

Original Research Article

Urea immobilized silica-coated Fe₃O₄ MNPs as a heterogeneous magnetic nanocatalyst for the synthesis of 2-amino-4H-benzo[b]pyran derivatives

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Magnetic Nanoparticle

Multicomponent reaction

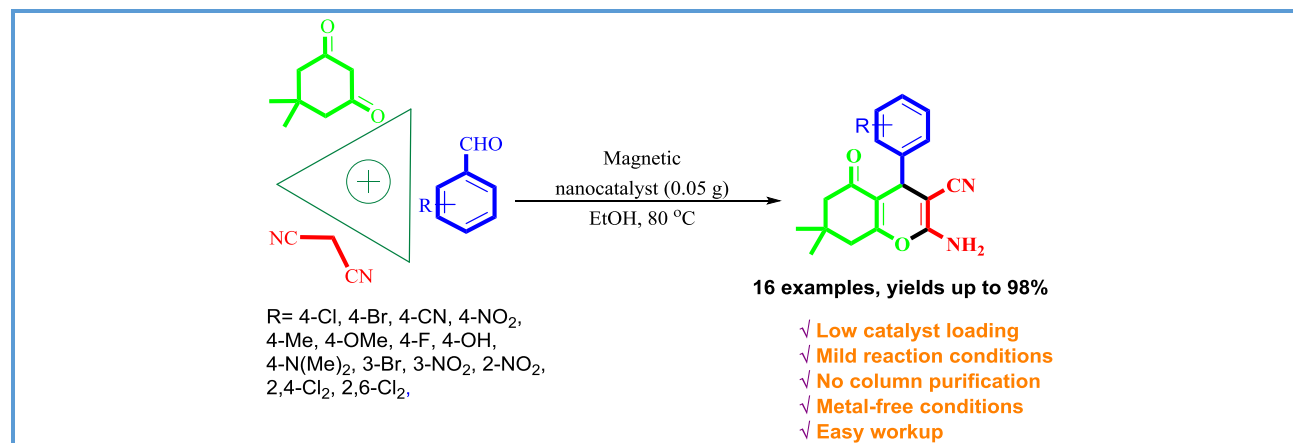
Pyran derivatives

ABSTRACT

In this work, a novel urea immobilized silica-coated Fe₃O₄ MNP (Fe₃O₄@SiO₂-(CH₂)₃-Urea) as a magnetically recoverable and metal-free nanocatalyst was designed and synthesized, and characterized using FT-IR, XRD, FE-SEM, TEM, EDX, and VSM. This system was explored in a three-component reaction to synthesize 2-amino-4H-benzo[b]pyran derivatives of dimedone, malononitrile, and aromatic aldehydes in ethanol at 80 °C. This new method has numerous merits, such as using a green and nontoxic catalyst, excellent yield, shorter reaction time, broad substrate scope, operational simplicity, and functional group compatibility. Moreover, the synthesized nanocatalyst was recovered by a magnetic field, and it was reused eight times without any appreciable change in the catalytic activity.

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Graphical Abstract



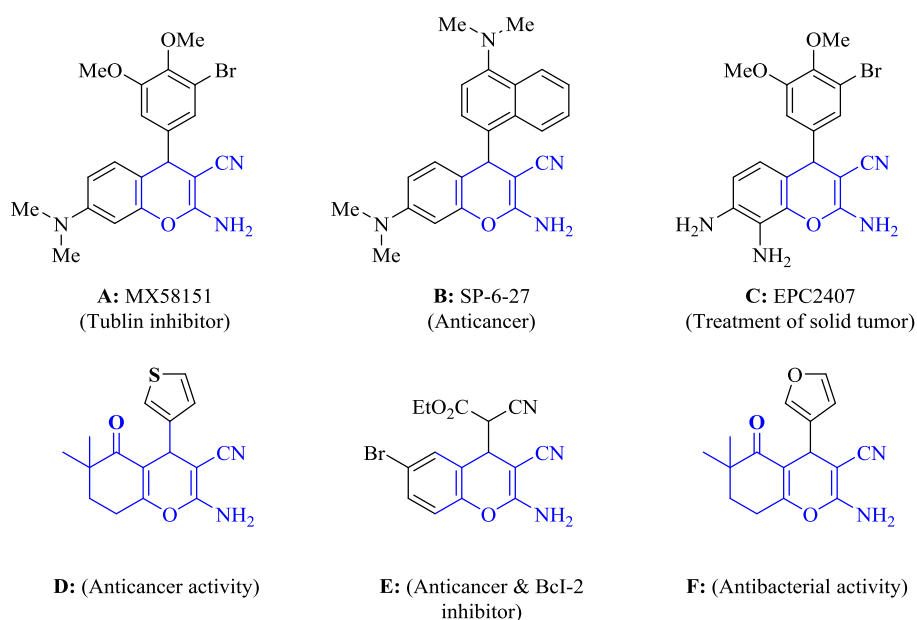
Introduction

The main aims of green chemistry are to design eco-friendly chemical processes by lowering the number of by-products and wastes produced in a chemical reaction, using fewer toxic reagents, and minimizing work-up and energy consumption as much as possible [1]. One of the most frequent strategies for achieving these green chemistry goals is using heterogeneous catalysts that increase the efficiency of chemical reactions and selectively manufacture the desired products [2]. Among the catalysts, magnetic nanoparticles have been widely investigated. Magnetic nanoparticles based on Fe_3O_4 have been used as alternative supports for catalysis. They have great potential in industries such as magnetic data storage [3], enzyme and protein separations [4], catalysis [5], medical therapeutics [6], MRI [7], diagnostics, and environmental remediation [8]. Therefore, much attention has been paid to using of Fe_3O_4 due to various advantages like low toxicity, easy separation from the reaction medium using an external magnet, high thermal

stability, simplicity, ease of synthesis, dispersed into solvents, large specific surface area, and pore volume.

Ideal procedures like multicomponent reactions (MCRs) have been used for the synthesizing of heterocyclic compounds. In this context, the desired product is generated by a one-pot reaction, and also starting materials with inexpensive resource-effective, and readily available materials. MCRs have several advantages in organic synthesis over multi-step synthesis, including lower energy costs, cost-effective, simple separation steps, short reaction time, less waste, and excellent yield [9, 10].

The 4*H*-pyrans and their derivatives are a key structural motif and essential in synthesizing many natural products and pharmaceutically active compounds. Pyrans and fused pyrans have antifungal, anticoagulant, anticancer, spasmolytic, anti-inflammatory, antibacterial, anti-anaphylactic diuretic, vasorelaxant, antiviral, antimicrobial, anti-Alzheimer's, and anti-malarial properties (Scheme 1) [11–15].

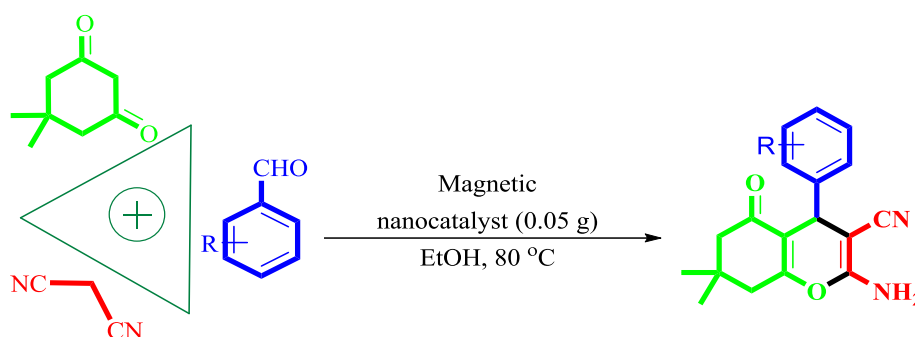


Scheme 1. Representative structures of drugs containing benzo[*b*]pyran scaffold

Although various catalysts have been reported for the synthesis of 2-amino-4*H*-benzo[*b*]pyran derivatives such as [PEG(mim)₂][OH]₂ [16], sodium alginate [17], [EMIM][OH] [18], GO-Fc@ Fe_3O_4 [19], nano-SnO₂ [20], montmorillonite [21], Fe_3O_4 @SiO₂-NH₂@TCT-guanidine [22], boron Nitride@ Fe_3O_4 [23], magnetic organosilica-supported gold nanoparticles [24], KF-Al₂O₃ [25], G/MF@SiO₂@Cu(proline)₂ [26], PPh₃ [27], and MNP@dpa@AgPd nanocatalyst [28]. However, many of these methods suffer from drawbacks such as toxic solvents, long reaction times, expensive reagents and catalysts, tedious steps

for the catalyst preparation, tedious work-up procedures, and harsh reaction conditions. Therefore, the development of new methods and catalysts is still in demand.

To assess the catalytic potential of urea immobilized silica-coated Fe_3O_4 MNPs as a green and reusable catalytic system [29], we synthesized and developed the Fe_3O_4 @SiO₂[(CH₂)₃-Urea] system to promote the one-pot three-component reaction of dimedone, malononitrile, and aromatic aldehydes for the synthesis of 2-amino-4*H*-benzo[*b*]pyran in good to excellent yields in ethanol at 80 °C (Scheme 2).



Scheme 2. Fe_3O_4 @SiO₂[(CH₂)₃-Urea] catalyzed synthesis of 2-amino-4*H*-benzo[*b*]pyran derivatives

Experimental

Preparation of Fe_3O_4

The co-precipitation procedure was used for the synthesis of Fe_3O_4 nanoparticles. For this purpose, deionized water (120 mL) was added to a mixture of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.97 g) and $\text{Fe}_2(\text{SO}_4)_3$ (0.9 g) and stirred at 80 °C under an N₂ gas atmosphere for 10 min. Then, 10 mL ammonia solution (28%wt) was added dropwise at 80 °C under a nitrogen gas atmosphere. The black Fe_3O_4 was stirred under an N₂ gas atmosphere for 30 min. The reaction mixture was then allowed to cool at ambient temperature. The resulting black precipitate was separated using an external magnet, washed six times (6×50 mL) with distilled

water and dried at room temperature for 24 h to afford Fe_3O_4 nanoparticle [30].

Preparation of Fe_3O_4 @SiO₂

Fe_3O_4 (1 g) in a mixture of ethanol: distilled water (80:20; 100 mL) was dispersed by sonification for 30 min. Then, tetraethyl orthosilicate (2 mL) and NH₄OH 25% (2 mL) were added, and the resulting solution was kept under N₂ for 24 h. Finally, the resulting products were collected by an external magnetic field and washed five times with distilled water (5×50 mL) and one time with ethanol (1×50 mL), and dried at room temperature for 24 h to afford Fe_3O_4 @SiO₂ nanoparticles [30].

Preparation of Fe_3O_4 @SiO₂[(CH₂)₃Cl

$\text{Fe}_3\text{O}_4@\text{SiO}_2$ (1 g) in dry toluene (80 mL) was dispersed for 20 min by sonification. Then, (3-chloropropyl)triethoxysilane (10 mmol) was added to the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ under stirring, and the reaction mixture was refluxed under N_2 for 24 h. The product was filtered, washed three times (3×30 mL) with dry toluene and two times (2×30 mL) with diethyl ether, and dried in a vacuum at 50°C to afford $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{Cl}$ [31].

Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-Urea}$

Eventually, $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{Cl}$ (1 g) was dispersed in dry toluene (80 mL) for 20 min, then urea (10 mmol) was added and refluxed for 24 h. The product was separated by the external magnetic field, washed dry toluene and anhydrous diethyl ether, and dried under vacuum for 24 h at room temperature to afford $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-Urea}$.

General process to synthesize of pyran derivatives

To a mixture of various aldehydes (1 mmol), dimedone (1 mmol), and malononitrile (1.2 mmol), was added $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-Urea}$ (0.05 g) in EtOH (5 mL) reacted under reflux conditions for the appropriate time. The progression of reaction as analyzed by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. Then, the magnetic catalyst was recovered from the reaction mixture by an exterior super magnet, washed with ethanol, and dried in an oven for 24 h. The solid product came through simple filtration and was washed with ethanol thoroughly for purification and dried at room temperature.

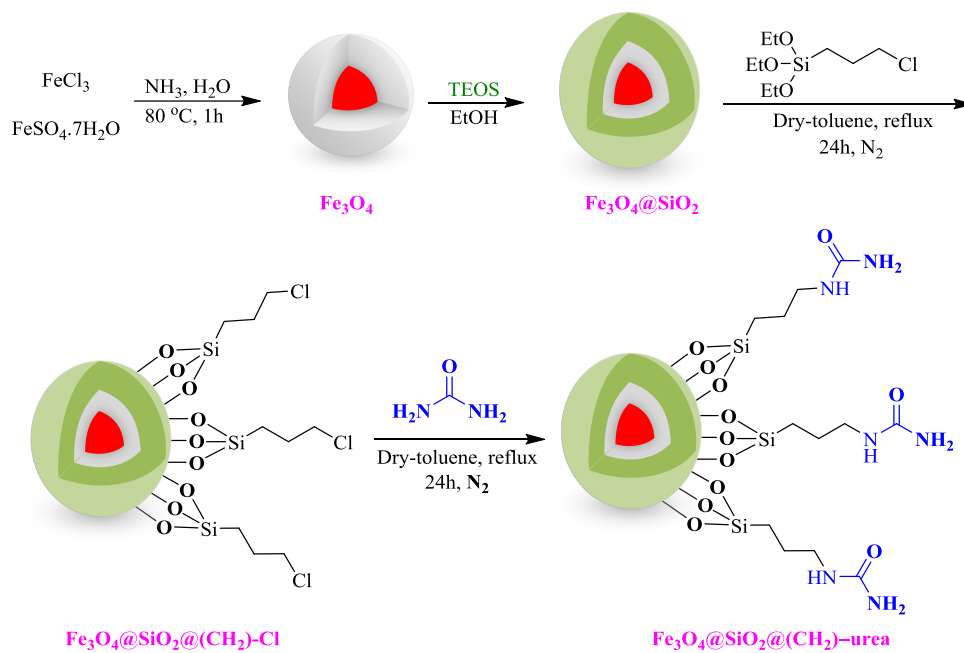
Results and Discussion

We described a facile strategy for synthesizing urea immobilized silica-coated Fe_3O_4 MNPs. For this purpose, the nanocatalyst was obtained by synthesizing Fe_3O_4 nanoparticles and coated with SiO_2 to give $\text{Fe}_3\text{O}_4@\text{SiO}_2$. Then, synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ functionalized with (3-chloropropyl) triethoxysilane to give $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{Cl}$. Finally, treatment of $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{Cl}$ with urea to produce the urea immobilized silica-coated Fe_3O_4 MNPs (Scheme 3).

The structure of synthesized nanocatalyst was characterized by FT-IR, SEM, TEM, EDX, XRD, and VSM analyses. The structure of the synthesized nanocatalyst was confirmed by an examination of FT-IR spectroscopy (Figure 1). Figure 1 reveals a sharp band of about 522 cm^{-1} , which is the characteristic of Fe–O stretching bands. Also, the characteristic absorption bands at 1090 cm^{-1} is related to Si–O–Si asymmetric stretching vibrations. This absorption indicated the existence of SiO_2 in $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs. Moreover, the weak peak at about 2859 cm^{-1} is related to C–H (sp^3) to confirm the existence of (3-chloropropyl) triethoxysilane functional groups on the surface of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs. Eventually, the peaks at 3422 and 1633 cm^{-1} were observed in NH_2 stretching vibrations and carbonyl group, respectively.

The FE-SEM and TEM analyses were used to determine the size and morphology of the synthesized nanocatalyst (Figure 2). As shown in Figure 2a,b, the images of synthesized nanocatalyst show that this nanocatalyst has a regular spherical shape with a size of about 45 nm.

EDX spectrum and elemental mapping analysis were used to confirm the presence of elements of synthesized nanocatalyst (Figures 3 and 4). Figures 3 and 4 show the synthesized nanocatalyst's EDX spectrum and elemental mapping analysis. As can be seen, EDX spectrum and elemental mapping analysis illustrate that



Scheme 3. Synthesis of urea immobilized silica-coated Fe_3O_4 MNPs

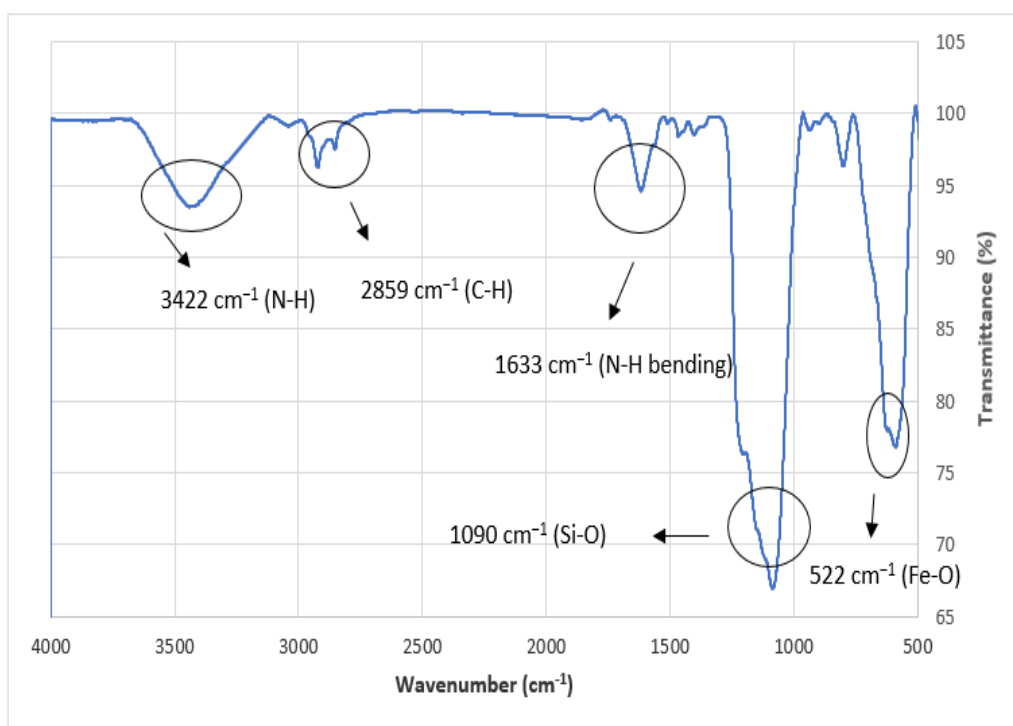


Figure 1. FT-IR spectra of synthesized nanocatalyst

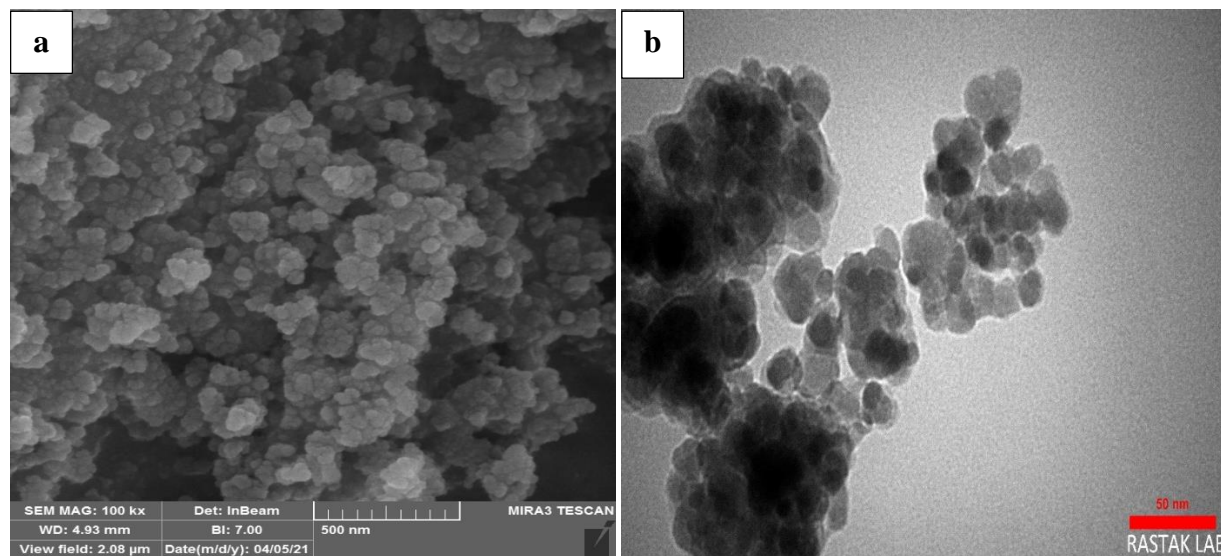


Figure 2. a) SEM and b) TEM images of synthesized nanocatalyst

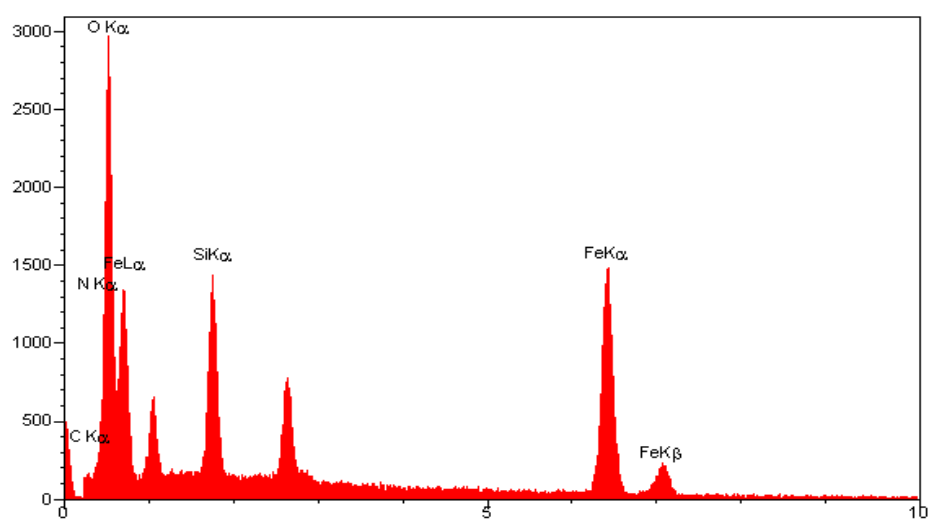
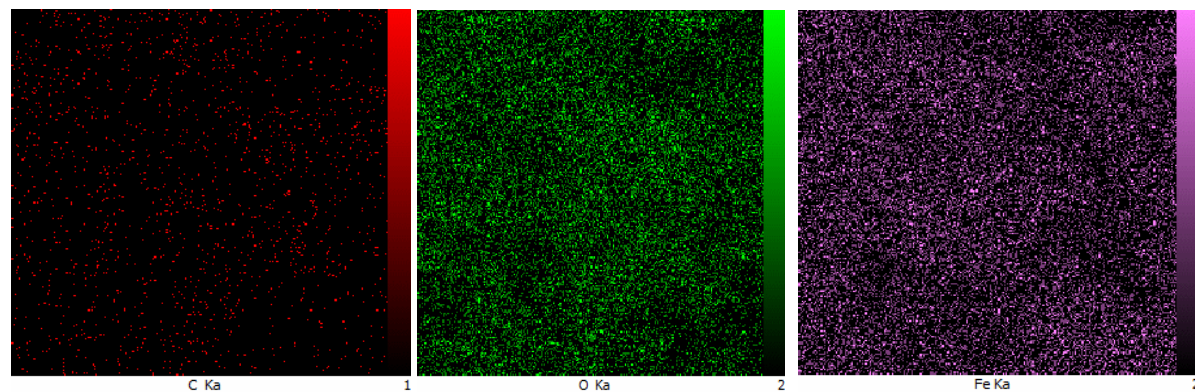


Figure 3. The EDX spectroscopy of synthesized nanocatalyst



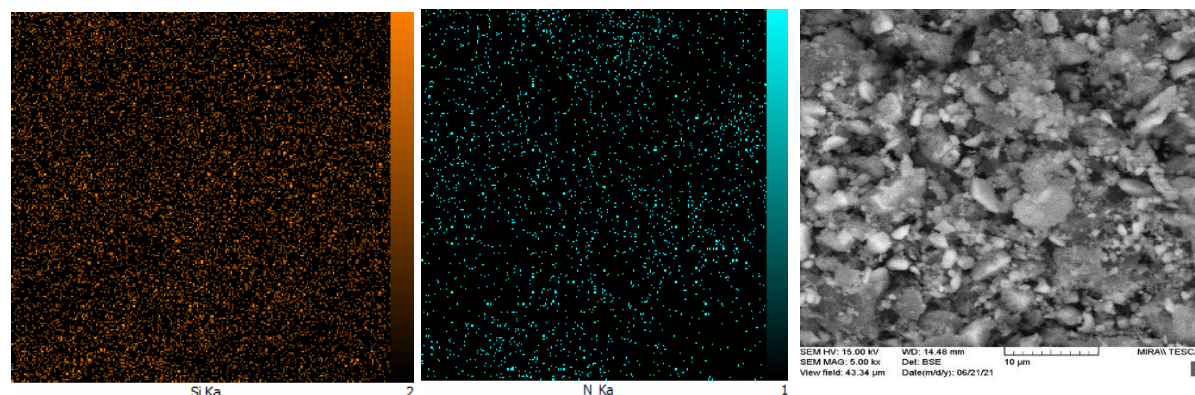


Figure 4. The elemental mapping analysis of synthesized nanocatalyst

the synthesized nanocatalyst has various elements such as Fe, Si, N, O, and C with mass percentages of 39.01, 6.13, 8.93, 38.51, and 7.42, respectively.

X-ray diffraction (XRD) analysis was used to determine the size and crystallinity of the synthesized nanocatalyst (Figure 5). The XRD patterns of the synthesized nanocatalyst indicated six characteristic peaks at $2\theta = 30.7$, 37.6 , 44.7 , 58.5 , 63.1° , that are the plates (220), (311), (400), (422), (511), and (440),

respectively. These peaks are related to the crystal planes in the Fe_3O_4 lattice and according to the standard XRD pattern of cubic Fe_3O_4 [JCPDS 88-0866] [30].

Figure 6 indicates the magnetic behavior of synthesized nanocatalyst by VSM analysis. The specific saturation magnetizations synthesized nanocatalyst is measured to be 23 emu g^{-1} . This decrease is relevant to the newly coated layer and affirms the favored synthesis of nanomagnetic catalysts.

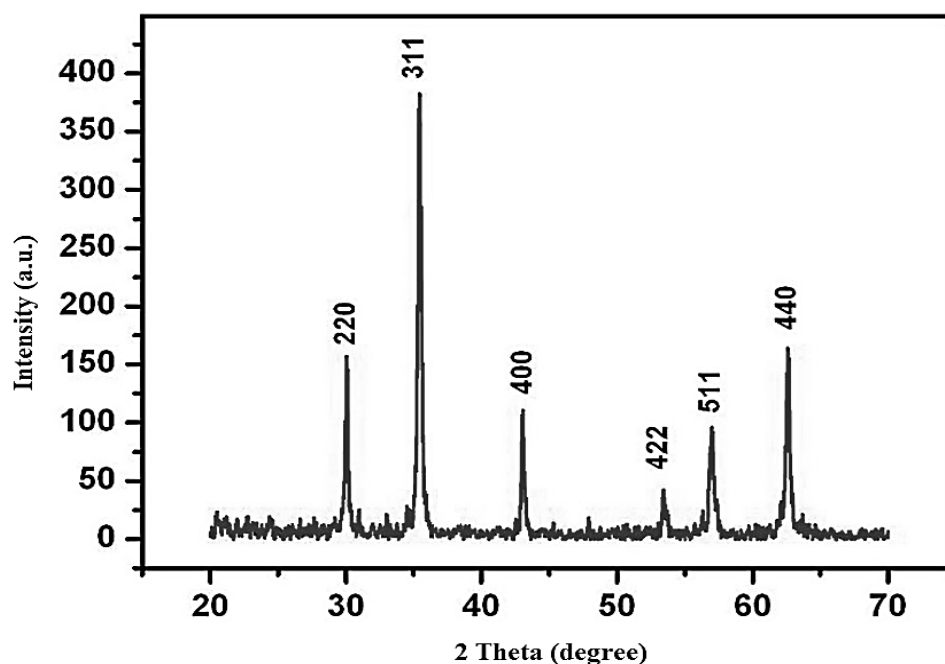


Figure 5. The XRD analysis of synthesized nanocatalyst

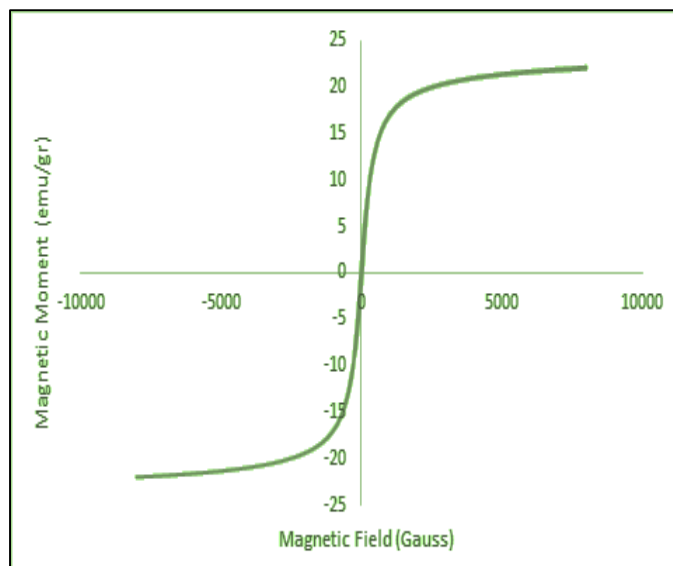


Figure 6. VSM analysis of the synthesized nanocatalyst

We choose the reaction between 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol), and malononitrile (1.2 mmol) as a model reaction to assess the catalytic effectiveness of the $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-Urea}$ and to optimize the reaction conditions. The model reaction was carried out at various temperatures and with different amounts of catalyst in the presence of various solvents and in solvent-free conditions to optimize the reaction conditions. The finding results are summarized in Table 1. The desired product 3a was not generated without a catalyst at different reaction conditions, including Solvent-free/room temperature and EtOH, room temperature, respectively (Table 1, entries 1 & 2). We repeated the model reaction in EtOH under reflux conditions in the presence of a various amount of catalyst for further research, and a reasonable quantity of desired product was obtained (Table 1, entries 3-7). Increasing the amount of catalyst to 0.05 g in ethanol under reflux conditions the desired product 3a was obtained in 96% yield after 30 min (Table 1, entry 5).

Moreover, increasing the amount of catalyst to 0.07 and 0.1 g in ethanol under reflux conditions, the improvement of reaction time and yield were not observed (Table 1, entries 6 and 7). To evaluate the catalyst's efficiency in the presence of other solvents, we conducted a model reaction with MeOH, CH_2Cl_2 , Toluene, THF, and H_2O . The attempted reactions were carried out in reflux conditions, and the obtained results are summarized in Table 1 (entry 8-12). The study of solvents indicated that the EtOH gives the best result compared with that of the other solvents used. As a result, the 0.05 g catalyst in EtOH under reflux conditions was selected as the best result for further exploration of the scope of this unique approach.

The above-optimized conditions (including 0.05 g synthesized nanocatalyst, 5 mL EtOH under reflux conditions), we then extended the current approach to various aromatic aldehydes (i.e., either electron-donating or electron-withdrawing groups) and the results are presented in Table 2. As seen, the corresponding 2-amino-4*H*-benzo[*b*]pyran derivatives were obtained in excellent yields in

short reaction times without the formation of any by-products. Also, a suggested satisfactory and straightforward mechanism for synthesizing 2-amino-4*H*-benzo[*b*]pyran derivatives catalyzed by Fe₃O₄@SiO₂[(CH₂)₃-Urea is demonstrated in Scheme 4.

Also, we investigated the catalyst recyclability from the reaction mixture for future trials. For this purpose, we selected the reaction between 4-cyanobenzaldehyde (1

mmol), dimedone (1 mmol), and malononitrile (1.2 mmol) in the presence of 0.05 g Fe₃O₄@SiO₂[(CH₂)₃-Urea as a model reaction under optimizing the reaction conditions. After completing the reaction, using an external magnet, the magnetic nanocatalyst can be recovered and reused in the next run. It can be seen that the recovered catalyst does not significantly lose its activity after 8 times (Figure 7).

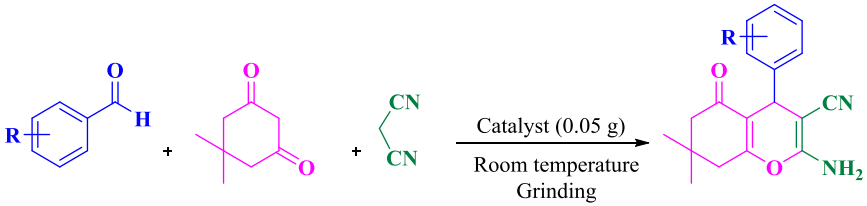
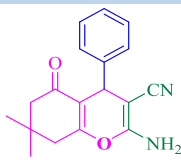
Table 1. Optimization of the reaction conditions

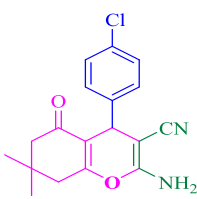
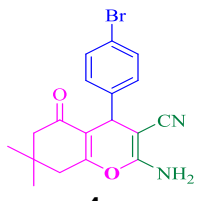
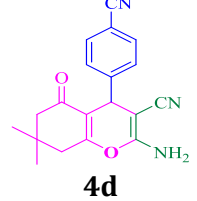
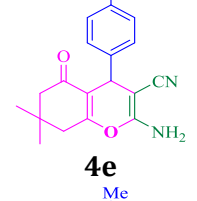
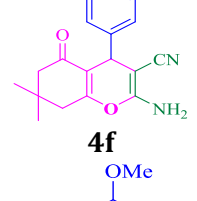
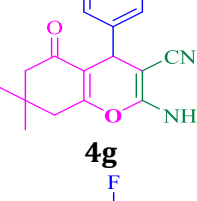
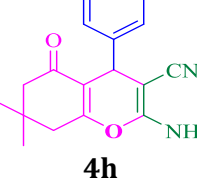
Entry	Catalyst loading (g)	Time (min)	Yield (%)	Conditions
1	-	6 h	Trace	Solvent-free/r.t.
2	-	6 h	Trace	EtOH, r.t.
3	0.01	60	55	EtOH, reflux
4	0.03	30	81	EtOH, reflux
5	0.05	30	96	EtOH, reflux
6	0.07	30	92	EtOH, reflux
7	0.1	45	89	EtOH, reflux
8	0.05	60	75	MeOH, reflux
9	0.05	110	65	CH ₂ Cl ₂ , reflux
10	0.05	130	60	Toluene, reflux
11	0.05	130	45	THF, reflux
12	0.05	60	66	H ₂ O, reflux

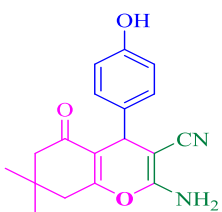
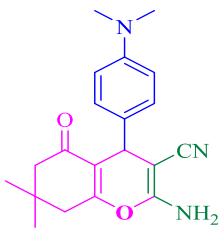
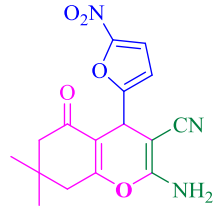
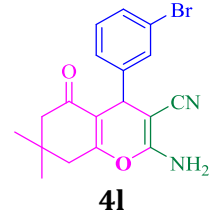
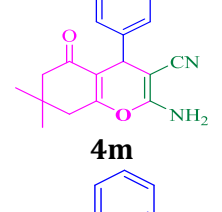
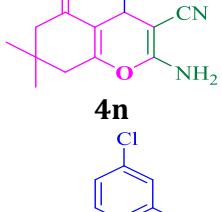
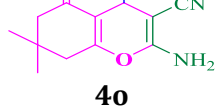
^a All reactions were carried out by 4-chlorobenzaldehyde (1 mmol), malononitrile (1.2 mmol), dimedone (1 mmol) in the presence of various amount of catalyst

^b Isolated yield

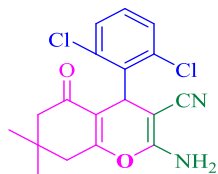
Table 2. Reaction scope^a

						
Entry	Products	Time (min)	Yield (%) ^b	Found	M.p (°C)	
					Found	Reported
1	 4a	40	92	230-232	233-235 [32]	

2	 4b	30	96	212-214	214-216 [32]
3	 4c	30	95	217-219	221-223 [32]
4	 4d	15	98	220-222	224-227 [32]
5	 4e	15	97	181-183	179-181 [32]
6	 4f	40	92	219-221	218-220 [32]
7	 4g	40	91	201-203	200-202 [32]
8	 4h	25	91	188-190	187-188 [32]

9	 4i	40	91	226-228	225-228 [32]
10	 4j	45	92		179-181
11	 4k	12	92	154-155	154-156 [32]
12	 4l	35	93		216-218
13	 4m	12	94	214-216	212-213 [32]
14	 4n	10	94	220-222	222-223 [32]
15	 4o	30	90	179-180	177-178 [32]

16

**4p**

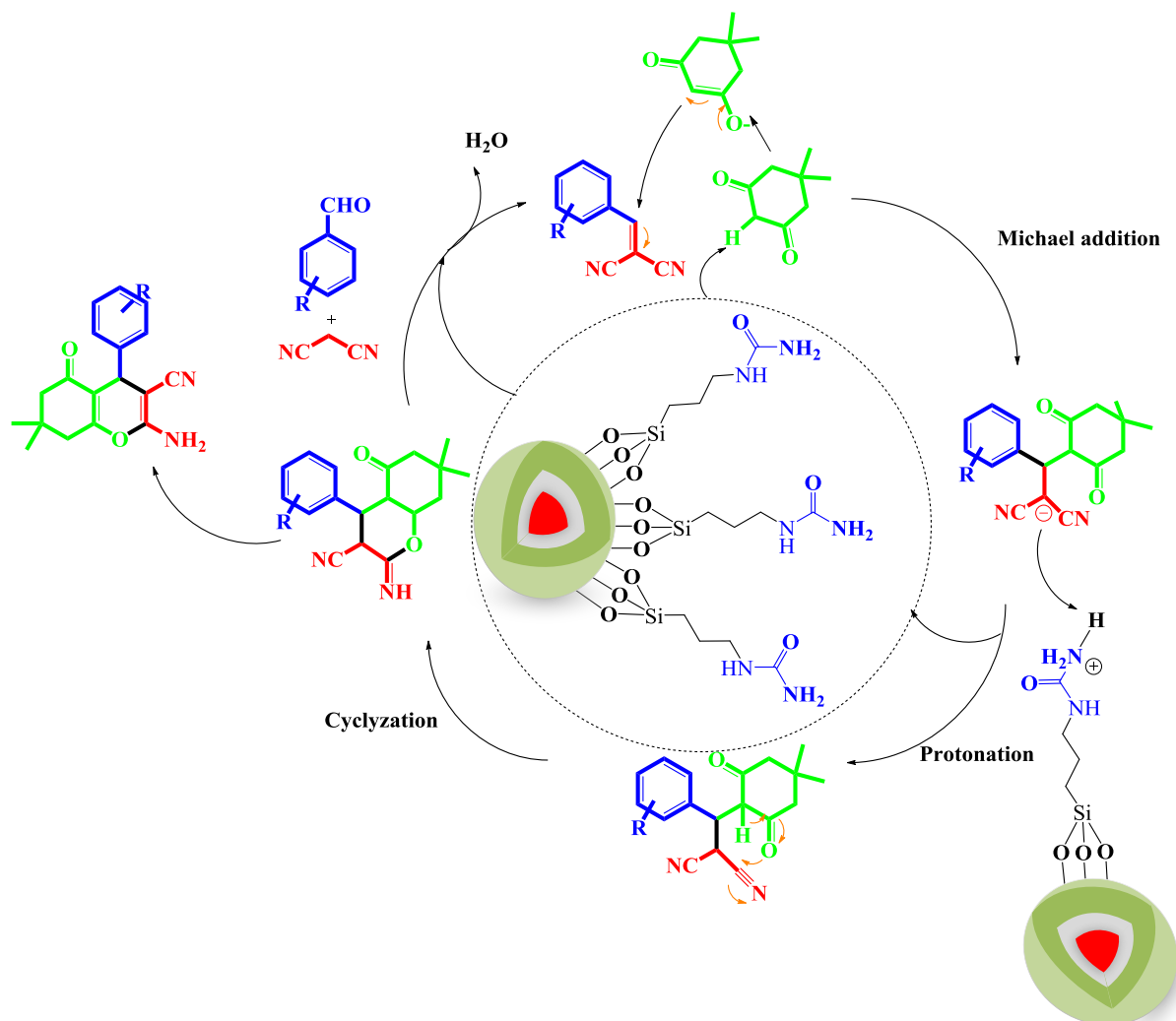
30

92

247-249

^a All reactions were carried out with various aldehyde (1 mmol), malononitrile (1.2 mmol), dimedone (1 mmol) in the presence of the $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-Urea}$ (0.05 g) in EtOH under reflux conditions

^b Isolated yield



Scheme 4. Plausible mechanism for the synthesis of 2-amino-4H-benzo[*b*]pyran derivatives catalyzed by $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-urea}$

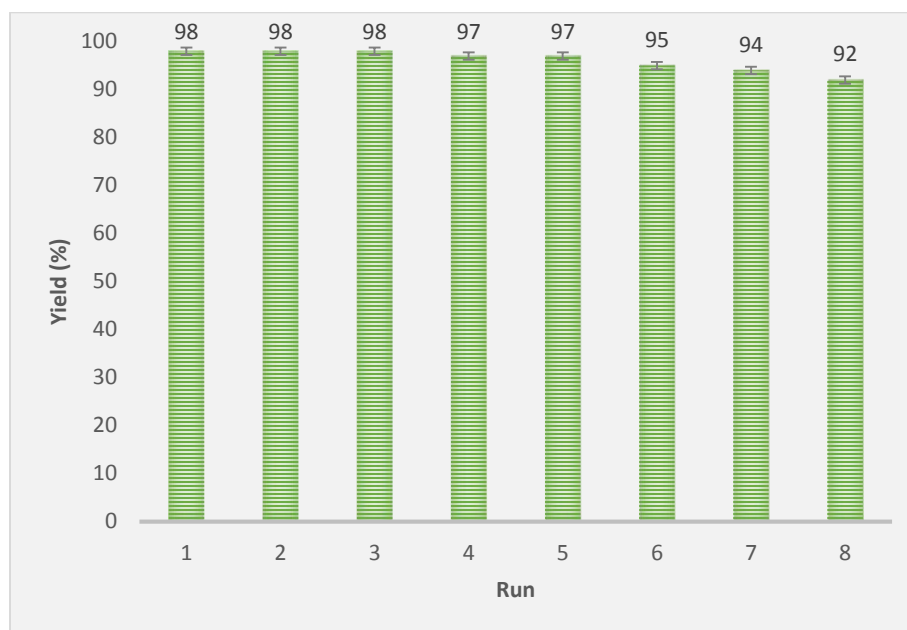


Figure 7. Study of catalyst recyclability

Conclusions

In summary, we have synthesized an environmentally friendly and efficient method for the synthesis of a novel urea immobilized silica-coated Fe_3O_4 MNP ($\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-Urea}$) as a magnetically recoverable and metal-free nanocatalyst, followed it was characterized using various analyses such as FT-IR, XRD, FE-SEM, TEM, EDX, and VSM. $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-Urea}$ exhibits high catalytic activity in synthesizing pyran derivatives of dimedone, malononitrile, and aromatic aldehydes at 80 °C within 10-45 min in ethanol. This method has various advantages, including clean reaction profiles, easy handling, a low-cost catalyst, no column purification, high yield, facile product isolation, and environmental compatibility.

Acknowledgments

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