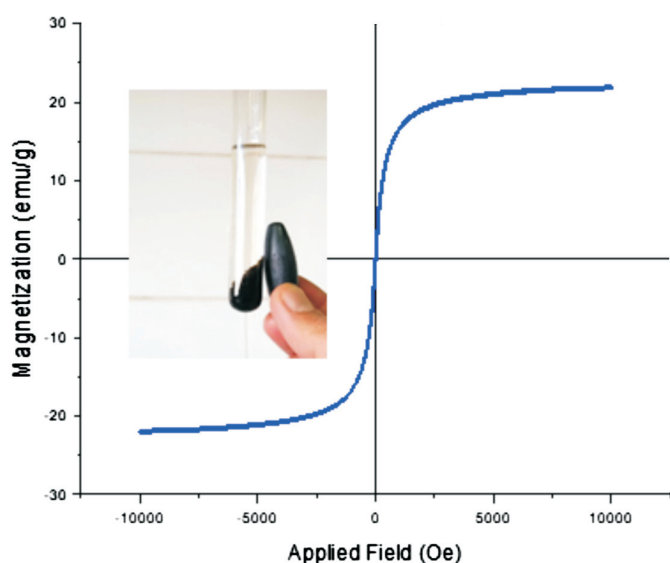


Figure 6 Magnetization hysteresis curve of Ag/Fe₃O₄@starch.

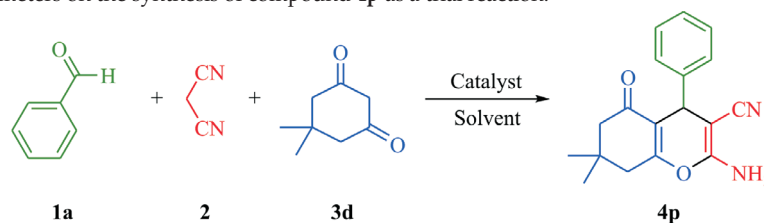
the desired product **4p** and even increasing the reaction times did not improve the yield (Table 1, entry 1). Several, tests were conducted to optimize the reaction conditions including solvent (CHCl₃, EtOH, H₂O and H₂O/EtOH) and the catalyst (starch, Fe₃O₄@starch, Ag@starch, and Ag/Fe₃O₄@starch), all parameters of which are summarized in Table 1. To optimize the reaction temperature, the model reaction was carried out at different temperatures ranging from room temperature to 80 °C. Moreover, it was observed that, in the presence of starch, Fe₃O₄@starch, or Ag@starch up to 79 % yield of compound **4p** was achieved after 10 min (Table 1, entries 2–4). The maximum yield (95 %) was in the presence of Ag/Fe₃O₄@starch 20 mg and ethanol as solvent at 50 °C in 10 min (Table 1, entry 16).

To evaluate catalyst loading in the model reaction, the procedure was optimized using Ag/Fe₃O₄@starch which afford the product at a range of trace-95 % yield (Table 1, entries 11–17). High yields (92 %) of product **4p** was achieved using 15 mg of Ag/Fe₃O₄@starch as a nanocatalyst in EtOH after 10 min of reaction time (Table 1, entry 15).

In contrast, low amounts of catalyst led to moderate outcomes of the product at longer reaction times; also, using larger amounts of Ag/Fe₃O₄@starch had no significant effect on the yields (Table 1, entry 15 *vs* entry 16). The yield plateaued when the temperature was further increased to 80 °C. Therefore, the most suitable reaction temperature is 50 °C. These results showed that Ag/Fe₃O₄@starch is an essential agent in promoting the reaction.

After optimizing the reaction conditions, this sustainable protocol was next successfully tested in producing **4a–t** in high to excellent yields (84 to 95 %) and short reaction times (9–17 min) in EtOH, by employing of a series of different aldehydes, 1,3-diketoesters [such as methyl acetoacetate (**3a**) and ethyl acetoacetate (**3b**)] or cyclic 1,3-diketones [such as cyclohexane-1,3-dione (**3c**) and dimedone (**3d**)] and malononitrile. Upon, completion of the reaction, the nanocatalyst was simply recovered by an external magnet, washed with ethanol, and reused directly with fresh reagents under the same conditions without the loss of activity. A summary of the experimental details including the substrate, product, reaction times, melting point, and yield of all target compounds are listed in Table 2. Moreover, the melting points were compared to the known products reported in the literature.

The proposed mechanism of reaction shows the influence of the nanocatalyst on the formation of products as illustrated in Scheme 1. The Knoevenagel condensation of activated aryl

Table 1 Effect of different parameters on the synthesis of compound **4p** as a trial reaction.^a

Entry	Catalyst/mg	Solvent	Temperature/°C	Time/min	Yield ^b /%
1	–	EtOH	50	10	–
2	Starch (20)	EtOH	50	10	Trace
3	Fe ₃ O ₄ @starch (20)	EtOH	50	10	30
4	Ag@starch (20)	EtOH	50	10	79
5	Ag/Fe ₃ O ₄ @starch (20)	–	RT	10	–
6	Ag/Fe ₃ O ₄ @starch (20)	–	80	20	–
7	Ag/Fe ₃ O ₄ @starch (20)	H ₂ O	80	10	–
8	Ag/Fe ₃ O ₄ @starch (20)	CHCl ₃	50	10	88
9	Ag/Fe ₃ O ₄ @starch (20)	CH ₃ CN	50	10	50
10	Ag/Fe ₃ O ₄ @starch (20)	H ₂ O/EtOH	60	30	25
11	Ag/Fe ₃ O ₄ @starch (1)	EtOH	50	10	Trace
12	Ag/Fe ₃ O ₄ @starch (5)	EtOH	50	10	61
13	Ag/Fe ₃ O ₄ @starch (8)	EtOH	50	10	70
14	Ag/Fe ₃ O ₄ @starch (10)	EtOH	50	10	78
15	Ag/Fe₃O₄@starch (15)	EtOH	50	10	92
16	Ag/Fe ₃ O ₄ @starch (20)	EtOH	50	10	95
17	Ag/Fe ₃ O ₄ @starch (30)	EtOH	50	10	88

^a Reaction was performed with benzaldehyde (**1a**, 1 mmol), malononitrile (**2**, 1 mmol), dimedone (**3d**, 1 mmol), and catalyst.

^b Isolated yield.

‘–’ indicates no reaction. RT: room temperature. The bold type (entry 15) refers to the best reaction conditions.

aldehydes **1** with malononitrile (**2**) form intermediate cyano-olefines **I**. The Michael type addition of activated 1,3-diketones or cyclic 1,3-diketones **3** to the intermediate **I** give the intermediate **II**, which intramolecular cyclization produce the final products **4**. In this method, Ag/Fe₃O₄@starch plays a crucial role in accelerating all stage of the reaction.

The behaviour, usefulness, and capability of Ag/Fe₃O₄@starch system for the formation of product **4p** were highlighted by a comparison of the results obtained with other reported systems, as shown in Table 3. As is evident from Table 3, our procedure in the presence of Ag/Fe₃O₄@starch as a nanocatalyst shows a greater or comparable efficiency such as short reaction times, using cheap and eco-friendly materials, and also simple magnetic recoverability compared with the other systems in the literature.

3.8. Catalyst Recycling

Furthermore, the recoverability of Ag/Fe₃O₄@starch as a key factor of a catalytic system was also studied for the synthesis of product **4p**. To this end, the catalyst was simply separated from the reaction mixture using an external magnet, recovered and reused for up to five sequential runs with an average efficiency of 90 % without any loss of activity (Fig. 7).

4. Conclusions

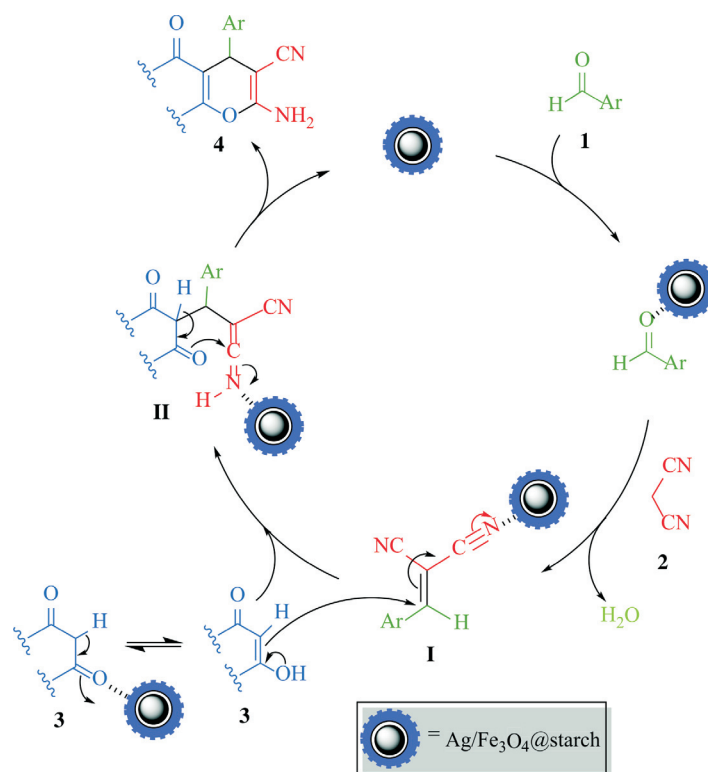
In this study, Ag/Fe₃O₄@starch was synthesized and used as a magnetic nanocatalyst, and it was characterized by XRD, EDX, VSM, FT-IR, TEM and TGA. Also, to examine the application of the nanocatalyst, it was used as a heterogeneous nanocatalyst for one-pot synthesis of 4H-pyrans and tetrahydro-4H-chromenes with 84–95 % substance yields, that are frequently applied as pharmacologically and biologically active products, *via* a three-component condensation of aryl aldehydes, malononitrile and 1,3-diketones or cyclic 1,3-diketones in the presence of ethanol at 50 °C. The prepared magnetic nanocatalyst was separated from the reaction mixture by a bar magnet, demonstrating its use as a recyclable nanocatalyst. Some of the considerable advantages of this inexpensive, new catalyst, are its low loading, simple recoverability, short reaction times, and high yields of the products resulting in an efficient and environmentally friendly procedure.

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Scheme 1

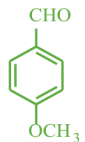
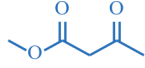
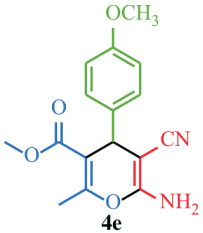

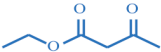
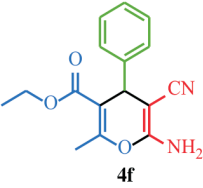
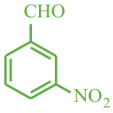
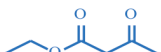
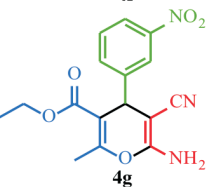
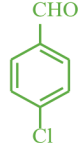
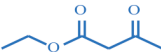
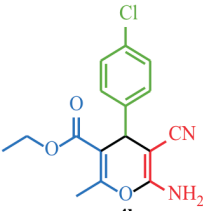
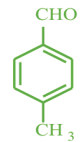
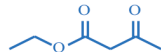
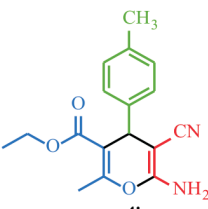
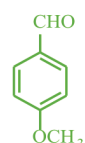
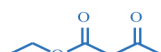
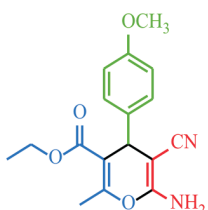
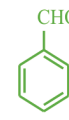
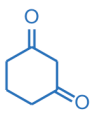
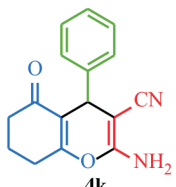
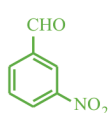
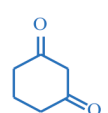
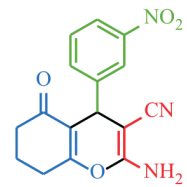
A plausible mechanistic pathway for the formation of final products in the presence of magnetic nanocatalyst.

Table 2 The reaction condition, yields and melting points of products 4a–t.

Entry	Aryl aldehydes	1,3-Diketoesters / Cyclic 1,3-diketones	Products	Time/min	Yield ^b /%	M _p /°C Observed	Reported
1				14	87	170–173	172–173 ¹⁴
2				16	90	212–214	212–213 ¹⁵
3				17	89	171–173	172–173 ¹⁵
4				13	84	173–175	174–175 ¹⁵

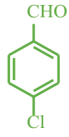
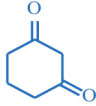
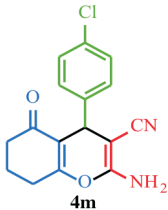
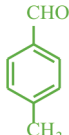
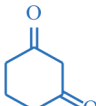
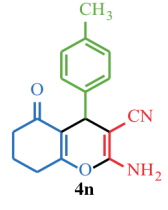
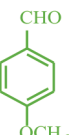
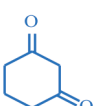
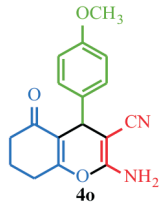
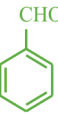
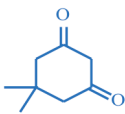
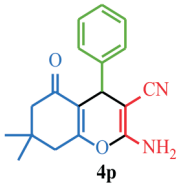
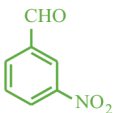
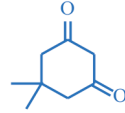
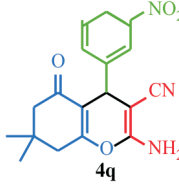
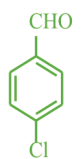
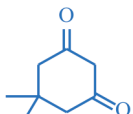
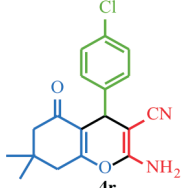
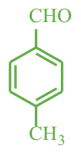
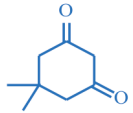
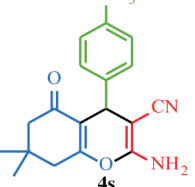
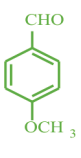
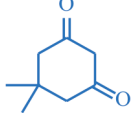
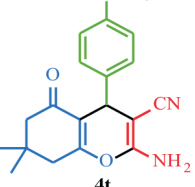
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Table 2 (continued)

Entry	Aryl aldehydes	1,3-Diketoesters / Cyclic 1,3-diketones	Products	Time/min	Yield ^b /%	M.p/ ^o C Observed	Reported
5			 4e	15	91	149–152	149–150 ¹⁵
6			 4f	9	90	194–196	193–195 ¹⁶
7			 4g	11	91	183–186	183–185 ¹⁷
8			 4h	8	95	172–174	173–175 ¹⁶
9			 4i	15	91	180–183	180–182 ¹⁶
10			 4j	16	86	139–142	140–142 ¹⁶
11			 4k	10	87	238–240	239–241 ¹⁶
12			 4l	12	92	202–205	201–202 ¹⁸

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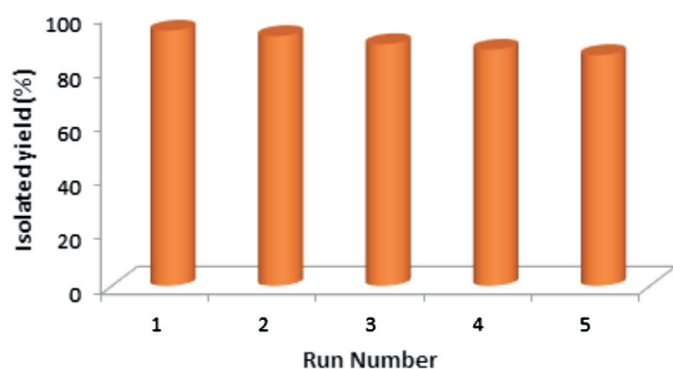
Table 2 (continued)

Entry	Aryl aldehydes	1,3-Diketoesters / Cyclic 1,3-diketones	Products	Time/min	Yield ^b /%	M.p/ ^c °C Observed	Reported
13			 4m	9	89	226–228	226–229 ¹⁶
14			 4n	14	86	213–215	214–216 ¹⁶
15			 4o	13	87	194–197	193–195 ¹⁶
16			 4p	11	92	230–232	228–230 ¹⁶
17			 4q	10	94	210–212	212–214 ¹⁸
18			 4r	12	91	208–211	207–209 ¹⁶
19			 4s	13	87	222–225	223–225 ¹⁶
20			 4t	15	88	201–203	201–202 ¹⁶

^a Reaction condition: aryl aldehyde (1 mmol), malononitrile (1 mmol) and 1,3-diketoester or cyclic 1,3-diketone (1 mmol) in 5 mL of ethanol at 50 °C in the presence of 15 mg of nanocatalyst. ^b Yields refer to isolated pure products.

Table 3 Comparison of the activity of different catalysts in the literature to the synthesis of 4p.

Entry	Catalyst	Temp	Time /°C	Yield/% /min	Ref.
1	MgO	RT	10	75	[19]
2	Nano-SiO ₂	70	8	94	[20]
3	Palladium nanoparticles	Reflux	5 h	87	[21]
4	NH ₄ Al(SO ₄) ₂ ·12H ₂ O	80	120	92	[22]
5	BF ₃ OEt ₂	Reflux	120	85–90	[23]
6	Fructose	40	45	86	[24]
7	Fe ₃ O ₄ @g-C ₃ N ₄	60–80	60	97	[25]
8	α-Zr(KPO ₄) ₂	60	120	93	[26]
9	γ-Al ₂ O ₃	50	10 h	95	[27]
10	ZnO	RT	240	86	[28]
11	Ag/Fe ₃ O ₄ @starch	50	11	92	This work

**Figure 7** Reusability of nanocatalyst in the synthesis of compound 4p.

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