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One-pot sonochemical synthesis of benzopyranophenazines using nano Fe_3O_4@ PAA-SO_3H

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ABSTRACT

A proper, atom-economical, straightforward one-pot multicomponent synthetic route for the synthesis of benzopyranophenazines has been presented by the reaction of hydroxynaphthoquinone, *o*-phenylenediamine, benzaldehydes, and malononitrile with crosslinked sulfonated polyacrylamide (Cross-PAA-SO_3H) attached to nano-Fe_3O_4 as an efficient heterogeneous solid acid catalyst under ultrasonic irradiations in ethanol. Experimental simplicity, wide range of products, excellent yields in short reaction times and applying the sonochemical methodology as an efficient method and innocuous means of activation in synthetic chemistry for the preparation of medicinally privileged heterocyclic molecules are some of the important features of this method. The present catalytic procedure is extensible to a wide diversity of substrates for the synthesis of a variety-oriented library of benzopyranophenazines.

***Keywords**: Ultrasonic irradiation, Sulfonated polyacrylamide, Pyranophenazines, Catalytic activity, Nano-Fe_3O_4.*

1. Introduction

Phenazines possess many biological activities such as anti-tumor [1], antimycobacterial [2], anti-proliferative [3], antibiotics [4], antifungal [5], and anti-inflammatory [6]. Some phenazines isolated from *Streptomyces* (a marine bacterium) have been described with biological significance (Fig. 1) [7-10]. Finding effective methods for the synthesis of phenazines through multicomponent reactions (MCRs) is a significant area of research in organic and medicinal chemistry. Recently, reports have been developed in the synthesis of phenazines using *p*-TSA [11], glacial acetic acid [12], 1,4-diazabicyclo[2.2.2]octane (DABCO) [13,14], thiourea-based organocatalysts [15], caffeine [16], theophylline [17], L-proline [18], 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH) [19], Et_3N [20], pyridine [21], oxalic acid [22] and nano-CuO [23]. However, some of the reported methods endure drawbacks including long reaction times, generate a large amount of waste, unpleasant reaction conditions, use of toxic and non-reusable catalyst. Therefore, to avoid these restrictions, the discovery of an efficient and retrievable catalyst with high catalytic activity for the synthesis of benzopyranophenazines is still favored. The modifying crosslinked polyacrylamides makes them attractive objects in chemistry and polymer science [24-26]. Sulfonated Polyacrylamides have unique characteristics such as high strength, hydrophilicity, and proton conductivity [27,28]. Recently, magnetic nanoparticles (MNPs) have been successfully utilized to immobilize enzymes, polymers, transition metal catalysts and organocatalysts [29,30]. We wish to report, herein, an efficient procedure for the preparation of benzopyranophenazines with the one one-pot four-component reaction of hydroxy naphthoquinone, *o*-phenylenediamine, benzaldehydes, and malononitrile with Nano Fe_3O_4@ PAA-SO_3H as a new catalyst under ultrasonic irradiations (Scheme 1). The ultrasound procedure decreases times, increases yields of title products by creating the activation energy in micro surroundings [31-36].

2. Experimental

2.1. Chemicals and apparatus

^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 MHz spectrometers in the presence of tetramethylsilane as the internal standard.

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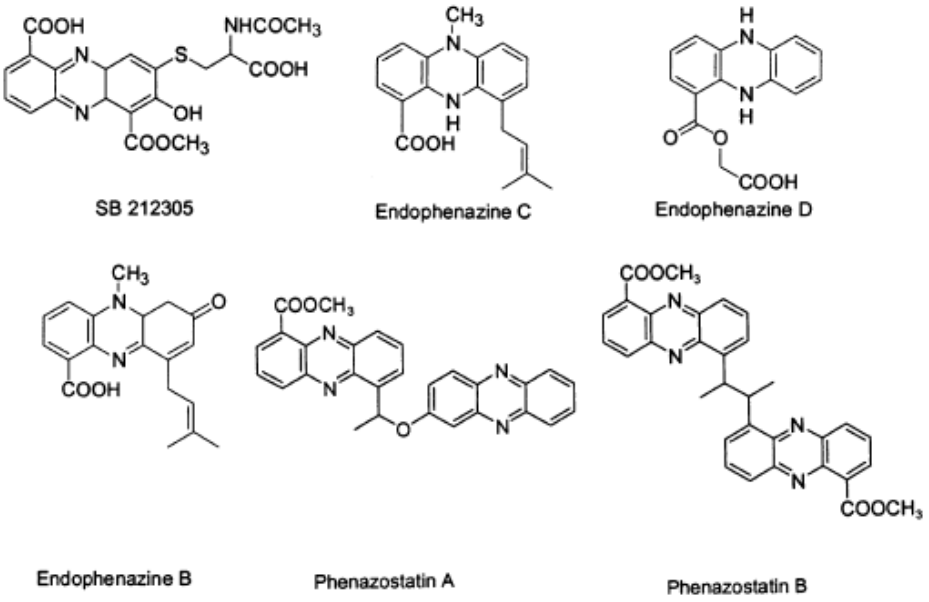


Fig. 1. Some phenazines isolated from *Streptomyces.*

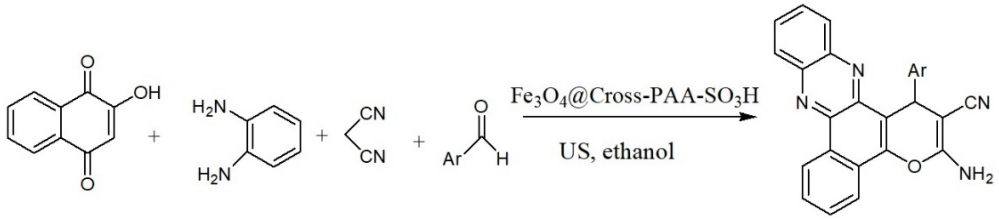
FT-IR spectra were recorded with KBr pellets by a Magna-IR, spectrometer 550 Nicolet. CHN compositions were measured by Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with monochromatized Cu Kα radiation (λ = 1.5406 Å). Microscopic morphology of nanocatalyst was visualized by SEM (MIRA3). The thermogravimetric analysis (TGA) curves are recorded using a V5.1A DUPONT 2000. The magnetic property of magnetite nanoparticle has been measured with a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co.; Kashan Kavir; Iran) at room temperature.

2.2. Preparation of Crosslinked Sulfonated Polyacrylamide (Cross-PAA-SO_3H):

In a round-bottom flask (200 mL) equipped with magnetic stirrer and condenser, 5 g of acrylamid (AAM) (70 mmol) and 5.17 gr of 2-acryloylamino-2-methylpropane-1-sulfonic acid (25 mmol) (AAMPS), (approximately AAM/AAMPS (3/1)) and 0.77 gr of N,N-methylene-bis-acrylamid (NNMBA) (5 mmol) as a crosslinking agent and benzoyl peroxide as an initiator were added to 80 mL EtOH under reflux condition for 5 h. After completion of the reaction, the white precipitate was formed, filtered, washed and dried in a vacuum oven in 70 ℃ for 12 h [37,38]. The weight of the polymer was 10.1 gr with the yield of 91.8 %.

2.3. Preparation of Crosslinked Sulfonated Polyacrylamide@nano-Fe_3O_4

1 gr of synthesized polymers was poured in a 100 mL round bottom flask under stirring at room temperature, then 50 mL HCl (0.4 M) was added to it. Our target molecules were synthesized by a magnetic nanocatalyst with the mass ratio of polymer/nano-Fe_3O_4 = 2/1. So, 0.43 g (2.1 mol) $FeCl_2.4H_2O$ and 1.17 g (2×2.1) $FeCl_3.6H_2O$ were added and the mixture was stirred until dissolved completely (flask1). In another 500 mL round-bottom flask no 2, 400 mL aqueous solution of NH_3 (0.7M) was poured under argon gas. Then flask 1 was added to the flask 2 immediately. Nanocatalyst was filtered and washed with water (2×25 mL) and dried in oven on 50 ℃. The catalyst has been characterized by FT-IR, SEM, XRD, EDS, TGA and VSM.



Scheme 1. Synthesis of benzopyranophenazines using Nano Fe_3O_4@ PAA-SO_3H.

This catalyst was characterized with infrared spectroscopy and back titration acid-base to confirm sulfonation and determine accurate sulfonation levels. The concentration of sulfonic acid groups was quantitatively estimated by back titration using HCl (0.01 N). 2 mL of KOH (0.01 N) was added to 0.02 g of the magnetic nanoparticles and the mixture was stirred for 30 min. The catalysts were magnetically separated and washed with deionized water. The excess amount of KOH was titrated with HCl (0.01 N) in the presence of phenolphthalein as an indicator. Averages of 3 separate titrations were performed to obtain an average value for the acid amount of Nano Fe_3O_4@ PAA-SO_3H. The results revealed that the samples of Nano Fe_3O_4@ PAA-SO_3H possessed 0.74 mmol g-1 acid amount.

2.4. General procedure for the preparation of benzopyranophenazines

A mixture of hydroxynaphthoquinone (1 mmol), *o*-phenylenediamine (1 mmol) aldehydes (1 mmol) and malononitrile (1.5 mmol) and Cross-PAA-SO_3H@nano-Fe_3O_4 (8 mg) in EtOH (15 mL) was sonicated at 40 W power for the appropriate times. The progress of the reaction was monitored by TLC (EtOAc/*n*-hexane 2:1). After completion of the reaction, the mixture was cooled to room temperature and nanocatalyst was easily separated using an external magnet. The solvent was evaporated and the obtained solid was filtered and then washed with EtOH and water (ratio: 5:5). The pure products were characterized by comparison of their physical data (melting points, IR, and H NMR) with those of known compounds in the literature.

Selected spectral data

3-Amino-1-(4-cyano-phenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (**5h**):

Yellow solid. m.p.= 288-290 °C. IR (KBr): $\bar{\nu}$= 3322, 3176, 3045, 2831, 2182, 2139, 1644, 1622, 1584, 1483, 1455, 1444, 1392, 1383, 1355, 1337, 1292, 1256, 1160 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ= 5.42 (s, 1H, CH), 7.23 (s, 2H, NH_2), 7.38 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.42 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.83-8.08 (m, 4H, Ar-H), 8.12-8.15 (m, 1H, Ar-H), 8.17-8.22 (m, 1H, Ar-H), 8.42 (d, 1H, *J* = 7.6 Hz, Ar-H), 9.17 (d, 1H, *J* = 7.2 Hz, Ar-H) ppm. ^{13}C NMR (100MHz, DMSO-d_6): δ= 37.3, 57.9, 113.8, 115.3, 118.3, 122.1, 124.3, 125.5, 126.3, 127.8, 128.2, 128.6, 129.0, 129.2, 130.1, 130.3, 130.6, 130.8, 139.9, 140.1, 140.7, 141.4, 145.6, 146.5, 159.5 ppm. Anal. Calcd. for $C_{27}H_{15}N_5O$: C, 76.22; H, 3.55; N, 16.46; Found: C, 76.18; H, 3.43; N, 16.35.

3- Amino-1- (4- methoxy- phenyl)- 1H- benzo[a]pyrano [2,3-c]phenazine-2-carbonitrile (**5m**):

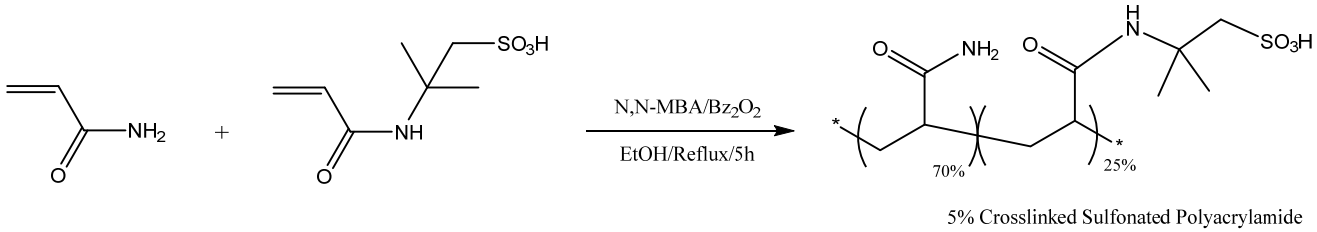
Yellow solid. m.p.= 268-269 °C. IR (KBr): $\bar{\nu}$= 3315, 3174, 3048, 2829, 2180, 1652, 1620, 1585, 1487, 1465, 1450, 1394, 1384, 1350, 1330, 1293, 1258, 1163 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ= 3.84 (s, 3H, OCH_3), 5.83 (s, 1H, CH), 6.65 (d, 2H, *J* = 7.6 Hz, Ar–H), 6.90 (d, 2H, *J* = 7.6 Hz, Ar–H), 7.35 (s, 2H, NH_2), 7.85-7.93 (m, 4H, Ar–H), 7.98-8.40 (m, 3H), 9.10 (d, 1H, *J* = 8.0 Hz, Ar–H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ= 37.5, 55.2, 58.3, 112.1, 115.2, 115.5, 120.2, 120.4, 121.4, 125.2, 127.0, 129.1, 129.3, 129.7, 130.1, 130.5, 130.8, 130.9, 140.3, 141.2, 141.9, 146.4, 147.3, 159.4, 160.5 ppm. Anal. Calcd. for $C_{27}H_{18}N_4O_2$: C, 75.34; H, 4.21; N, 13.02; Found: C, 75.25; H, 4.15; N, 12.93.

3. Results and Discussion

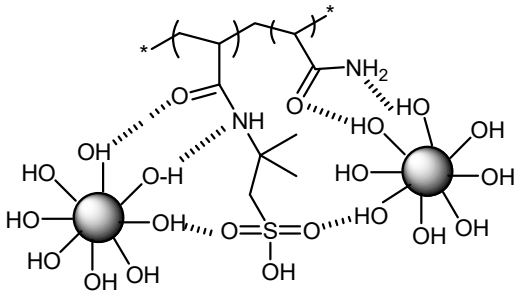
3.1. Characterization of the nanocatalyst

In this study, we synthesized the crosslinked sulfonated polyacrylamide (Cross-PAA-SO_3H) with simultaneous radical co-polymerization in the presence of an initiator and a crosslinking agent. Also, a schematic illustration of the reaction is shown in Scheme 2 and Scheme 3 [39-42]. The FT-IR absorbance spectra of the dried crosslinked sulfonated polyacrylamide (poly AAM-*co*-AAMPS), Fe_3O_4 and Cross-PAA-SO_3H@nano-Fe_3O_4 are shown in Fig. 2. The N–H stretching vibration of the amide groups in AAm and AAMPS and overlapping O–H stretching vibration of a sulfonic acid group in AAMPS are observed in the region 3100–3500 cm^{-1}. The strong absorption band in the 1658 cm^{-1} can be attributed to the stretching vibrations of C=O groups in both AAm and AAMPS. Secondary amide band of AAMPS unit has a peak in 1545 cm^{-1}. The sharp peak at 1042 cm^{-1} is related to the sulfonic acid (–SO_3H) group. The symmetric band of SO_2 is observed in the 1178-1216 cm^{-1}. The band at 1453 cm^{-1} is assigned to the stretching vibration of the C–N bond (amide) and the asymmetric bending of the C–H bond in methyl groups of AMPS [37,38]. The absence of the olefinic band at 1620–1635 cm^{-1} confirms that there is no residual monomer in the system. The results in Fig. 2 (c) suggest the integration of Fe_3O_4 NPs and Cross-PAA-SO_3H.

The particle size and morphology of Nano Fe_3O_4@PAA-SO_3H was determined by SEM. The statistics of results from SEM images clearly demonstrated that the average size of Cross-PAA-SO_3H@nano-Fe_3O_4 is about 7-25 nanometers (Fig. 3).



Scheme 2. Preparation of crosslinked sulfonated polyacrylamide (Cross-PAA-SO_3H).



Scheme 3. A schematic illustration for the formation of Nano Fe_3O_4@PAA-SO_3H.

The XRD pattern agrees well with the reported pattern for Fe_3O_4 (JCPDS No. 75-0449). The crystallite size of Nano Fe_3O_4@PAA-SO_3H calculated by the Debye–Scherer equation is about 20-25 nm, in good agreement with the result obtained by SEM (Fig. 4).

An EDS (energy dispersive X-ray) spectrum of Nano Fe_3O_4@PAA-SO_3H (Fig. 5) shows that the elemental compositions are carbon, oxygen, sulfur, iron and nitrogen.

The magnetic properties of nano-Fe_3O_4 and Nano Fe_3O_4@PAA-SO_3H were determined with the help of a vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping between ±10,000 Oe (Fig. 6).

The amount of saturation-magnetization for nano-Fe_3O_4 and Cross-PAA-SO_3H@nano-Fe_3O_4 is 57.2 emu/g and 26.8 emu/g. These results demonstrate that the magnetization property decreases by coating and functionalization.

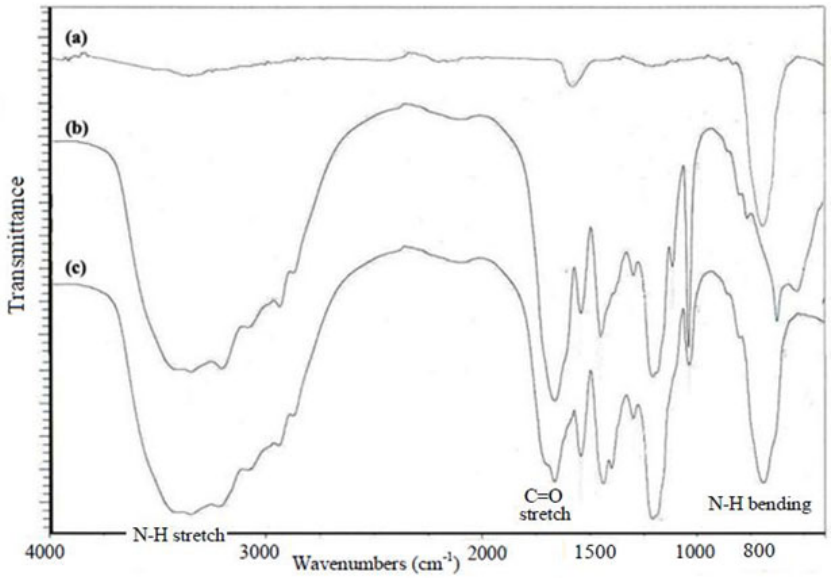


Fig. 2. The FT-IR spectra of (a) Fe_3O_4 NPs, (b) Cross-PAA-SO_3H and (c) Cross-PAA-SO_3H@ nano-Fe_3O_4.

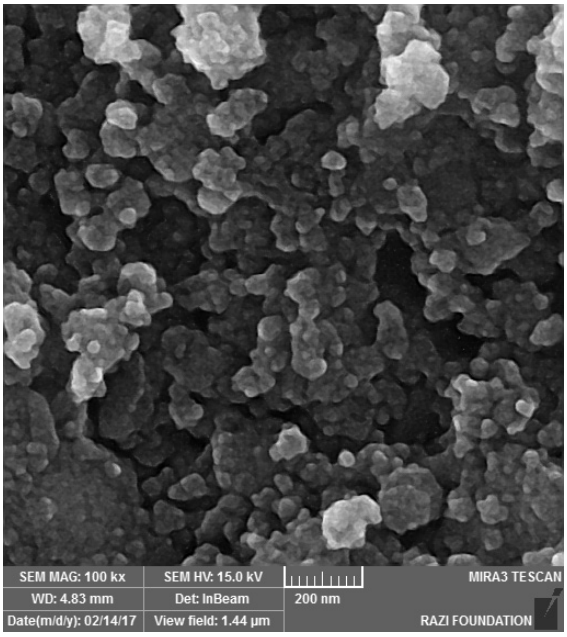


Fig. 3. SEM image of Nano Fe_3O_4@ PAA-SO_3H.

Thermogravimetric analysis (TGA) evaluates the thermal stability of the Nano Fe_3O_4@ PAA-SO_3H. These nanoparticles show suitable thermal stability without a significant decrease in weight (Fig. 7). The weight loss at temperatures below 200 °C is due to the removal of physically adsorbed solvent and surface hydroxyl groups. The curve shows a weight loss of 20 % from 250 to 600 ºC, resulting from the decomposition of the organic spacer grafting to the nano-Fe_3O_4 surface.

The amount of PAA-SO_3H grafted onto the Fe_3O_4 was calculated through the following equation [43,44] using the nitrogen content of Nano Fe_3O_4@ PAA-SO_3H from EDS analysis:

$$\text{Amount (mol g}^{-1}) = \frac{\left[\frac{wt\times 100}{X}\right]\times\left[\frac{100}{100-\left(wt\times\frac{100}{X}\right)}\right]}{Y}$$

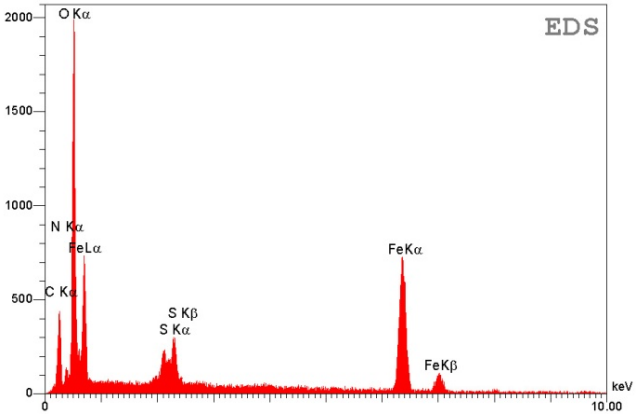


Fig. 5. EDS spectrum of Nano Fe_3O_4@ PAA-SO_3H.

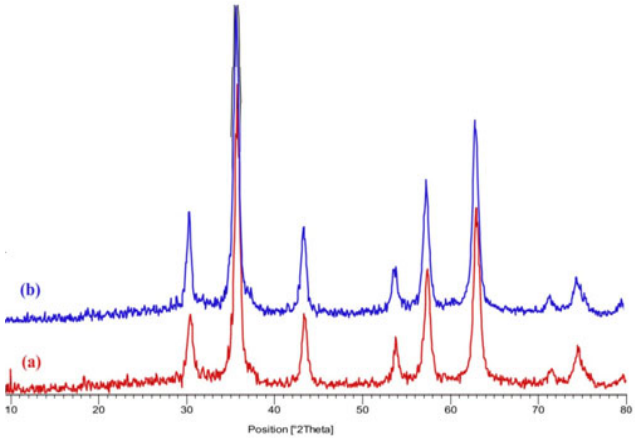


Fig 4. The XRD pattern of (a) Fe_3O_4 (b) Nano Fe_3O_4@PAA-SO_3H.

Where Wt is the weight percent of the element measured, X is the theoretical weight percent of the element in the molecule Y is the theoretical molecular weight of the molecule. PAA-SO_3H has carbon, hydrogen, nitrogen and sulfur contents. Based on this equation, the amount of PAA-SO_3H detected from the nitrogen content is 0.85 mol g^{-1}.

3.2. Catalytic Behaviors of Cross-PAA-SO_3H@nano-Fe_3O_4 for the Synthesis of benzopyranophenazines

Initially, we focused on the systematic evaluation of different catalysts for the model reaction of hydroxynaphthoquinone, *o*-phenylenediamine, 4-chlorobenzaldehyde, and malononitrile under different conditions. To obtain the ideal reaction conditions for the synthesis of compound **5b**, we studied some other catalysts and solvents which are shown in Table 1.

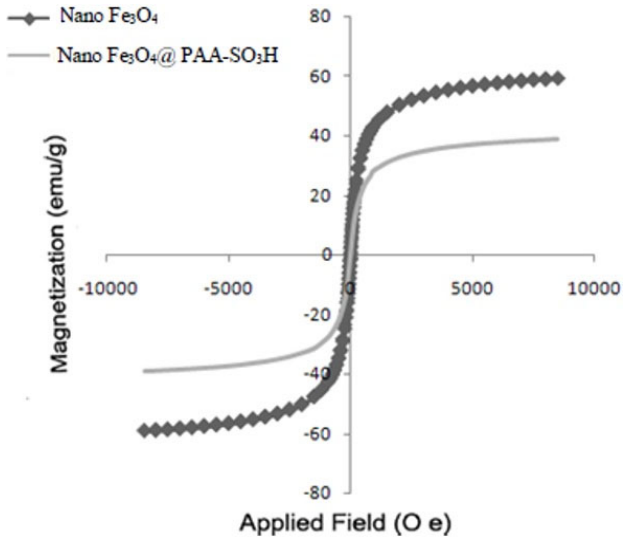


Fig. 6. The VSM curve of: (a) nano-Fe_3O_4 and (b) Nano Fe_3O_4@ PAA-SO_3H.

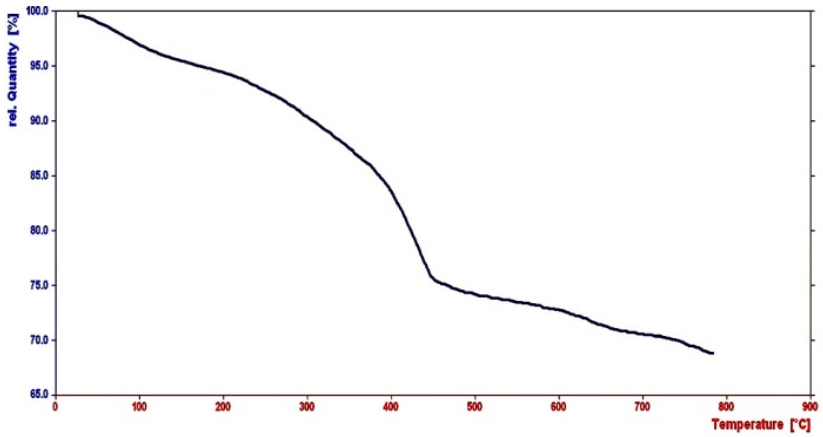


Fig. 7. TGA curve of Nano Fe_3O_4@ PAA-SO_3H.

Screening of diverse catalysts such as $NiCl_2$, imidazole, $ZrOCl_2$, *P*-TSA, nano-Fe_3O_4 and Cross-PAA-SO_3H@nano-Fe_3O_4 revealed Cross-PAA-SO_3H@nano-Fe_3O_4 (8 mg) as the most effective catalyst to perform this reaction under ultrasonic irradiations (40 W) in ethanol. The results illustrated that the sonication certainly affected the reaction system. It could reduce the reaction time and increase the yield of the products. When the reaction was carried out under reflux conditions, it gave low yields of products and took longer reaction times, while the same reaction was carried out under ultrasonic irradiation to give excellent yields of products in short reaction times. The results show the present catalytic method is extensible to a wide diversity of substrates to create a variety-oriented library of benzopyranophenazines.

Table 1. Optimization of reaction conditions using different catalysts under different conditions.[a]

Entry	Solvent (conditions)	Catalyst	Time (min)	Yield (%)[c]
1	EtOH (reflux)	No catalyst	500	trace
2	EtOH (reflux)	$NiCl_2$ (5 mol%)	500	45
3	EtOH (reflux)	$ZrOCl_2$ (5 mol%)	600	48
4	EtOH (reflux)	Imidazole (7 mol%)	400	35
5	EtOH (reflux)	*p*-TSA (8 mol%)	200	52
6	EtOH (reflux)	Nano-Fe_3O_4 (7 mol%)	250	48
7	H_2O (reflux)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (15 mg)	150	45
8	DMF (reflux)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (15 mg)	150	50
9	CH_3CN (reflux)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (15 mg)	150	62
10	EtOH (reflux)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (15 mg)	150	72
11	H_2O (US: 40 W)[b]	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (10 mg)	15	55
12	DMF (US: 40 W)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (10 mg)	15	65
13	CH_3CN (US: 40 W)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (10 mg)	15	77
14	EtOH (US: 20 W)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (8 mg)	15	73
15	EtOH (US: 30 W)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (8 mg)	10	85
16	EtOH (US: 40 W)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (8 mg)	10	95
17	EtOH (US: 50 W)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (8 mg)	10	95
18	EtOH (US: 40 W)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (6 mg)	10	88
19	EtOH (US: 40 W)	Cross-PAA-SO_3H attached to nano-Fe_3O_4 (10 mg)	10	95

[a]Reaction conditions: 2-hydroxynaphthalene-1,4-dione (1 mmol), *o*-phenylenediamine (1 mmol), 4- chlorobenzaldehyde (1 mmol), and malononitrile (1.5 mmol) as a model reaction.
[b]Ultrasonic irradiation.
[c]Isolated yield.

From the above observation, it is important to mention that electron-withdrawing groups increased the rate of reaction and gave better yields than that with electron-donating groups. Several functional groups, such as Cl, OMe, CN, and CH_3, are compatible under the reaction conditions. Interestingly, a variety of aromatic aldehydes, including *ortho*, *meta* and *para*-substituted aryl aldehydes, participated well in this reaction and gave the corresponding products in a good to excellent yield (Table 2). In addition, we examined aliphatic aldehydes such as *n*-pentanal instead of arylaldehydes in the reaction, but we could not find the considerable amount of the title product from aliphatic aldehydes.

We investigated reusability of the Cross-PAA-SO_3H@nano-Fe_3O_4 as the catalyst for the preparation of product **5b** and it was found that product yields reduced to a small extent on each reuse (run 1, 95%; run 2, 95%; run 3, 94%; run 4, 94%; run 5, 93%, run 6, 92%). After completion of the reaction, the nanocatalyst was easily separated using an external magnet. The catalyst was washed four times with ethanol and dried at room temperature for 24 h.

To compare the efficiency of Nano Fe_3O_4@ PAA-SO_3H with the reported catalysts for the synthesis of benzopyranophenazines, we have tabulated the results in Table 3. As Table 3 indicates, Nano Fe_3O_4@ PAA-SO_3H is superior to the reported catalysts in terms of reaction time, yield and conditions. As expected, the increased surface area due to small particle size increased the reactivity of catalyst. This factor is responsible for the accessibility of the substrate molecules on the catalyst surface.

Table 2. Synthesis of benzopyranophenazine derivatives.

Entry	R (aldehyde)	Product	Time (min)	Yield (%)[a]	m.p. (°C)	
					Found	Reported[b]
1	H	**5a**	10	90	297-300	298-300
2	4-Cl	**5b**	10	95	290-292	288-290
3	2-Cl	**5c**	10	92	299-302	301-303
4	4-Br	**5d**	10	96	282-284	283-285
5	4-F	**5e**	10	97	273-276	274-276
6	2-NO_2	**5f**	10	92	277-281	278-279
7	3-NO_2	**5g**	10	92	280-282	281-283
8	4-CN	**5h**	10	91	288-290	-
9	4-NO_2	**5i**	15	95	261-263	261-263
10	4-Me	**5j**	15	84	293-295	293-294
11	2-OMe	**5k**	15	80	268-270	270-272
12	3-OMe	**5l**	15	82	239-241	240-242
13	4-OMe	**5m**	15	80	268-269	-
14	2,4-dichloro	**5n**	10	96	306-309	308-310

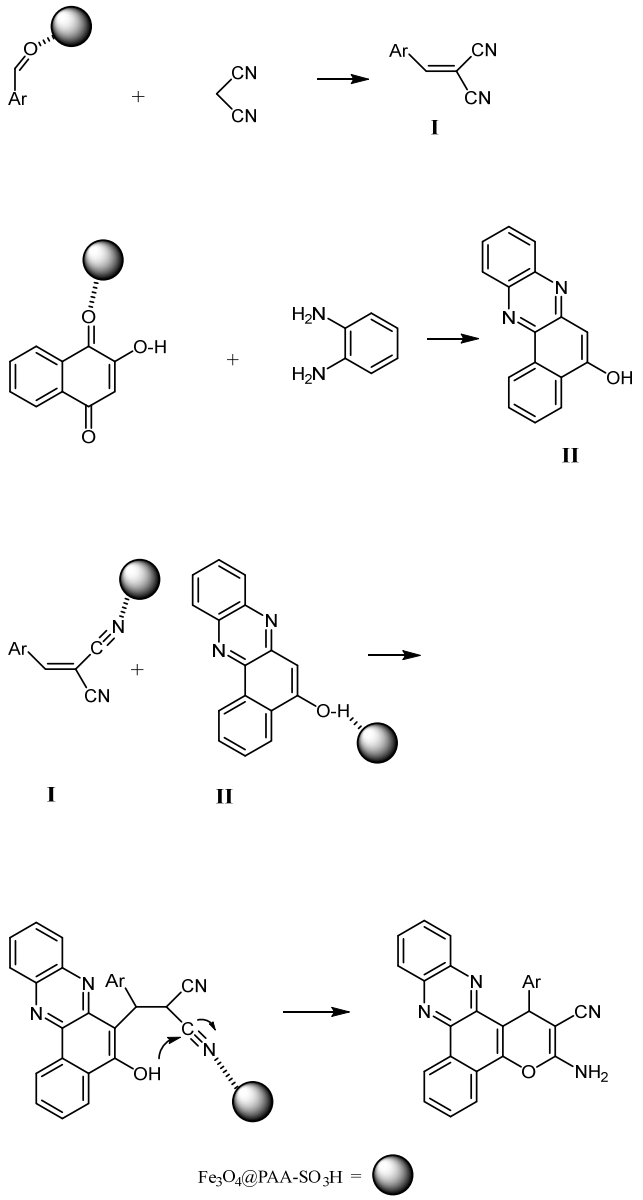
[a]Isolated yield.
[b]All from Ref. [45].

Table 3. Comparison of the catalytic activity of Nano Fe_3O_4@ PAA-SO_3H with other reported catalysts for the synthesis **5b**.

Entry	Catalyst (condition)	Time (min)	Yield (%) [a]	Ref.
1	DABCO (10 mol%, EtOH)	100	80	[13]
2	thiourea-based organocatalysts (10 mol%, H_2O)	240	79	[15]
2	caffeine (20 mol%, EtOH)	60	90	[16]
3	ionic liquid (15 mol%, 75 °C)	10	89	[19]
4	Nano CuO (10 mol%, 75 °C)	10	93	[23]
5	Theophylline (20 mol%, microwave irradiation)	10	94	[17]
6	Nano Fe_3O_4@ PAA-SO_3H (8 mg, EtOH (Ultrasonic irradiation, 40 W)	10	95	This work

[a]Isolated yield.

A proposed mechanism for the synthesis of benzopyranophenazines using Cross-PAA-SO_3H@Fe_3O_4 is shown in Scheme 4. (i) The initial condensation of hydroxynaphthoquinone with *o*-phenylenediamine affords intermediate **I**; (ii) Knoevenagel condensation of malononitrile and benzaldehydes to form the intermediate **II**; (iii) The Michael addition of intermediate **I** with intermediate **II** formed intermediate **III**, which in subsequent cyclization and tautomerism affords the corresponding products. In this mechanism, the surface atoms of Cross-PAA-SO_3H@Fe_3O_4 activate the C=O and C≡N groups for better reaction with nucleophiles. This proposed mechanism has been supported by literature [15, 19, 36].



Scheme 4. Proposed mechanism for the synthesis of benzopyranophenazines.

4. Conclusions

In conclusion, we have developed a straightway and efficient method for the preparation of benzopyranophenazines using crosslinked sulfonated polyacrylamide (Cross-PAA-SO_3H) attached to nano-Fe_3O_4 an efficient heterogeneous solid acid catalyst under ultrasonic irradiations. The method offers several advantages including rapid assembly of medicinally privileged heterocyclic molecules, high yields, shorter reaction times, the reusability of the catalyst, the low amount of catalyst and use of ultrasonic irradiation as a valuable and powerful technology.

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