IRANIAN JOURNAL OF CATALYSIS

Fe$_3$O$_4$@SiO$_2$@Vitamin C@Fe$_2$O$_3$ Nanoparticles as a Novel Green Catalyst for One-pot Synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile Derivatives

Naghmeh Darya, Hassan Tajik*

Department of Chemistry, Faculty of Science, University of Guilan, Rasht P.O. Box 41335-1914, Iran

ABSTRACT

In this research, we report a novel and green magnetic nanocatalyst; Fe$_3$O$_4$@SiO$_2$@Vitamin C@Fe$_2$O$_3$ for clean synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles with high-yield in water as solvent at room temperature. The nanocatalyst is stable under the synthetic conditions and it can be reused several times without considerable reduction in its catalytic activity. The catalyst structure was characterized by using various analytical techniques; SEM, FT-IR, thermogravimetric analysis (TGA), UV-vis spectroscopy, VSM and EDS. Also, the products were separated and characterized by determining their melting points, IR spectra and compared to those of the authentic samples. Environmentally friendly, availability, high catalytic activity and ease of separation are the main reasons for using Fe$_3$O$_4$@SiO$_2$@Vitamin C@Fe$_2$O$_3$ as a green catalyst.

Keywords: *Green chemistry, Magnetite nanocatalyst [Fe$_3$O$_4$@SiO$_2$@Vitamin C@Fe$_2$O$_3$], Multi-component Reactions, 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile*

1. Introduction

Using catalysts in a synthesis is one of the basic principles of green chemistry. In recent years, nanoparticles as a catalyst have attracted the attention of organic chemists [1-10]. Also, the easily separable magnetic nano-catalysts have found interesting applications in the field of catalytic processes [11-18].

On the other hand, 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles derivatives systems constitute an important class of organic compounds. The most straightforward synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles derivatives involves the three-component reaction of aromatic aldehydes, 2-naphthol and malononitrile. Regarding the importance of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles derivatives, many research efforts in recent years have attention drawn toward the development of new methodologies for the synthesis of these compounds [19-24].

These methods, however, suffer from drawbacks such as the use of expensive devices, extended reaction time, elevated temperature, tedious work-up and in some cases are pollutant to the environment. Therefore, we design a powerful recoverable catalyst Fe$_3$O$_4$@SiO$_2$@Vitamin C@Fe$_2$O$_3$ under "layer-by-layer" technique and employed it in the preparation of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles derivatives (**Scheme 1**).

2. Experimental

2.1 General

The products were characterized by FT-IR spectra recorded on a BRUKER-ALPHA spectrometer on KBr disk. TGA thermogram was recorded using a THERMO-NIKOLET TGA spectrometer. UV-Vis analysis was reported using a UV-vis Array spectrophotometer (PHOTONIX2017). Also, the progress of reactions were monitored by Thin Layer Chromatography (TLC) by using UV light.

2.2 Clean synthesis of Fe$_3$O$_4$@SiO$_2$ nano-capsule

FeCl$_2$·4H$_2$O (10.059 mmol, 2.000g), anhydrous FeCl$_3$ (32.059 mmol, 5.200 g) and hydrochloric acid (1.5 mL, 12 mol. L^{-1}) were dissolved in 25 mL deionized water.

*Corresponding author:
E-mail address: Tajik2014@Gmail.com (**H. Tajik**)
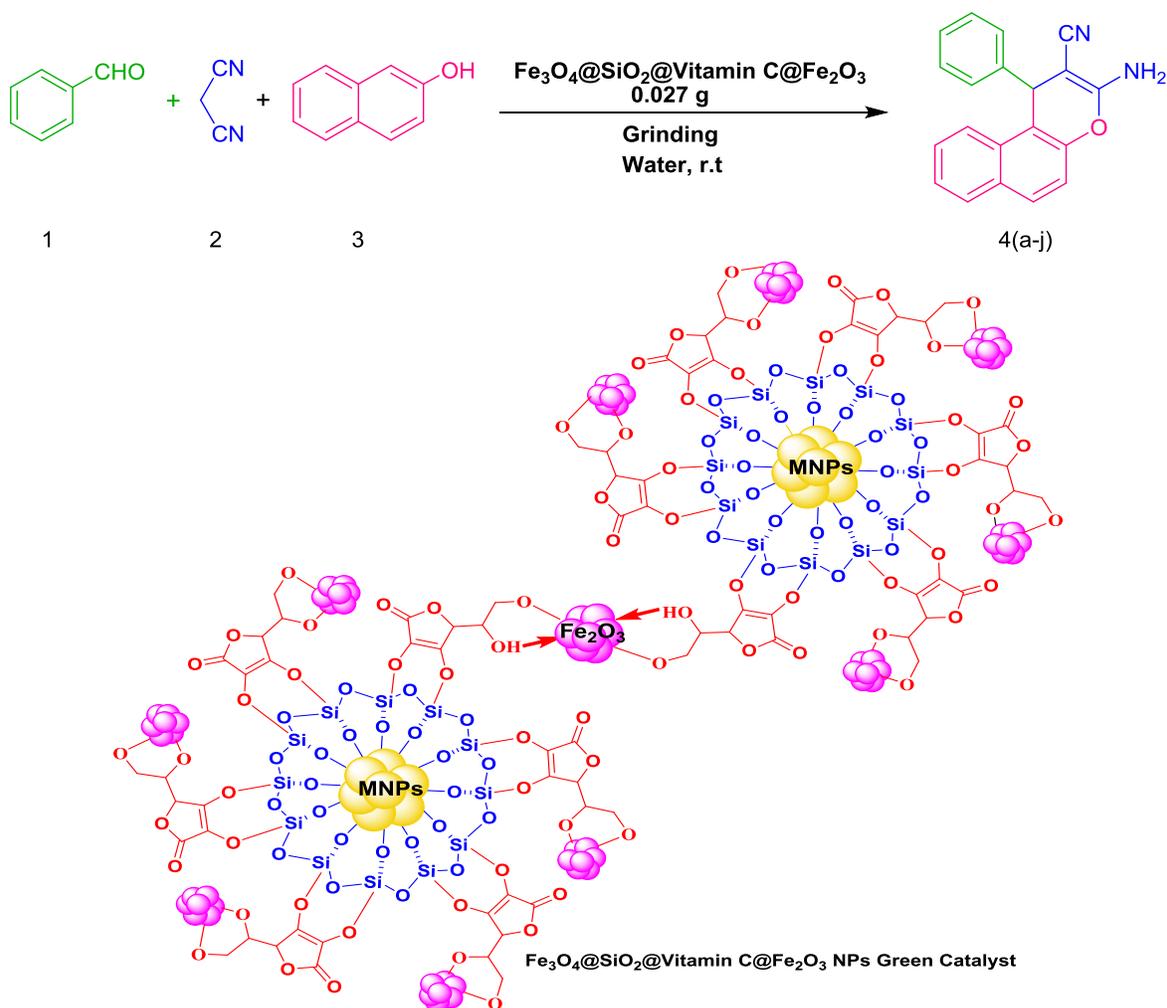
Scheme 1. Green synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles synthesis using Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 green catalyst

Then, NaOH solution (250 mL, 1.5 mol. L^{-1}) was added and mixed at room temperature for 10 minutes. The black suspension of nanoparticles was precipitated out of the reaction mixture. The resulting nano-solid was separated by using a magnet and washed with EtOH (2×5mL). In order to coat the silicon oxide layer on the nanoparticles, 10 mL NaOH solution (1.5 mol. L^{-1}) was added to maintain the reaction pH between 11 and 12, and then 1.000 g nanoparticles and tetraethyl orthosilicate, TEOS (4 mL, 0.017mol), was added to the reaction mixture and ground by a mortar and pestle at room temperature for 30 minutes and then stirred and mixed at 40°C for 8 hrs. The resulting Fe_3O_4@SiO_2 was separated by using a magnet, washed with ethanol (3×5ml) and dried at room temperature for 24hrs.

2.3 Clean synthesis of magnetite multilayer Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 green catalyst

Functionalized vitamin C on the nano-capsule silicon dioxide coated iron oxide NPs was prepared by the addition of a solution of 0.25 g vitamin C in water (20 drops) to nano-capsules (1.000 g) and ground by a mortar and pestle for 2h at room temperature and the mixture was then kept at room temperature for 48 hrs. The silicon dioxide coated iron oxide nanoparticles functionalized vitamin C were collected by a permanent magnet, followed by washing with H_2O (2×5mL) and drying at room temperature. Then $FeCl_2.4H_2O$ (1mmol, 0.198g) in EtOH/water (50 drops) was added to Fe_3O_4@SiO_2@Vitamin C and ground at room temperature for 1h. The resulting Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 NPs were collected by a permanent magnet, followed by washing with H_2O (2×5mL) and drying at room temperature.

2.4 General procedure for the synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles derivatives (3a-3j).

2-naphthol (1mmol), aldehydes (1mmol), malononitrile (1mmol) were added to the Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 (0.027 g) and mixed in water as a solvent (10

drops) in a mortar at room temperature for the appropriate amount of time (22-44 minutes). The reaction progress was monitored by TLC. The catalyst was separated from the product by using a magnet. The products were purified by recrystallization in ethanol. Also, $Fe_3O_4@SiO_2@$Vitamin $C@Fe_2O_3$ was washed by deionized water (3×5ml) and dried at room temperature for 24 hrs for use in the next cycle (the results are given in Table 2).

2.5 *The spectral data of compound* **4a**

3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles (**4a**); Yield: (94 %), IR (KBr, cm^{-1}) = 3433 cm^{-1}, 3341 cm^{-1}, 2960 cm^{-1}, 2929 cm^{-1}, 2183cm^{-1}, 1728cm^{-1},1643 cm^{-1}, 1568 cm^{-1}, 1441 cm^{-1}, 1279 cm^{-1},1125 cm^{-1}, 1073 cm^{-1},815 cm^{-1},718 cm^{-1}, 697 cm^{-1},558 cm^{-1}.

In this study, uniform sized spherical MNPs as a magnetic core were synthesized via a "co-precipitation method" from ferric and ferrous ions [25]. Then, a layer of nano-silica as a natural catalyst was coated on Fe_3O_4 via hydrolysis of TEOS in order to conjugate with Fe_3O_4 and Vitamin C ($Fe_3O_4@SiO_2@$Vitamin C). Then $Fe_3O_4@SiO_2$ was coated by a layer of Vitamin C and a layer of Fe_2O_3 NPs as a natural catalyst by the addition of $FeCl_2.4H_2O$ powder (**Scheme 2**). $Fe_3O_4@SiO_2@$Vitamin $C@Fe_2O_3$ is an excellent catalyst as it is magnetically recoverable and the chemicals required for the preparation of $Fe_3O_4@SiO_2@$Vitamin $C@Fe_2O_3$ are readily available. The catalyst was characterized by using various techniques including SEM (**Fig. 1a-c**), TGA (**Fig. 2**), FT-IR (**Fig. 3a-3b**), UV-vis spectroscopy (**Fig. 4a and 4b**), VSM analysis (**Fig. 5)** and EDS analysis (**Fig. 6**).

3. Results and Discussion
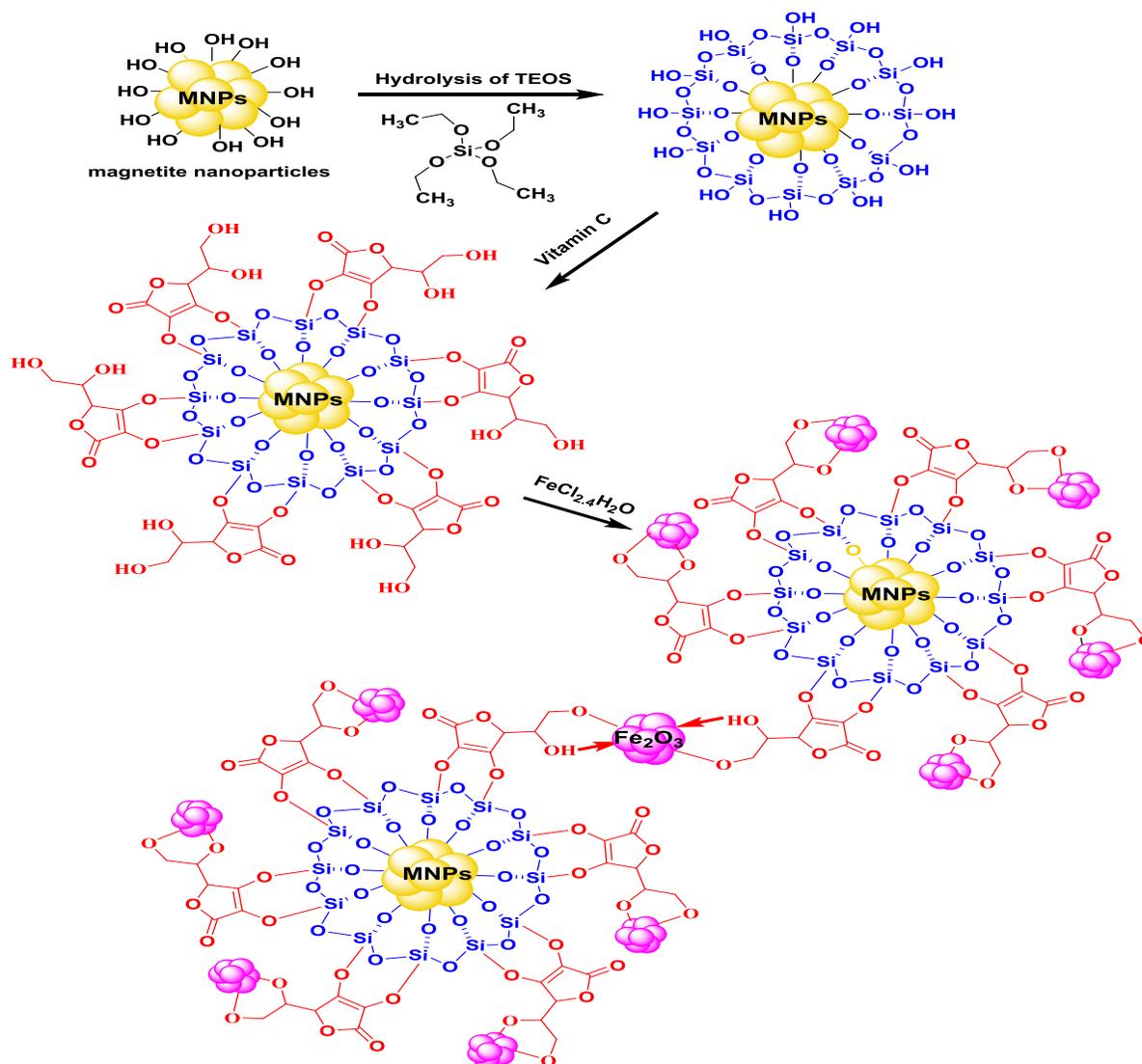
Scheme 2. Clean synthesis of magnetite multilayer $Fe_3O_4@SiO_2@$Vitamin $C@$ Fe_2O_3 green catalyst

3.1 Scanning electron microscopy analysis (SEM)

The size and surface morphology of iron oxide nanoparticles before and after encapsulation were analysed by scanning electron microscopy. (**Fig. 1a-c**). The SEM images of the Fe₃O₄@SiO₂@Vitamin C@Fe₂O₃ nano-catalyst shows a spherical morphology, with an average size range of 54 nm. Also, SEM imaging showed that the nano-capsules (Fe₃O₄@SiO₂) have uniform morphologies with average size of 27 nm. The nanoparticles, have a core–shell structure, and a uniform magnetic core (Fe₃O₄) with a diameter of 9 nm in **Fig. 1a**, surrounded by SiO₂ shell and coated with Vitamin C@ Fe₂O₃NPs (**Fig. 1b and 1c**).
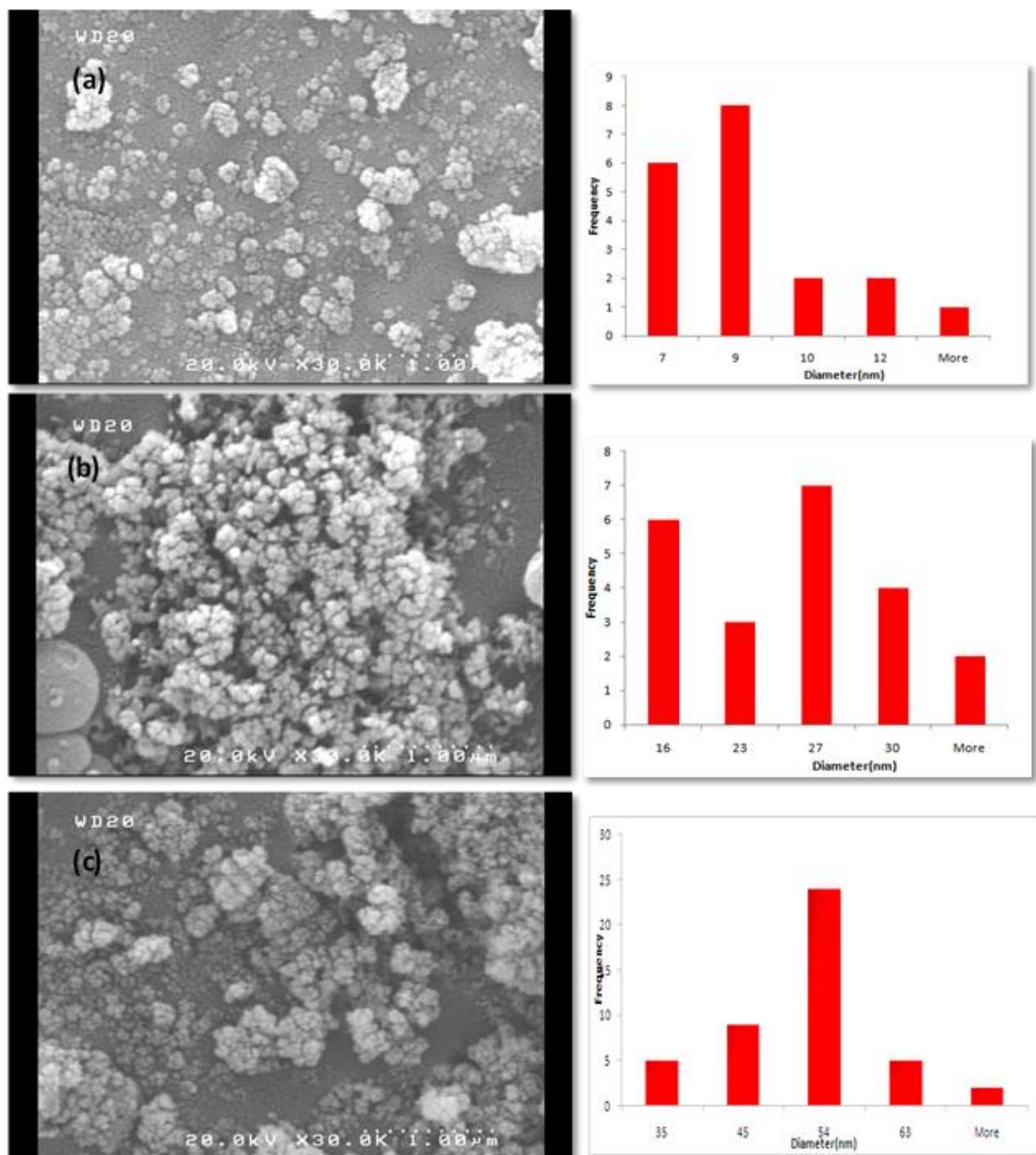
Fig.1 Scanning electron microscopy (SEM) and Histogram of Nanoparticle (a) Fe₃O₄ (MNPs) (b) Fe₃O₄@SiO₂. (c) Fe₃O₄@SiO₂@Vitamin C@ Fe₂O₃

3. 2 Thermogravimetric Analysis (TG-DTG)

According to the *TG-DTG* thermogram (**Fig. 2**), the iron oxide nanoparticles are stable up to 457°C. The *TG-DTG* also shows an initial small weight loss due to the evaporation of moisture from the sample. The weight loss at 457°C temperature is due to the thermal crystal phase transformation from MNPs (Fe_3O_4) to Fe_2O_3.

3.3 Infrared spectroscopy analysis (FT-IR)

The FT-IR spectra of (a) $Fe_3O_4@SiO_2@$Vitamin C (b) $Fe_3O_4@SiO_2@$Vitamin C@Fe_2O_3 were recorded and are given below (**Fig. 3a-3b**). According to the FT-IR spectra, the O-H stretching are appeared at 3422 cm^{-1}, the Fe-O bond stretching appeared at around 582 cm^{-1} in iron oxide nanoparticles (**Fig. 3a**). The results of FT-IR analysis observed for Fe-O and Si-O bonds in $Fe_3O_4@SiO_2$ were then compared to the literature [26].

After the immobilization of Fe_2O_3 NPs on $Fe_3O_4@SiO_2@$Vitamin C (**Fig. 3a-3b**), the IR spectrum exhibits a new absorbance peak at 615 cm^{-1} for Fe-O in Fe_2O_3 that stabilized and capping by Vitamin C, also the absorbance peaks attributed to Si-O in silicon dioxide groups are at 1000-1200 cm^{-1}. The Si-O-C groups appeared at 1072-1281 cm^{-1}. This means that vitamin C is immobilized on the surface of the nanoparticles ($Fe_3O_4@SiO_2$). Also, a comparison of the spectrum of $Fe_3O_4@SiO_2@$Vitamin C @Fe_2O_3 and $Fe_3O_4@SiO_2$ @Vitamin C FT-IR (**Figure 3a-b**) revealed the formation of nanocomposite, because the IR spectrum in Figure 3b exhibits a new absorbance peak at 615 cm^{-1} which corresponds to the Fe-O stretching vibration in Fe_2O_3 NPs and the peak at 900-1000 cm^{-1} is assigned to Fe-O-C bond and its formation is because of an interaction between the Fe-O in Fe_2O_3 complexes on $Fe_3O_4@SiO_2$ @Vitamin C via stabilized and capping by Vitamin C. Also, major broad bands at 400-743cm^{-1} are attributed to the stretching vibrations of Fe-O group in Fe_2O_3 and Fe_3O_4.
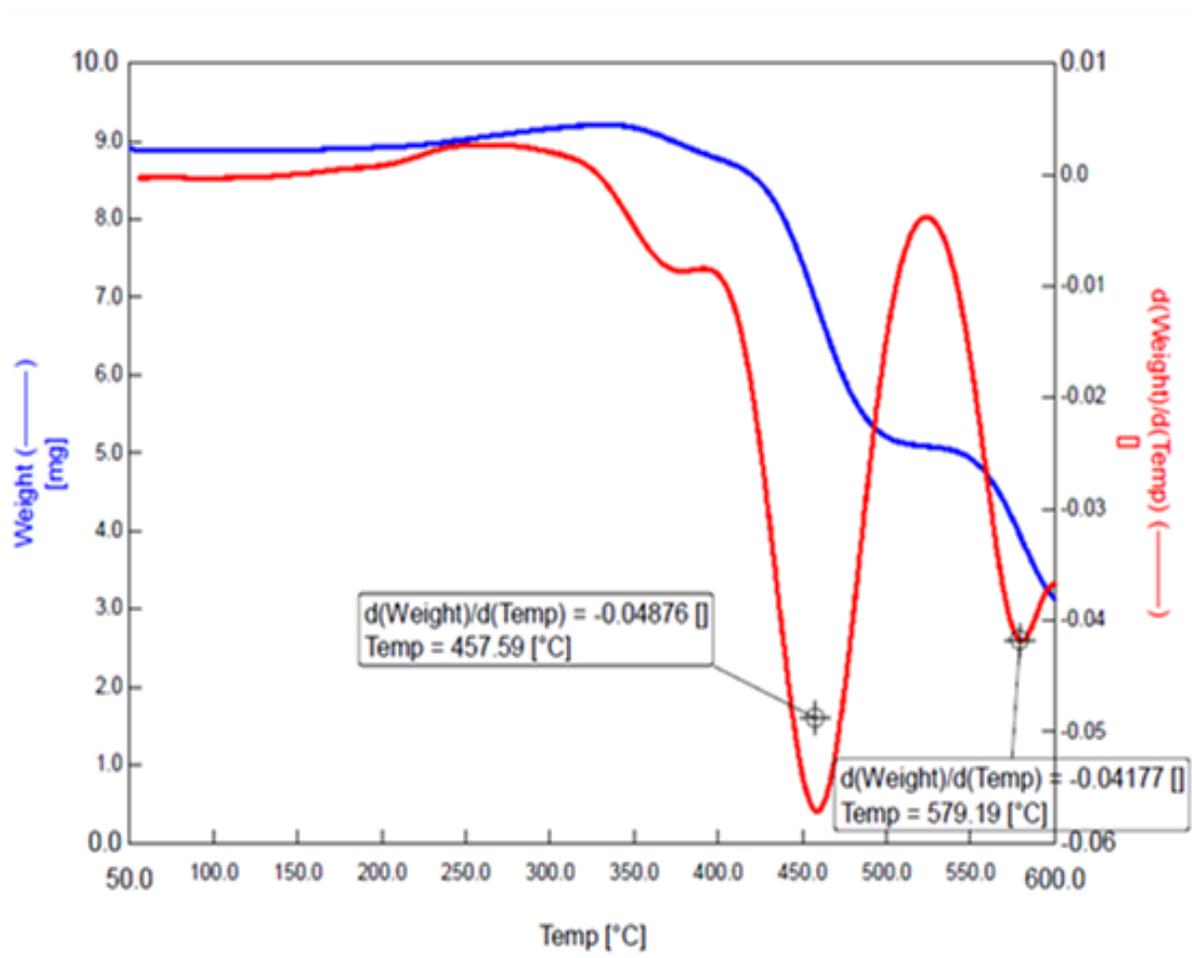

Fig. 2 TG-DTG analysis of MNPs
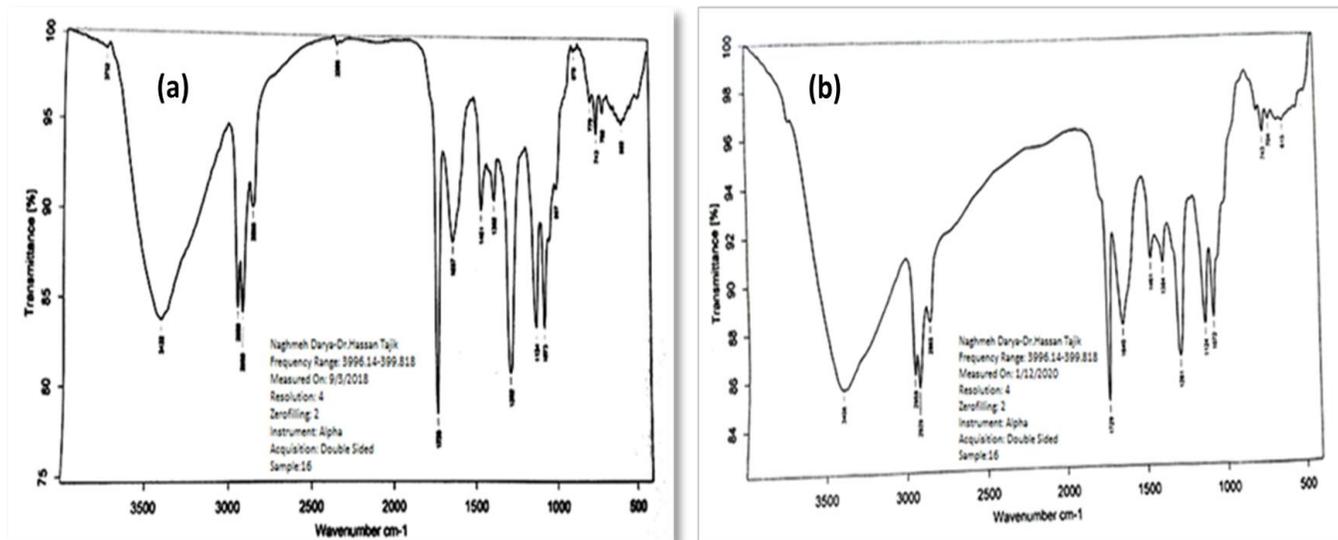
Fig. 3 FT-IR spectra of (a) Fe$_3$O$_4$@SiO$_2$@Vitamin C (b) Fe$_3$O$_4$@SiO$_2$@Vitamin C@ Fe$_2$O$_3$

Therefore, the FT-IR spectra of the nanoparticles prepared, (Fig. 3a-3b), show the immobilization of Fe$_2$O$_3$ nanoparticles on nano-Fe$_3$O$_4$-supported@silicon dioxide@Vitamin C. Therefore, the vitamin C has both linker, stabilizer and capping capabilities. Based on the spectral analysis it seems that the active site of Vitamin C is immobilized on nano-capsule via hydroxyl groups. Furthermore, the active site of the catalyst is immobilized on vitamin C via hydroxyl and carboxyl groups. In this catalyst, molecular chains of the catalyst are attached via cross-linked bonds to the other chains by using Fe$_2$O$_3$ nanoparticles. Cross-linked bonds are the key factors that link one catalyst chain to another and create a network of 3D structure.

3.4 UV-vis analysis

The process of catalyst formation (supernatant of catalyst) was checked by the UV-vis spectra (**Fig. 4, a-b**). Comparison of UV-vis spectra of Fe$_3$O$_4$@SiO$_2$@Vitamin C@Fe$_2$O$_3$ and Vitamin C, shows that the catalyst has a single absorption band around 316 nm for Fe$_3$O$_4$@SiO$_2$@Vitamin C@ Fe$_2$O$_3$ catalyst.

There was a blue shift in the absorption peak (**4a**) which is probably be due to the formation of the composite structure and exhibits the interaction between nanoparticles. In addition, no other peak was observed in the spectrum except for the characteristic peak that indicates the catalyst [Fe$_3$O$_4$@SiO$_2$@Vitamin C@Fe$_2$O$_3$] prepared possesses high purity.

3.5 VSM analysis

Superparamagnetic properties of [Fe$_3$O$_4$@SiO$_2$@Vitamin C@Fe$_2$O$_3$] were analyzed by

magnetometer (VSM) (**Fig. 5**). The magnetic catalyst is a superparamagnetic material due to the zero remanence and since hysteresis loop was not observed. This catalyst exhibits a high permeability in magnetization. Their magnetization is sufficient for magnetic separation by a simple external magnet.
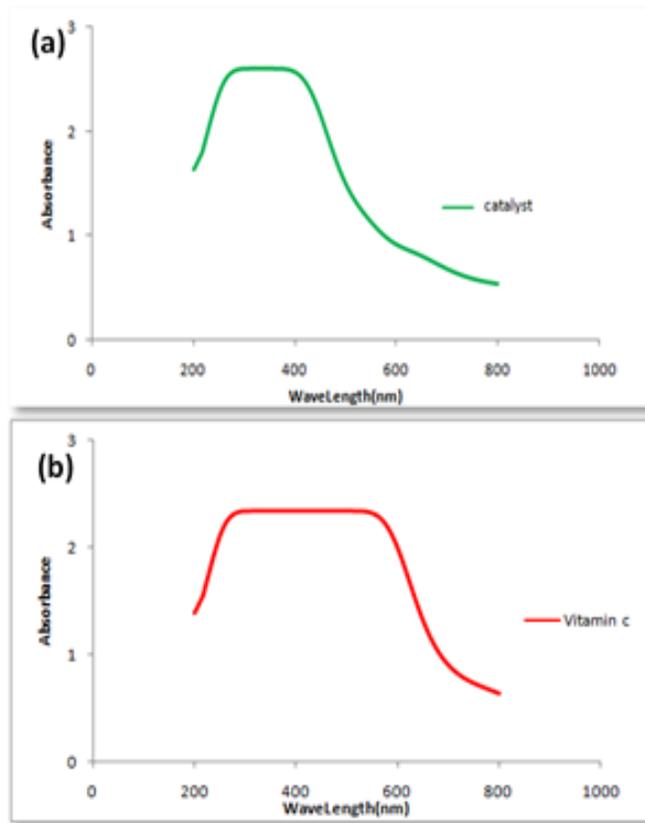

Fig. 4 UV-vis Spectra of (a) Fe$_3$O$_4$@SiO$_2$@Vitamin C@Fe$_2$O$_3$, (b) Vitamin C

3.6 EDS analysis

The EDS analysis clearly reveals the existence of the expected elements and the chemical composition in the structure of the catalyst, namely iron, oxygen, silicon, and carbon. Therefore, the above results fully confirmed the synthesis of the catalyst (**Fig. 6**).

3.7 Catalytic activity and optimization of the reaction conditions

We report a green synthesis and new method for one-pot synthesis of 3-amino-1aryl-1H-benzo[f]chromene-2-carbonitriles using Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 nano catalyst; Magnetite nanoparticles Fe_3O_4 was chosen as a solid support for the development of magnetic recyclability and ease of separation of the catalyst. Considering the agglomeration tendency of the nano-Fe_3O_4, we coated the magnetic nanoparticles with silica as a natural catalyst. Furthermore, vitamin C as a natural linker coated on nano-capsule in order to link with Fe_2O_3 and SiO_2[Fe_3O_4@SiO_2-Vitamin C- Fe_2O_3].
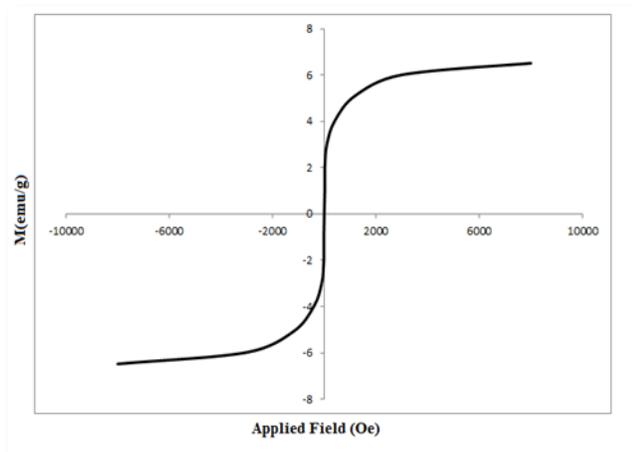

**Fig. 5** VSM diagram of Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 nanoparticles
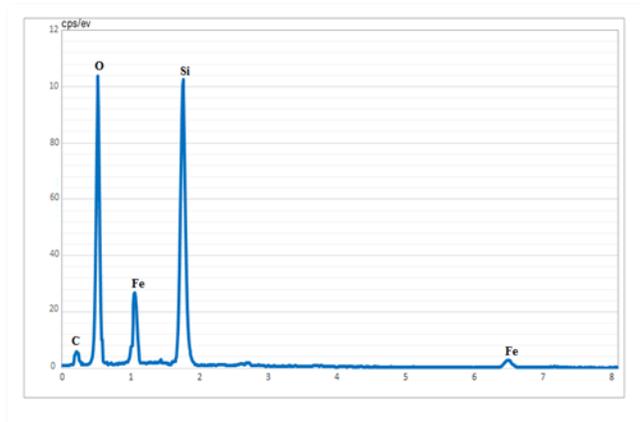
Fig 6. The EDS spectra of the Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 nanoparticles

After the synthesis of Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3, 3-amino-1aryl-1H-benzo[f]chromene-2-carbonitriles was chosen to optimize conditions such as, green solvent, type and amount of catalyst under ambient pressure at room temperature and grinding condition. We found that 0.027 g of [Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3] and water as solvent at room temperature was the optimum conditions for the synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles (**Table 1**). Therefore, the best result was obtained under mild reaction conditions, water as solvent, room temperature and atmospheric pressure.

According to **Table 1** the results of catalytic performance test revealed that, nano-Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 served as a highly efficient and easily recyclable catalyst for the efficacious one-pot synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile under mild condition in water as a green solvent at room temperature (**Table 1, entry 1**).

In order to study the generality of this new method, a variety of aldehydes containing electron-withdrawing and electron-donating groups were used for the synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile derivatives under the selected conditions. It was observed that a variety of aldehydes were successfully reacted with malononitrile and 2-naphthol by using Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 green catalyst to produce the corresponding 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile derivatives in excellent yields, short reaction times and with product's purity of 90-96% (**Table 2**).

The results of analysis and characterizations (SEM, EDS, VSM, and FT-IR) revealed that the catalytic activity is accomplished between each active layer supported on surface of core. It seems that the unique form of nanostructure gives the high catalytic performance of [Nano-Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3] due to the increase in the number of active surfaces between the layers in the Nano-Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3. Thus, the application of Nano-Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 improve the yield of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile derivatives.

3.8 Suggested mechanism for the synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles in the presence of Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 green catalyst

The reaction mechanism for the synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles in the

Table 1. Optimization of the reaction conditions for the synthesis of **-**amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile[a] under ambient pressure at room temperature.

Entry	Catalyst	Condition	Time (min)	Yield(%)[a]
1	Nano- $Fe_3O_4@SiO_2@Vitamin\ C@Fe_2O_3$ (0.027 g)	Room temperature /Water-grinding	30	94
2	Nano- $Fe_3O_4@SiO_2@Vitamin\ C@Fe_2O_3$ (0.027 g)	Room temperature /Solvent-free-grinding	30	90
3	Nano- $Fe_3O_4@SiO_2@Vitamin\ C@Fe_2O_3$ (0.01g)	Room temperature / Water-grinding	30	91
4	Nano- $Fe_3O_4@SiO_2@Vitamin\ C@Fe_2O_3$ (0.05g)	Room temperature / Water-grinding	30	94
5	----	Room temperature / Water-grinding	80	5
6	Fe_2O_3 (0.027 g)	Room temperature / Water-grinding	30	56
7	Nano-$Fe_3O_4@\ SiO_2@Vitamin\ C$ (0.027 g)	Room temperature / Water-grinding	30	82

a)   Isolated Yield.

Table 2. The green synthesis of 3-amino-1aryl-1H-benzo[f]chromene-2-carbonitriles[a,b] using $Fe_3O_4@SiO_2@Vitamin\ C@Fe_2O_3$ as a Green Catalyst

Entry	ArCHO	Product	Time(min)	Yield(%)	M.p (°C)	M.p.(°C) [Rf]
1		**4a**	30	94	277-278	278 [22]
2		**4b**	22	96	184-186	186 [24]

3	O₂N—CHO	**4c**	25	96	284-285	283–284 [24]
4	F—CHO	**4d**	26	96	236-238	231–232 [27]
5	Cl—CHO	**4e**	26	96	206-208	209–210 [27]
6	CHO (2-Cl)	**4f**	26	96	270-272	270–271 [27]
7	Br—CHO	**4g**	26	95	241-242	238-240 [28]
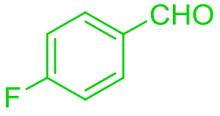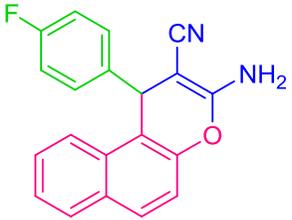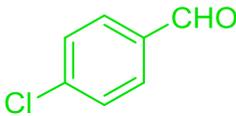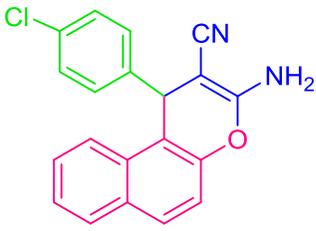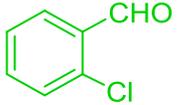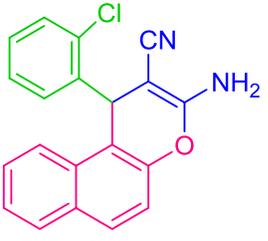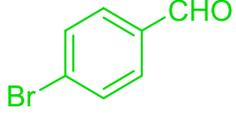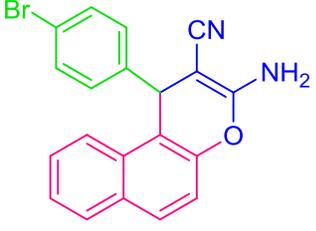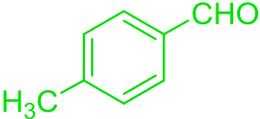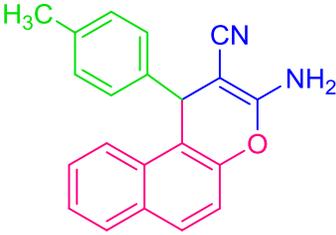
8		**4h**	40	90	273-275	270–271[27]
9		**4i**	30	95	290-292	289–291 [29]
10		**4j**	44	90	180-182	181 [22]
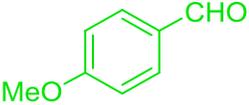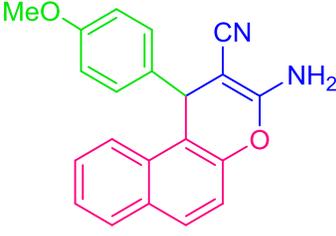
a Reaction conditions: 2-naphthol (1mmol), benzaldehyde (1mmol), malononitrile (1mmol), Fe₃O₄@SiO₂@Vitamin C@Fe₂O₃ green catalyst (0.027 g), Water/ room temperature
b isolated yields

presence of $Fe_3O_4@SiO_2@$Vitamin C@Fe_2O_3 smart green catalyst proposed in **Scheme 3** and reaction mechanism was compared to the literature [30].

According to this mechanism, firstly, carbonyl group of the aldehyde (**1**) is activated in the presence of [$Fe_3O_4@SiO_2@$Vitamin C@Fe_2O_3]. Then this activated carbonyl group is attacked by nucleophilic compound **2** to give key intermediate **5**. Then, compound **5** is attacked by 2-naphthol (**3**) in the Michael manner and follows neutralization, cyclization, and tautomerization to give the final product **4**.

3.9 Comparison of catalytic activity of $Fe_3O_4@SiO_2@$Vitamin C@Fe_2O_3 with some different catalysts reported for the synthesis 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles

In the present research the catalytic activity of $Fe_3O_4@SiO_2@$Vitamin C@Fe_2O_3 was investigated in the synthesis of 3-amino-1aryl-1H-benzo[f]chromene-2-carbonitriles at room temperature and water as a green solvent. The catalytic efficacy of the present method was compared to some of the previously reported methods in the synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles (**Table 3**). As shown in **Table 3**, it can be seen that the reaction is more efficient in the presence of $Fe_3O_4@SiO_2@$Vitamin C@Fe_2O_3 and also this method is superior in terms of the reaction temperature and yields. According to **Table 2**, most of the earlier reported methods require high-temperature synthesis (Reflux and Microwave) or using ultrasonic to assure comparable yields of the products, long reaction times or tedious workup. Also, other methods need catalysts that are mainly non recyclable.

As shown in **Table 3**, this green method is more superior, cleaner and more efficient in the presence of $Fe_3O_4@SiO_2@$Vitamin C@Fe_2O_3 than the comparable

previously reported methods. Also, the reaction in this research describes the catalytic activity of a nano-composite made of the materials which are readily available and quite prevalent in nature.

3.10 Catalyst stability and recyclability

The nano-catalyst is stable under the synthetic conditions, and it can be reused several times without

any reduction in its catalytic activity (**Fig. 7**). Also, the product yield remained nearly unchanged after using the recovered catalyst which may be due to the stability of the nanoparticles. In fact, if the nanoparticles had just adsorbed on the surface of the nano-capsules, the catalyst should have been deactivated in the subsequent runs.
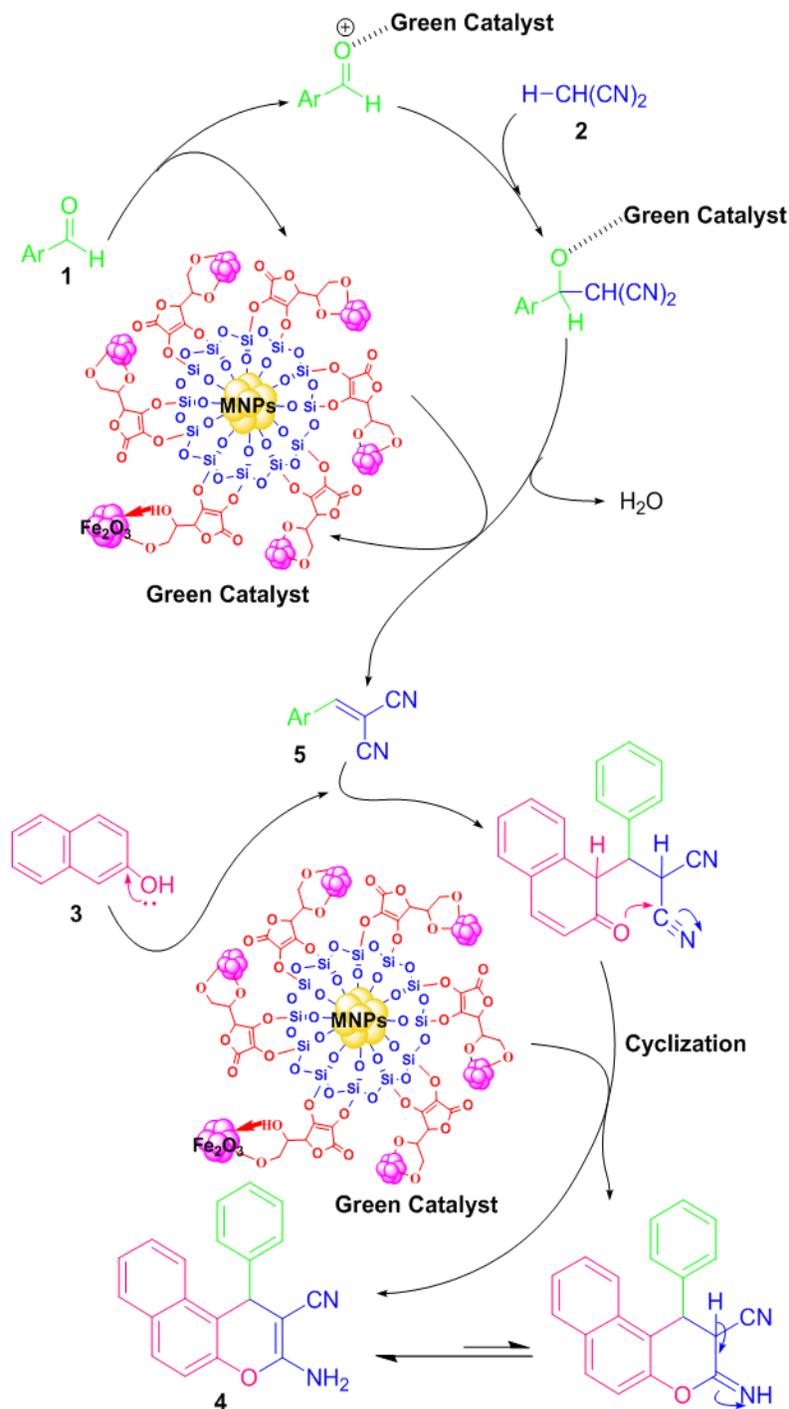
Scheme 3 Clean synthesis of 3-amino-1aryl-1H-benzo[f]chromene-2-carbonitriles using $Fe_3O_4@SiO_2@Vitamin C@ Fe_2O_3$ (NC@VC@Fe₂O₃) Green Catalyst

Table 3. Comparison of the catalytic efficiency of Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 to some reported catalysts for the synthesis of 3-amino-1aryl-1H-benzo[f]chromene-2-carbonitriles

Entry	Catalyst	Solvent	Reaction condition	Time	Yield (%)	Ref.
1	Fe_3O_4@SiO_2@Vitamin C@ Fe_2O_3 NPs	Water	*Room temperature*	30 min	94	This work
2	$Fe(HSO_4)_3$	MeCN	Refluxed	4.5 h	86	[22]
3	NiFe2O4@propyl-Pip	Solvent-free	110ºC	40 min	95	[23]
4	KF	Solvent-free	110ºC	5 min	95	[24]
5	TPOP-2	Water	80 ºC	6h	87	[31]
7	MOF-5	Solvent-free	80 ºC	40 min	80	[32]
8	Nano-sawdust–BF_3	EtOH,	Reflux	20 min	92	[33]
9	PTO	EtOH	Ultrasound bath sonicator at 40 kHz frequency and 40 ºC	20 min	90	[34]
10	CTABr	H_2O	Ultrasound Irradiation/r.t.	2.5 h	78	[35]
11	3-hydroxypropanaminium acetate	Solvent-free	70 ºC	7min	82	[36]
12	Piperazine	Solvent-free	Microwave irradiation	8 min	84	[37]
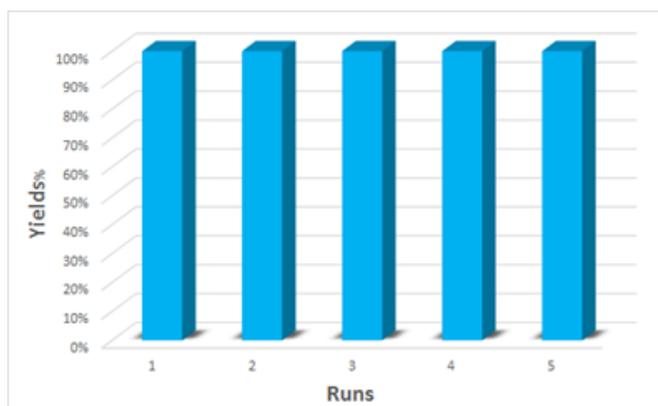
Fig. 7 Catalyst reusability

4. Conclusions

This research presented a clean strategy and green method in preparation of Fe_3O_4@SiO_2@Vitamin C@Fe_2O_3 as a green catalyst and a new method for the green synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles derivatives in water as solvent at room temperature in excellent yields, which makes this procedure an excellent alternative to the available methodologies.

References

[1] S. Sajjadifar, I. Amini, M. Karimian, Iran. J. Catal. 11 (2021) 59-67.
[2] E. Babaei, B. Mirjalili, Iran. J. Catal. 10, (2020) 219-226.
[3] F. Hasanzadeh, F. K. Behbahani, Russ. J. Org. Chem. 56 (2020) 1070 –1076.
[4]. J. Safaei-Ghomi, R. Teymuri, *Iran. J. Catal. 11, 2021, 113-123*.
[5] Z. Jalili, R. Tayebee, F, M. Zonoza. RSC Adv. 11 (2021) 18026-18039.
[6]. M. Jafarpour, A. Rezaeifard, M. Ghahramaninezhad, F. feizpour, Green Chem. 17 (2015) 442-452.
[7] M. Hakimi, M. Alikhani, Inorg Organomet Polym Mater. 30 (2020) 504–512.
[8] M. Blanco, D. Mosconi, C. Tubaro, A. Biffis, D. Badocco, P. Pastore, M. Otyepka, A. Bakandritsos, Zh. Liu, W. Ren, S. Agnoli, G. Granozzi, Green Chem. 21 (2019) 5238-5247.
[9] N. Khatun, A. Gogoi, P. Basu, P. Das, B. K. Patel, RSC Adv. 4 (2014) 4080-4084.

[10] Y. Zhao, Y. Kang, H. Li, H. Li, Green Chem. 20 (2018) 2781-2787.

[11] N. Tandon, Sh. M. Patil, R. Tandon, P. Kumara, RSC Adv. 11 (2021) 21291-21300.

[12] R. Li, J. Zhao, F. Yang, Y. Zhang, D. Ramella, Y. Peng, Y. Luan, RSC Adv. 7 (2017) 51142 -51150.

[13] J. Zhou, Y. Li, H. Sun, Zh. Tang, L. Qi, L. Liu, Y. Ai, Sh. Li, Z. Shao, Q. Liang, Green Chem. 19 (2017) 3400-3407.

[14] M. Kazemnejadi, M. A. Nasseri, S. Sheikh, Z. Rezazadeh, S. Ameneh Alavi Gol, RSC Adv, 11 (2021)15989-16003.

[15] J. Afsar, M. Ali Zolfigol, A. Khazaei, *ChemistrySelect.,* **3** (2018) 11134– 11140.

[16] Aqeel Ashraf, M.; Liu, Zh.; Li, Ch.; Zhang, D. *Synth. Commun*. 50 (2020) 2629-2646.

[17] J. Zeng, F. Yi, M. Cai, *Synth. Commun*. 50 (2020) 1936-1945

[18] S. Veysipour, M. Nasr-Esfahani, Z. Rafiee, B. Eftekhari far, *Iran. J. Catal. 11, (2021), 125-136.*

[19] N. Orooji, A. Takdastan, R. Jalilzadeh Yengejeh, S. Jorfi, A. H. Davami, Res. Chem. Intermed. 46 (2020) 2833-2857.

[20] L. Chen , Ch. Lin , Y. Lan , Zh. Li , D. Huang , W. Yang ,Y. Li, Environ. Chem. Lett. 18 (2020) 2157–2163.

[21] Z. Abshirini, A. Kohzadian, Z. paryav, A. Zar, Iran. J. Catal. 9, (2019), 251-257.

[22] H. Eshghi, S. Damavandi, G. H. Zohuri, Inorg, Nano-Met. Chem. 41 (2011) 1067-1073.

[23] B. Pourhasan, A. Mohammadi-Nejad, J Chin Chem Soc. 66 (2019) 1356-1362.

[24] B. Maleki, S. Sheikh, Org. Prep. Proced. Int. 47 (2015) 368–378.

[25] Y. S. Kang, S. Risbud, J. F. Rabolt, P. Stroeve, Chem. Mater. 8 (1996) 2209 –2211.

[26] L. Zhang, H Shao, H Zheng, T Lin, Zh Guo, Int. J. Miner. Metall. Mater. 23 (2016) 1112.

[27] K. Gong, H. L.Wang, D. Fang, Z. L. Liu, Catal. Commun. 9 (2008) 650–653

[28] M.G. Dekamin, M. Eslami, A. Maleki, Tetrahedron. 69 (2013) 1074-1085.

[29] A. R. Moosavi-Zare, M. A. Zolfigol, O. Khaledian, V. Khakyzadeh, M. Darestani farahani, M.H Beyzavi, H. Gerhardus Kruger, Chem. Eng. Technol. 248 (2014) 122–127.

[30] K. Azizi, M. Karimi, H.Reza Shaterian and A. Heydari, RSC Adv. 4 (2014) 42220-42225.

[31] S. K. Kundu, A. Bhaumik, RSC Adv. 5 (2015) 32730-32739.

[32] Z. Arzehgar, V. Azizkhani, S. Sajjadifara, M. H. Fekri, Chem. Methodol. 3 (2019) 251-260

[33] B. Sadeghi, I. Zarepour, J Nanostruct Chem. 5 (2015) 305–311

[34] A.P. Manake, S.R. Patil , V. Patil, Mater. Today: Proc. 26 (2020) 3487-3491

[35] T. Jin, J. Xiao, S. Wang, T.Li, Ultrason Sonochem. 11 (2004) 393–397.

[36] H. R Shaterian, M, Mohammadni, Res Chem Intermed 41 (2015) 1301–1313

[37] A. Mobinikhaledi, H. Moghanian, F. Sasani, Inorg. Nano-Met. Chem. Inorg nano-met. 41(2011) 262–265.