A novel poly(ethyleneoxide)-based magnetic nanocomposite catalyst for highly efficient multicomponent synthesis of pyran derivatives

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ABSTRACT
In the present work, a new magnetically recyclable nanocomposite catalyst was designed, prepared, and characterized by Fourier transform infrared (FT-IR) spectroscopy, field-emission scanning electron microscopy (FE-SEM) images, X-ray diffraction (XRD) pattern, energy-dispersive X-ray (EDX), vibrating sample magnetometer (VSM), and transmission electron microscopy (TEM) analyses. Then, the catalytic activity of the prepared Fe3O4/PEO/SO3H nanocatalyst was examined on multicomponent synthesis of 2-amino-3-cyano-4H-pyranes. Short reaction time, room temperature, good-to-excellent yields, easy catalyst separation and catalyst reusability, environmentally benign and efficient conditions are some advantages of this green protocol.

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1. Introduction
Multicomponent reactions (MCRs) are that involve at least three reactants, which combined in the one-step process and generate a product that involves ideally whole parts of starting reactants. In compared with classical methods, MCRs have many merits that make them a valuable method to substitute. Atom economy, less use of solvents, low cost, low energy and time using are some advantages of MCRs. Therefore, these types of reactions can be an effective strategy to approaching green and sustainable protocols (1).

Catalysts are an important part of a chemical process. One common classification of catalyst divides them into two general fields: the homogeneous and heterogeneous catalysts according to compare their active sites phase with reactants phase. Both have their own advantages and disadvantages. Nanocatalysts are heterogeneous catalysts with a high surface to volume ratio due to their size, and accordingly more catalytic sites can efficiently interact with components in the reaction mixture and they can be separated from a reaction mixture and recycled thereby they have advantages of both heterogeneous and homogeneous catalysts at the same time. Applying nanocatalyst to MCRs helps to approach a green route for the synthesis of complex and diverse molecules (2). As it is told before, nanocatalysts are separable from the reaction mixture but separation of them by conventional methods failed due to their nanoscale size. Using magnetic nanocatalysts provides an easily separation way by an external magnetic field (3) and solve the problem. Magnetic nanocatalysts can be recovered efficiently and reused in reactions and are green catalysts (4).

Heterocycles are an important class of molecules with wide variety. Most of them are biological active molecules. 2-Amino-4H-pyran derivatives are one of the
important heterocyclic compounds with various biological and pharmaceutical activities such as antitumor, antibacterial, antiviral, antiallergic, spasmyloytic, diuretic, anti-coagulant, and anti-anaphylactic. In addition, these compounds are used in the treatment of Alzheimer, Schizophrenia, and Mycolonous diseases (5–8). Furthermore, they are building blocks of some natural products (9–13). 2-Amino-4H-pyrans are also useful as photoactive materials (14,15). MCR between an aryl aldehyde, malononitriles, and 1,3-dicarbonyl compounds that produce 2-amino-4H-pyrans is widely studied. Some examples of the catalysts used for synthesis are molecular iodine (16), Ammonia solution (17), Urea (5), MgO (6), Mg/La (18), SiO₂ (19), SnCl₂/nano-SiO₂ (20), Cu(II) oxymetasilicate (21), KF-Al₂O₃ (22), ionic liquids like [2-aemim][PF₆] (23), C₄(DABCO-SO₃H)₂.4Cl (24), and chitosan-CTAB (25). Most of published reports in the literature suffer from disadvantages such as high temperature, non-recyclable catalyst and long reaction time, use of volatile solvent and tedious work-up procedures. Therefore, still finding an efficient method for green synthesis of 4H-pyrans seems necessary.

Fe₃O₄ magnetic nanoparticles (MNPs) were applied in reactions as catalyst or core of magnetic catalysts (26–33). Magnetic nanoparticles can easily agglomerate and it decreases their reachable active sites. Modification of their surface like coating overcomes this problem (2). Various materials are used for coating MNPs (34). Cellulose (29), SiO₂ (35, 36), triethylamine (37), chitosan (27, 38, 39) are some of examples. Poly(ethylene oxide) (PEO) is a nontoxic, chemically stable, inexpensive, and affordable material used for coating MNPs (40). PEO has many hydroxyl groups that make it hydrophilic and soluble in water; therefore, it can be used in green synthesis methods.

Sulfated catalyst has been recently studied widely. Because, grafting of sulfonic acid groups to heterogeneous magnetic nanocatalysts provides recyclable solid acid catalysts that can apply efficiently in numerous organic reactions (32, 41, 42).

Scheme 1. Synthesis of 2-amino-4H-pyrans by using Fe₃O₄/PEO/SO₃H nanocatalyst.
Due to inconvenient reported methods and in continuation of our interest in the application of new catalysts in organic synthesis to obtain green procedures (27, 29, 36, 38, 43–46), a novel magnetic nanocomposite, polyethylene oxide-coated ferrite-sulfonic acid, Fe₃O₄/PEO/SO₃H, is prepared and used as catalyst in three-component reaction of aryl aldehydes 1, malononitrile 2, and ethyl acetoacetate 3 for the synthesis of 2-amino-4H-pyran derivatives 4 (scheme 1). To the best of our knowledge, this is the first time that Fe₃O₄/PEO/SO₃H has been synthesized and applied as a catalyst in this three-component reaction.

2. Result and discussion
2.1. Characterization of the prepared Fe₃O₄@PEO-SO₃H nanocatalyst

As can be seen in Figure 1, FT-IR spectra of sulfonated modified magnetite nanocatalyst, Fe₃O₄@PEO-SO₃H, PEO modified, Fe₃O₄@PEO, unmodified, Fe₃O₄ and PEO were clearly shown, for Fe₃O₄@PEO-SO₃H, the strong broad peaks at about 594 and 1631 cm⁻¹ are due to the bending and stretching vibration bands of Fe–O bonds, respectively. The bands around 2862, 2927, and 955 cm⁻¹ correspond to CH₂ stretching vibrations and CH out-of-plane bending vibrations, respectively. Absorption bands at 1095 and 1193 cm⁻¹ are related to S=O stretching vibrations that approved the functionalization of SO₃H groups on Fe₃O₄@PEO surface. As a consequence from the FT-IR spectra, a broad O–H stretch around 3440 cm⁻¹ was observed in the PEO-coated MNPs as well as the C–H and S=O peaks are strong evidences that PEO-SO₃H was successfully coated onto the surface of Fe₃O₄ nanoparticles.

2.2. Morphological study

As shown in Figure 2, the morphology of obtained nanocatalyst was investigated by SEM and TEM images. The images indicate that the obtained Fe₃O₄@PEO-SO₃H is composed of spherical nanoparticles with average grain size 35 nm. It can be seen that the nanocatalyst was uniformly prepared and the main structure of nanocatalyst along with the spherical ferrite nanoparticles. Therefore, the nanosized structure and morphology of the catalyst was proved by SEM and TEM images.

2.3. EDX study

The surface composition of Fe₃O₄@PEO-SO₃H magnetic nanoparticles was qualitatively determined by energy-
dispersive X-ray (EDX) that shows the presence of Fe, C, O, and S elements by their peaks (Figure 3). It is therefore assumed that PEO is coated onto the surface of Fe3O4 nanoparticles and also SO3H functionalizing of nanocatalyst was taken place.

2.4. X-ray study

Figure 4 clearly shows the X-ray diffraction (XRD) pattern of Fe3O4@PEO-SO3H with the dried powder samples to identify the crystal phases present in the samples. The XRD pattern of a representative Fe3O4@PEO-SO3H along with bare Fe3O4 NPs showed all the major peaks corresponding to Fe3O4. The diffraction angles (2θ) of 30.28, 35.64, 43.28, 57.24, 62.87, and 74.42 can be assigned to 220, 311, 400, 511, 440, and 533 planes, respectively, which are in accordance with Fe3O4 reference pattern (JCPDS#19–0629).

In conclusion, these results implied that the spinal structure of Fe3O4 in duration preparation and the surface modification of the Fe3O4 NPs with PEO-SO3H have been retained.

2.5. Magnetic study

Figure 5(a)–(c) represents magnetic field-dependent magnetization parameters, M (H) for Fe3O4, Fe3O4@PEO, and Fe3O4@PEO-SO3H, using vibrating sample magnetometer curves at room temperature. The hysteresis loops for above coated and uncoated nanoparticles with coercivity (Hc = 0.0 Oe) and remanence (Mr = 0) indicate a superparamagnetism properties with a saturation magnetization of 56, 38 and 27 emu g⁻¹ for Fe3O4, Fe3O4@PEO and Fe3O4@PEO-SO3H respectively. The lower values for coated and functionalized nanoparticle than that of neat Fe3O4 confirmed the successful surface coating of Fe3O4 nanoparticles.

2.6. Application of Fe3O4/PEO/SO3H in the synthesis of 2-amino-4H-pyran

To optimize the reaction conditions, 4-chlorobenzaldehyde (1 mmol = 0.14 g) was chosen as a substrate. Thus its reaction with malononitrile and ethyl acetoacetate was subjected to the synthesis of pyran derivatives. In this regard, various parameters were studied in the presence of PEO, Fe3O4@PEO and Fe3O4@PEO-SO3H as catalysts in different solvents. It has been known that the reaction temperature has a significant effect on the
reaction rate and product selectivity. On the other hand, the catalytic activity is greatly efficient at room temperature. As the results are summarized in Table 1, we have provided various effects with above preliminary consideration. First, the effect of the catalyst amount on the reaction yield was investigated using (0.005, 0.007, 0.008 and 0.01 g) of Fe$_3$O$_4$@PEO-SO$_3$H. The results revealed that using 0.008 g of the nanocatalyst is adequate to complete the reaction and give 4b after 25 min in 95% yield in 4 mL of EtOH as a green solvent at room temperature and a higher amount of catalyst did not have any effect on the completion of the reaction or improve the yield. To study the solvent effect and comparing the efficiency of ethanol, the model reaction was performed in several solvents with different polarities in the presence Fe$_3$O$_4$@PEO-SO$_3$H. As shown,

| Entry | Catalyst (g) | Solvent | Temperature (°C) | Time (min) | Yield (%) |
|-------|--------------|---------|------------------|------------|-----------|
| 1     | –            | EtOH    | Reflux           | 240        | 50        |
| 2     | 0.005        | EtOH    | r.t.             | 25         | 75        |
| 3     | 0.007        | EtOH    | r.t.             | 25         | 89        |
| 4     | 0.008        | EtOH    | r.t.             | 25         | 95        |
| 5     | 0.01         | EtOH    | r.t.             | 25         | 95        |
| 6     | 0.008        | EtOH    | r.t.             | 35         | 95        |
| 7     | 0.008        | EtOH    | Reflux           | 30         | 95        |
| 8     | 0.008        | H$_2$O  | r.t.             | 60         | 80        |
| 9     | 0.008        | H$_2$O/ EtOH | r.t.   | 30         | 87        |
| 10    | 0.008        | CH$_3$CN | r.t.             | 30         | 88        |
| 11    | 0.008        | CH$_3$OH | r.t.             | 30         | 85        |
| 12    | 0.008        | –       | r.t.             | 70         | 82        |
| 13    | 0.01         | –       | r.t.             | 70         | 85        |
| 14    | 0.015        | –       | reflux           | 70         | 89        |

$^a$Isolated yield.

Figure 4. The XRD patterns of Fe$_3$O$_4$@PEO-SO$_3$H composite nanocatalyst. The symbol ‘*’ represents the PEO-SO$_3$H peak.

Figure 5. VSM magnetization curves of (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$@PEO, and (c) Fe$_3$O$_4$@PEO-SO$_3$H.

Table 1. Optimizing of the reaction conditions in the synthesis of 4b.
ethanol due to the relatively good solubility of the catalyst and starting materials was the superior solvent in the presence of 0.010 g of Fe3O4@PEO-SO3H catalyst at room temperature. The results are summarized in Table 1. As shown in Table 2, a comparison was done between the nanocatalyst and its components for the synthesis of 4b. The results clearly demonstrate the superiority of the nanocatalyst over its component. Then these conditions were taken onto the synthesis of other derivatives to determine catalyst applicability (Table 3).

The experimental procedure is very simple, convenient, and has the ability to tolerate a variety of other functional groups such as methoxy, nitro, hydroxyl, and halides under the reaction conditions. Thus in order to examine the generality of this nanocatalyst, Fe3O4@PEO-SO3H, for the synthesis of pyran derivatives as well as investigation of the scope and limitations of the present protocol, a variety of products were synthesized under the optimized conditions. A ratio of 1:1:1 mixture of 4-chlorobenzaldehyde, malononitrile, ethyl acetocacetate acetate and 0.008 g of nanocatalyst in 4 mL absolute ethanol is a choice green solvent leading to high yields of products at room temperature. The results shown in Table 3 indicated that both electron rich and electron deficient aldehydes worked well and undergo this condensation reaction. Electron-withdrawing substituents give the products with higher yields in shorter reaction times than electron-donating substituents. For example, 4-chlorobenzaldehyde gave higher yield than 4-methoxybenzaldehyde. The structure of the corresponding products can be seen in Scheme 1.

To investigate the effect of molecular weight on the intrinsic properties of the nanocatalyst, two different low and high molecular weight PEOs were applied (MW = 400 that briefly represented PEG and MW = 900,000 represented PEO). Both of their prepared nanocatalysts were used on the model reaction. Evaluation of the parameters such as temperature, amount of catalyst, reaction time, stability, and reusability of catalyst under different circumstances gave notable and interesting results. When PEO was used instead of PEG, the efficiency of the reaction was improved. Therefore, due to the advantages of PEO, it was selected as a surface modifier of MNPs and further studies in this work.

### 2.7. Catalyst recycling

The reusability of the catalyst was studied in the model reaction. In this regard, after completion of the reaction, the catalyst was separated by an external magnet, washed with ethanol and water, dried and reused in the next runs. It was observed that the catalyst can be reused at least six times without any significant decrease in yield of the products (Figure 6). These results were confirmed by FT-IR spectrum of reused catalyst after six runs that clearly indicated, the prepared catalyst, Fe3O4@PEO-SO3H, was highly stable (Figure 7).

### 3. Conclusion

In summary, Fe3O4@PEO-SO3H as an eco-friendly and reusable superparamagnetic nanocatalyst was synthesized through a facile process and characterized completely by FT-IR spectroscopy, SEM images, XRD pattern, and EDX and VSM analyses. Furthermore, a green, efficient, and environmentally benign multicomponent

### Table 2. Synthesis of 2-amino-4H-pyrans derivatives using Fe3O4@PEO-SO3H nanocatalyst.

| Entry | Ar          | R      | Product | Time (min) | Yield (%) | Observed  | Reported  |
|-------|-------------|--------|---------|------------|-----------|-----------|-----------|
| 1     | Benzaldehyde| C6H5   | 4a      | 35         | 88        | 190–192   | 195–196   |
| 2     | 4-Chlorobenzaldehyde| C6H5     | 4b      | 20         | 95        | 174–175   | 171–172   |
| 3     | 4-Methylbenzaldehyde| C6H5 | 4c      | 35         | 88        | 174–176   | 177–179   |
| 4     | 4-Bromobenzaldehyde| C6H5     | 4d      | 30         | 93        | 178–179   | 175–176   |
| 5     | 4-Methoxybenzaldehyde| C6H5     | 4e      | 40         | 84        | 151–153   | 142–144   |
| 6     | 3-Hydroxybenzaldehyde| C6H5     | 4f      | 40         | 85        | 168–169   | 164–165   |
| 7     | 3-Nitrobenzaldehyde| C6H5     | 4g      | 25         | 93        | 186–187   | 182–184   |
| 8     | 4-Nitrobenzaldehyde| C6H5     | 4h      | 25         | 92        | 180–181   | 175–176   |
| 9     | 4-Nitrobenzaldehyde| CH3       | 4i      | 25         | 91        | 174–176   | 170–172   |
| 10    | Benzaldehyde  | CH3    | 4j      | 35         | 83        | 157–158   | 158–160   |
| 11    | 3-Nitrobenzaldehyde| CH3     | 4k      | 25         | 91        | 197–198   | 204–206   |
| 12    | 4-Methoxybenzaldehyde| CH3     | 4l      | 40         | 85        | 161–163   | 158–160   |

*Isolated yield.

### Table 3. Comparison of catalysts and its components effects on the model reaction.

| Entry | Catalyst | Temperature (°C) | Time (min) | Yield (%) |
|-------|----------|------------------|------------|-----------|
| 1     | PEO      | Reflux           | 70         | 35        |
| 2     | PEO-SO3H | Reflux           | 70         | 50        |
| 3     | Nano-Fe3O4 | r.t.     | 70         | 76        |
| 4     | Nano-Fe3O4@PEO | r.t.  | 70         | 84        |
| 5     | Nano-Fe3O4@PEO-SO3H | r.t. | 15         | 95        |
| 6     |        | Reflux           | 240        | 50        |

*Isolated yield.
synthesis of 2-amino-4H-pyran via a novel magnetic nanocatalyst was represented at room temperature under mild reaction conditions. Several advantages of this method include high yields of the products, use of ethanol as a green solvent, short reaction times, inexpensive reagents, simple isolation of the products, and the compatibility and versatility toward various functional groups such as methoxy, nitro, hydroxyl, and halides make this procedure very efficient and convenient. Simple separation, easy recovery by an external magnet, stability and reusability for several runs without significant loss of activity make it a highly efficient and attractive nanocatalyst. As far as we know, this is the first report on design, in situ synthesis, functionalization, and characterization of the present nanocomposite and also its performance as a heterogeneous catalyst in the synthesis of pyran derivatives. Green inexpensive reusable catalyst, short reaction times, green solvent, ease of catalyst separation, simple work-up procedure, good-to-excellent yields, room temperature, and mild conditions are advantages of the presented work.

4. Experimental

4.1. General

All the solvents, chemicals, and reagents were purchased from Merck, Sigma, and Aldrich. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Fourier transforms infrared spectroscopy (FT-IR) spectra were recorded on a Shimadzu IR-470 spectrometer using KBr pellet. 1H and 13C NMR spectra were recorded on a Bruker DRX-300 Avance spectrometer at 300 and 75 MHz, respectively. Scanning electron micrograph (SEM) images were taken with VEGA-TESCAN. Magnetic measurements of the solid samples were performed using a Lakeshore 7407 vibrating sample magnetometer (VSM). Elemental analysis of the nanocatalyst was carried out by energy-dispersive X-ray (EDX) analysis recorded on a Numerix DXP-X10P. XRD patterns of the solid powders were recorded with an X’Pert Pro X-ray diffractometer operating at 40 mA, 40 kV. Transmission electron microscopy (TEM) images were recorded using a Zeiss-EM10C TEM.

4.1.1. Preparation of Fe3O4/PEO

Fe3O4/PEO nanoparticles were prepared via in situ coprecipitation method. In a typical procedure, 2.4 g FeCl3 and 3.0 g FeCl2·5H2O solved in 100 mL of deionized water. Then, 0.8 g of PEO-900000 was mixed with 10 mL of NH3·H2O at 30°C in a three-necked flask. Then, the mixture of FeCl3 and FeCl2·5H2O was added in NH3-PEG solution during 150 min at 30°C. The obtained Fe3O4/PEO precipitate was washed with deionized water until pH was reached to 7. Finally, it was dried at 80°C in an oven.

4.1.2. Preparation of Fe3O4/PEO/SO3H

A 500-mL suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution of alkali trap. Fe3O4/PEO (2.0 g) was added to the flask and dispersed by an ultrasonic bath for 10 min in CH2Cl2 (75 mL). Then, a solution of chlorosulfonic acid (1 mL) in CH2Cl2 (20 mL) was added dropwise over a period of 30 min at 0°C. After completion of the addition, the mixture was shacked for 90 min to remove residual HCl. After that Fe3O4/PEO/SO3H was separated from the reaction mixture by a magnetic bar and washed several times with dry CH2Cl2. Finally, Fe3O4/PEO-SO3H was dried under vacuum at 80°C.

4.2. General procedure for the synthesis of pyran derivatives 4a-l

To a solution of an aromatic aldehyde 1 (1 mmol), malononitrile 2 (1 mmol), and methyl acetoacetate or ethyl acetoacetate 3 (1 mmol) in absolute EtOH (4 mL), 0.01 g of Fe3O4@PEO-SO3H was added and stirred at room temperature for 20–40 min. The completion of the reaction was followed by thin layer chromatography.
(TLC) (n-hexane/ethyl acetate, 3:1). The solid product was gradually formed. After completion of the reaction, it was stopped and the catalyst was separated by an external magnet, washed with ethanol and water. The solvent of the reaction mixture was evaporated under vacuum and the pure products were obtained by further recrystallization by using hot EtOH and no more purification was required. All the products were known compounds and were identified by comparison of their physical data with those authentic samples.

4.3. Spectral data of the selected product

5-Ethoxycarbonyl-2-amino-4-(3-nitrophenyl)-3-cyano-6-methyl-4H-pyran (4 g): FT-IR (KBr) (νmax cm−1): 3402, 3326, 3080, 2987, 2925, 1691, 1691, 1674, 1604, 1529, 1344, 1267; 1H NMR (500 MHz, DMSO-d6): 1.02 (3H, t, J = 6.9 Hz, CH3), 2.35 (3H, s, CH3), 3.95-3.98 (2H, m, CH2), 4.52 (1H, s, CH), 7.08 (1H, s, NH2), 7.62-7.66 (2H, m, Ar), 7.98 (1H, s, H-Ar), 8.11 (1H, d, J = 6.8 Hz, H-Ar).

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Disclosure statement

No potential conflict of interest was reported by the authors.

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