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FULL PAPER

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Synthesis of quinazolines over recyclable $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} nanoparticles: A green, efficient, and solvent-free protocol

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A practical and efficient method is developed for efficient synthesis of quinazoline derivatives through condensation reaction of 2-aminoaryl ketone, an aldehyde, and ammonium acetate, over magnetic $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} NPs as a recyclable nanocatalyst, under solvent-free conditions. The as-prepared nanocatalyst was characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and vibrating sample magnetometer (VSM). Mild conditions, easy work up, high purity of the products, recyclability, readily availability, nontoxicity, economical, and environmental-friendly nature of the iron catalyst are the attractive features of this methodology.

KEYWORDS
Iron catalyst, Magnetic nanoparticles, Quinazoline, Recyclable, Solvent-free

1 | INTRODUCTION

One of the most important nitrogen heterocycles found in a wide variety of natural products is quinazoline. It has received great attentions in organic synthesis and medicinal chemistry.[1–5] Many of its derivatives exhibit a broad range of remarkable biological and pharmacological activities such as antimalerial,[6] antibacterial,[7] antiasthmatic,[8] antihypertensive,[9] antiviral,[10] antiinflammatory,[11] anticancer,[4,12] *etc*. Others are building blocks for naturally occurring alkaloids,[13–16] microorganisms[17] and in several life-saving drugs such as gefitinib (Iressa)[5,18] and erlotinib (Tarceva)[19] (Scheme 1).

Therefore, the design of new strategy for synthesis of quinazolinones has attracted many researchers. Recently, there has been exponential growth in creating magnetic nanoparticles (MNPs) and led to their potential applications in some fields such as biomedicine, catalysis, environmental protection, and energy storage.[20–27] Especially as catalyst, MNPs have attracted considerable attention because of their easy separation from the mother solution by magnetic decantation rather than time-consuming filtration.[28] The immobilization of catalytically active metal complexes on MNPs offers the advantages of a combination of high catalytic activity, selectivity and stability with easier separation of the catalysts from the reaction media, thus makes it a reusable and efficient system. In this context, some of MNPs have been coated with amorphous type silica which acts as a stabilizer and improves their chemical stability and dispersibility.[29,30] Silica-coated MNPs have appeared as versatile supports for the immobilization of metal complexes. Among transition metal catalysts, the readily available iron complexes have found increasing applications, as environmentally benign, economical, and nontoxic efficient catalysts in hydrogenation,[31] oxidation,[32] epoxidation,[33] *etc*. Herein, we have combined two complementary properties, high reactivity and stability of the catalyst by immobilization of Fe^{3+} on

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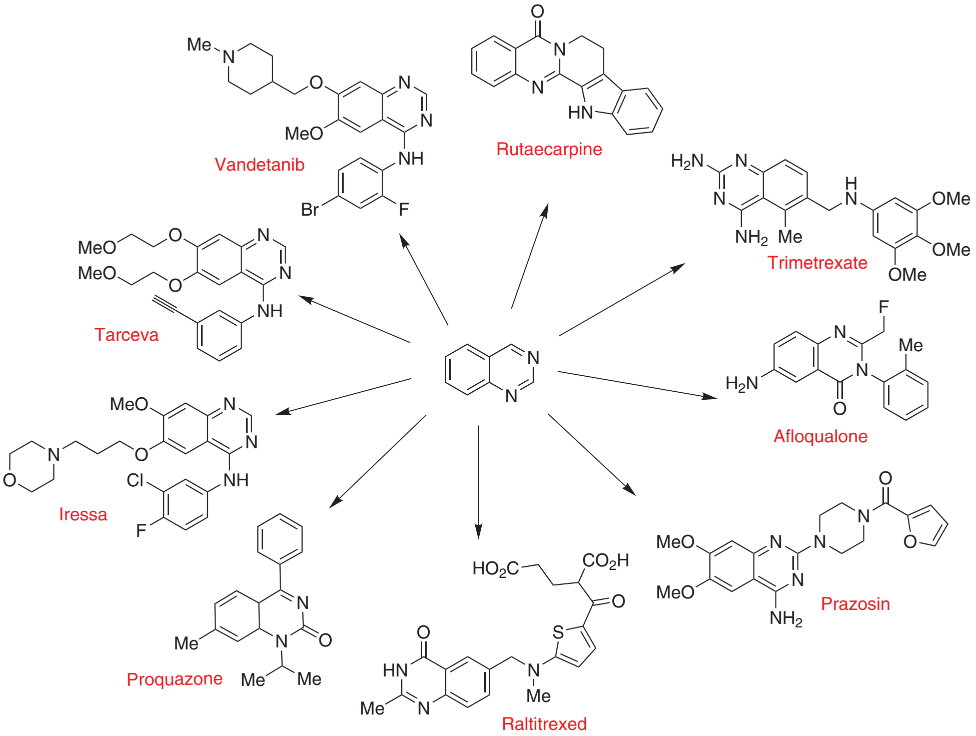


SCHEME 1 Occurrence of quinazolines in some important biological and pharmacological compounds

MNPs and its employment as a reusable heterogeneous catalyst for the synthesis of quinazoline derivatives *via* a one-pot three-component reaction of 2-aminoaryl ketones, aldehydes, and ammonium acetate, under eco-friendly solvent-free conditions (Scheme 2).

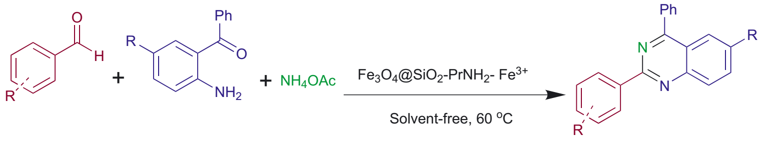
2 | Experimental

2.1 | Materials and physical techniques

All chemical reagents used in our experiments were purchased from Merck or Aldrich Chemical Company with high purity. All solvents were distilled, dried and purified using standard procedures. Thin layer chromatography (TLC) was performed using aluminium plates coated with silica gel 60 F-254 (Merck). Melting points were measured on an Electro-thermal 9100 apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance (DPX 500 MHz and DPX 125 MHz) in pure deuterated $CDCl_3$ solvent using tetramethylsilane (TMS) as an internal reference. Fourier transform infrared (FT-IR) spectra were recorded using KBr pellets on a Nicolet IR-100 infrared spectrometer. The powder X-ray diffraction spectrum was recorded at room temperature using a Philips X-Pert 1710 diffractometer with Co Kα (α = 1.79285 Å) voltage of 40 kV, current of 40 mA, in the range of 20°–80° (2θ) with a scan speed of 0.02°/s. TGA thermogravimetric analyzer was used to study the thermal properties of the compounds under an inert N_2 atmosphere and heating rate of 10 °C min^{-1}. An energy dispersive detector (EDS) coupled to the microscope was used to identify chemical elements of the prepared catalyst. The particle morphology was examined by scanning electron microscopy using SEM (HITACHI S-4160) on gold coated samples and TEM (Zeiss - EM10C - 100 KV). Magnetic properties were obtained by a vibrating magnetometer/Alternating Gradient Force Magnetometer (VSM/AGFM, MDK Co., Iran).

2.2 | Preparation of magnetic Fe_3O_4 magnetic nanoparticles (MNPs)

Magnetic nanoparticles were prepared *via* chemical co-precipitation using chlorine salts of Fe^{3+} and Fe^{2+} ions with molar ratio of 2:1, in the presence of NH_4OH, followed by the hydrothermal treatment. Typically, $FeCl_3 \cdot 6H_2O$ (1.76 g, 0.0065 mol) and $FeCl_2 \cdot 4H_2O$



SCHEME 2 Catalytic synthesis of quinazoline derivatives over $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+}

(0.65 g, 0.0033 mol), were dissolved in 100ml of deionized water and vigorously stirred under Ar atmosphere for 1 h. Then 6ml of 25% NH_4OH was dropped into the reaction mixture. The reaction was continued for another 60 min at 80°C, the cooled mixture was separated by an external magnet, washed with distilled water, and dried overnight under vacuum at 50 °C.

2.3 | Preparation of silica coated magnetic nanoparticles (Fe_3O_4@SiO_2)

Magnetic nanoparticles (1 g) was dispersed in a solution of ethanol and water (40:10 ml) in an ultrasonic bath for 30 min. The pH was adjusted to 10 with an ammonia solution and 0.5 ml tetraethylorthosilicate (TEOS) that was added drop-wise into the mixture over a period of 10 min. Then, the mixture was stirred using a mechanical stirrer for 12 hr at 60 °C. The obtained Fe_3O_4@SiO_2 nanoparticles were collected using an external magnet, subsequently washed with ethanol several times and dried under vacuum.

2.4 | Preparation of amino-functionalized magnetic nanoparticles (Fe_3O_4@SiO_2-$PrNH_2$)

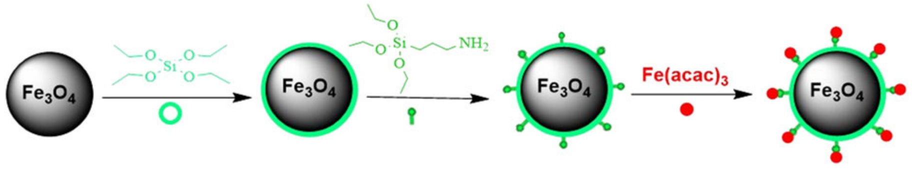
The surface of the silica coated magnetic nanoparticles was functionalized with amino groups by adding 3-aminpropyltriethoxysilane (APTES) (1 ml) to a suspension of Fe_3O_4@SiO_2 (1 g) in dry toluene (25 ml) and refluxing for 24 hr under N_2 atmosphere. The product was separated by an external magnetic, washed with toluene and anhydrous ethanol, and dried under vacuum for 24 hr at 60 °C.

2.5 | Preparation of iron (III) Schiff base grafted onto Fe_3O_4@SiO_2-$PrNH_2$

1 g Fe_3O_4@SiO_2-$PrNH_2$ was sonicated in dry dichloromethane (25 ml), then an aqueous solution of Fe $(acac)_3$ (100 mg in 10 ml) was added slowly into the above mixture and refluxed for 24 hr. After cooling to room temperature, the mixture was separated by an external magnet, washed with copious amounts of dichloromethane and ethanol to remove the ungrafted Fe $(acac)_3$. Finally, Fe_3O_4@SiO_2-$PrNH_2$-Fe^{3+} was dried under vacuum at 60 °C for 12 hr.

2.6 | General procedure for the synthesis of quinolones

A mixture of 2-aminoaryl ketone (1 mmol), aromatic aldehyde (1 mmol), ammonium acetate (2.5 mmol) and catalyst (10 mg) was placed in a round bottom flask and heated in an oil bath at 60 °C. After completion of the reaction which was indicated by TLC, ethanol (5 ml) was added to the reaction mixture, the catalyst was separated using an external magnet, washed several times with water and ethanol and dried under vacuum at room temperature to be ready for the next run. Then, solvent



SCHEME 3 Preparation of magnetic nanocatalyst Fe_3O_4@SiO_2-$PrNH_2$-Fe^{3+}

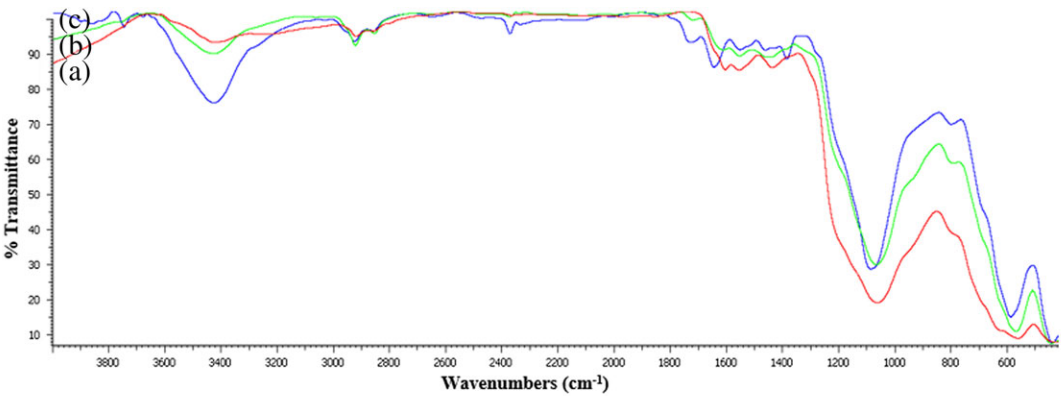


FIGURE 1 FT-IR spectra of: (a) Fe_3O_4@SiO_2, (b) Fe_3O_4@SiO_2–$PrNH_2$, (c) Fe_3O_4@SiO_2-$PrNH_2$-Fe^{3+}

was evaporated under reduced pressure. To afford pure quinazoline derivatives, the solid residue was recrystallized from ethanol.

3 | RESULTS AND DISCUSSION

In this section, we discuss the preparation, characterization and application of $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} as an efficient, eco-friendly and reusable heterogeneous nanocatalyst for the synthesis of quinazoline derivatives. The magnetic system is prepared in three steps (Scheme 3). Then, characterization of catalyst is done *via* FT-IR, SEM, TEM, VSM, TGA/DTA and XRD.

The FT-IR spectra of $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$–$PrNH_2$, and $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} in Figure 1 show an adsorption peak at around 565 cm^{-1} that is attributed to the vibration of Fe–O bonds and the bands at 450, 1075, 1618 and 3430 cm^{-1} which show silica has coated as a shell on surface of Fe_3O_4. The presences of bands in the 2925–2858 cm^{-1} region in spectra of $Fe_3O_4@SiO_2$–$PrNH_2$ are assigned to the stretching of C—H bonds. Moreover, the band at 1558 cm^{-1} is due to the bending vibrations of H—N—H bond; however absorption bands of the stretching vibration of –NH_2 are overlapped with the–OH stretching vibration. Thus, it can be confirmed that surface modification of the silica shell by APTES is successful (Figure 1b). After immobilization of the metal complex on the $Fe_3O_4@SiO_2$–$PrNH_2$ surface, increasing the intensity of the C—H stretching vibration can indirectly suggest that metal acetylacetonate has been successfully grafted onto the modified Fe_3O_4 (Figure 1c).

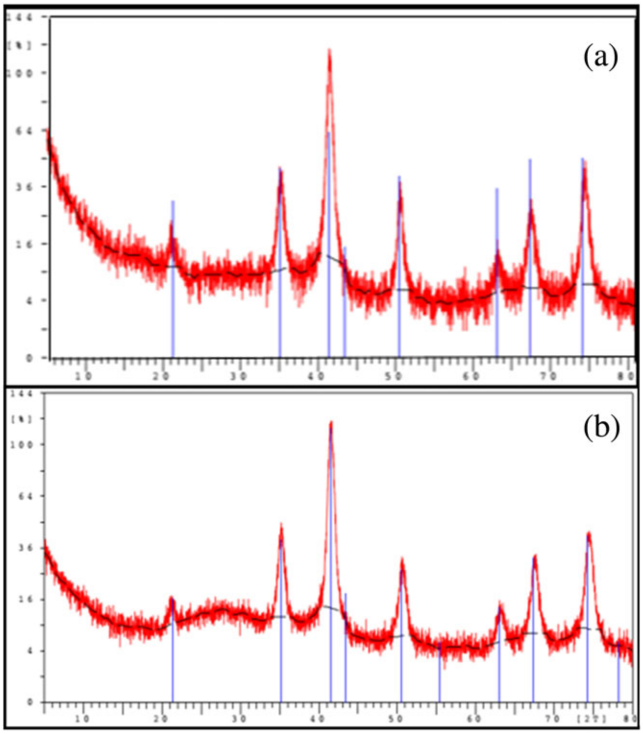


FIGURE 2 Wide-angle XRD patterns of (a) Fe_3O_4 and (b) $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} catalyst

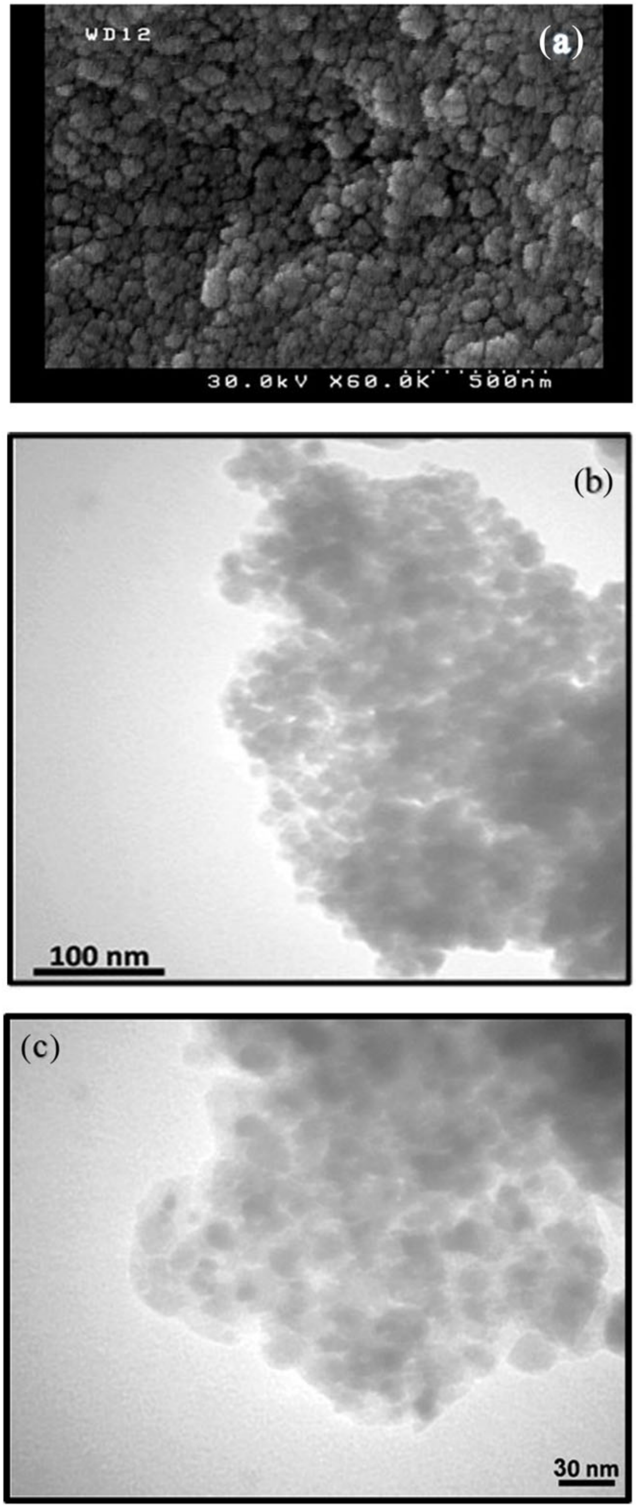


FIGURE 3 Images of: (a) SEM, (b) TEM of $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} and (c) TEM of recycled catalyst after last run

The properties of crystallinity and phase purity of the as-synthesized Fe_3O_4 and $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} are investigated by wide angle XRD. For $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} NPs, XRD pattern are in agreement with standard patterns of inverse cubic spinel magnetite (Fe_3O_4) crystal structure, showing six diffraction peaks at 2θ about 35.1°, 41.5°, 50.5°, 63.1°, 67.3° and 74.3° corresponding to the respective (220), (311), (400), (422), (511), and (440) planes, respectively (Figure 2). Sharp peaks confirm the good crystallinity of the prepared samples. The small and weak broad bands in around 25 is related to the existence of amorphous silica shell.

The size and morphology of the $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} NPs are determined *via* SEM and TEM analyses. In SEM image, particles with uniformly spherical morphology are observed. TEM image shows Fe_3O_4 nanoparticles covered with organic and inorganic groups (Figure 3).

Thermal stability of $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} is obtained from the thermogravimetric (TG) and differential thermal analysis (DTA), under an air flow from room temperature to 800 °C at a rate of 10 °Cmin^{-1}. In TGA diagram, the first weight loss below 200 °C is due to physically adsorbed water and solvents. This was followed by a gradual decrease in the weight between 200 °C and 650 °C which is attributed to the decomposition of the grafted organic molecule on the surface. These result are indicate that the surface modification has occurred (Figure 4).

The magnetic properties of the as-synthesized Fe_3O_4 and $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} are measured by VSM at room temperature, in the range from +1 to −1 T. The magnetization hysteresis loops of them are S-like curves that indicate they are super paramagnetic (Figure 5). The magnetic saturation (M_{sat}) values are 24.0 emu g^{-1} and 68.0 emu g^{-1} for $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} and Fe_3O_4, respectively. The decrease in M_{sat} for $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} can be attributed to the modification on the surface of the Fe_3O_4 with nonmagnetic material [$PrNH_2$-Fe^{3+}]. These properties cause to facilitate separation of magnetic nanoparticles with a conventional magnet which is efficient for recovery of the catalyst.

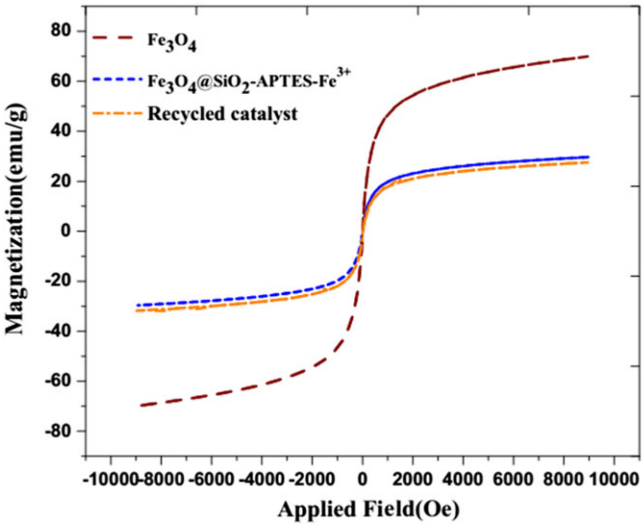


FIGURE 5 VSM curve of Fe_3O_4 NPs, $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} NPs and recycled catalyst after last run

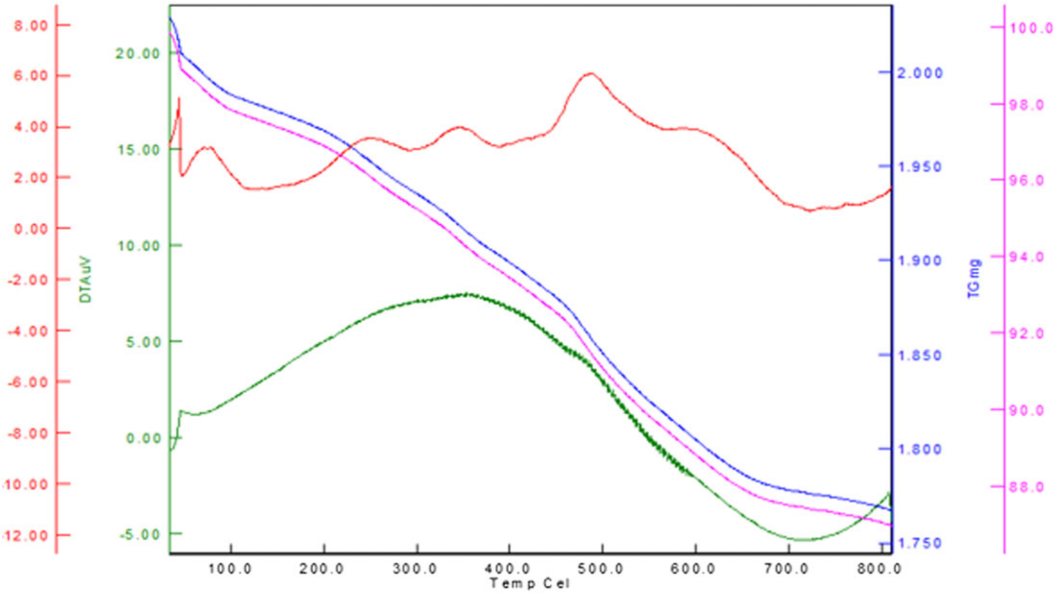


FIGURE 4 TGA/DTA/DTG analysis of $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+}

TABLE 1 Optimization of the catalytic synthesis of quinazoline derivatives over $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+a}

Entry	Catalyst (mg)	Solvent	T/°C	Time (h)	Yield[b] (%)
1	10	-	25	5	37
2	10	-	40	4	70
3	15	-	40	4	73
4	10	-	40	5	75
5	10	-	60	4	95
6	15	-	60	4	95
7	10	H_2O	60	4	68
8	10	H_2O	80	4	80
9	10	EtOH	60	4	84
10	10	EtOH	70	4	89
11	10	CH_3CN	60	4	39
12	-	-	60	4	Trace

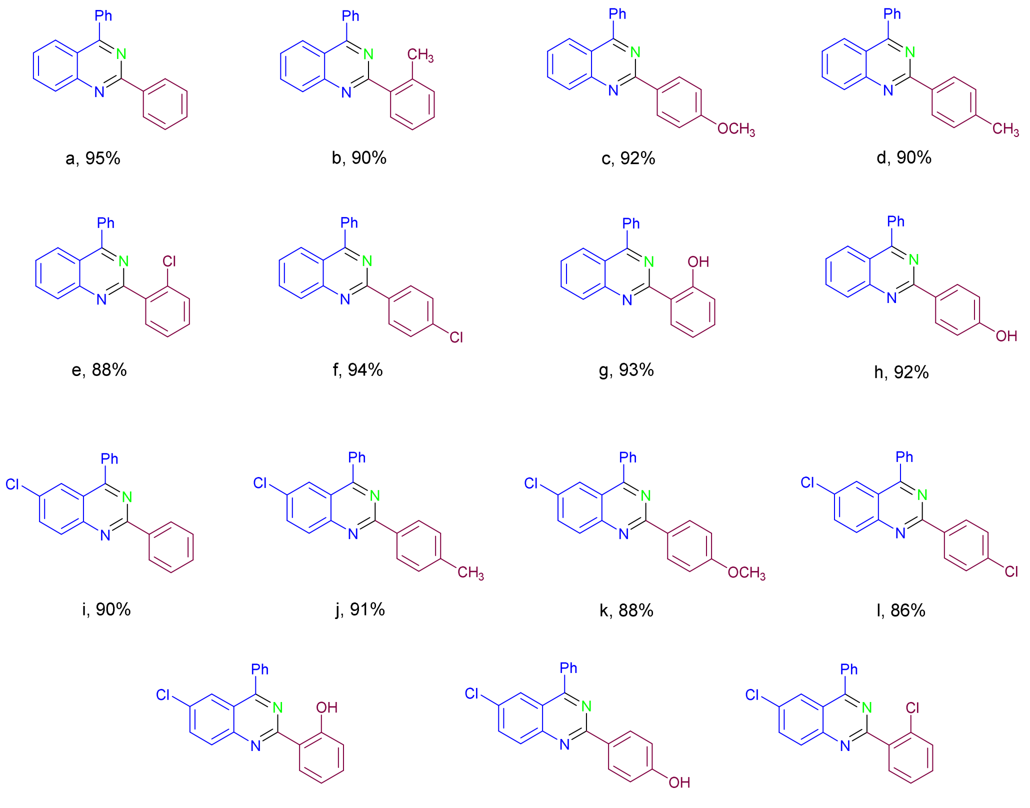
[a] Reaction conditions: 2-aminobenzophenone (1 mmol), benzaldehyde (1 mmol), ammonium acetate (2.5 mmol).

[b] Isolated yield.

4 | CATALYST ACTIVITY

Catalytic activity of $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} is probed through synthesis of quinazoline derivatives in a three component condensation reaction of 2-aminoaryl ketones, aldehydes, and ammonium acetate. Firstly, to optimize conditions, model reaction is performed by using 2-aminobenzophenone, benzaldehyde, and ammonium acetate. Effects of different amounts of the catalyst, time and temperature of the reaction, as well as the solvent effects are explored on the overall yield of the reaction. In the absence of the catalyst, reaction yield in low, while in its presence (10 mg) the yield of the product increases at 40 °C. However, an amount higher than 10 mg does not improve the yield to an appreciable extent at this temperature. It is found that the yield improves to 95% at 60 °C and in solvent-free conditions. The effect of solvent is investigated for the model reaction using H_2O, EtOH, and CH_3CN. The results show that conducting the reaction under solvent-free condition generates the desired product in an excellent yield. Based on these results, the optimal conditions are determined as that

TABLE 2 Synthesis of quinazoline derivatives over $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} under solvent-free condition[a,b]



a, 95% b, 90% c, 92% d, 90%

e, 88% f, 94% g, 93% h, 92%

i, 90% j, 91% k, 88% l, 86%

m, 91% n, 94% o, 93%

[a] Reaction conditions: 2-aminoaryl ketone (1 mmol), aldehyde (1 mmol), ammonium acetate (2.5 mmol). 60 °C, 4 hr.

[b] Isolated yield.

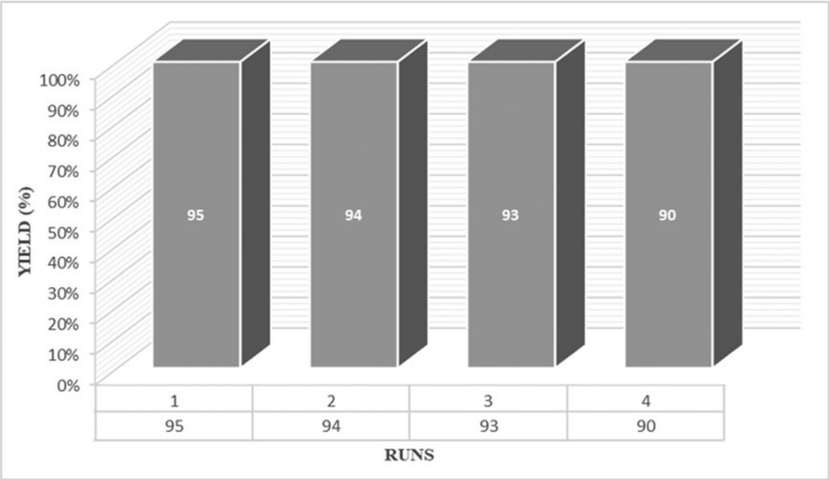
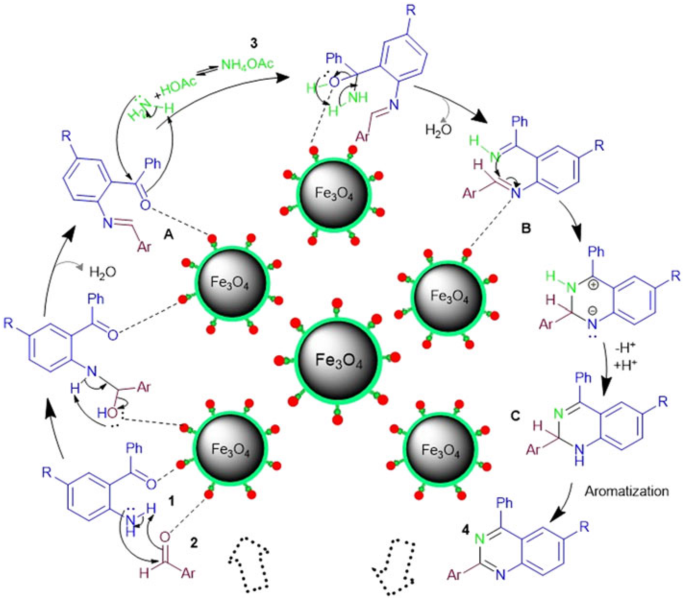


FIGURE 6 Recyclability of $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} NPs in catalytic synthesis of quinazolines



SCHEME 4 A proposed mechanism for the synthesis of quinazolines over $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} NPs

the reaction is catalyzed by 10 mg of catalyst under solvent-free conditions at 60 °C (Table 1).

In order to further demonstrate the utility of this methodology, we extend our studies with a wide range of aldehydes. It can be clearly observed that electronic and steric effects of substitutions on the aldehyde do not appreciably affect the yield of the desired product. Moreover, the reaction is well tolerated with other functional group halide (Cl) substituent on the substrates of 2-aminobenzophenone (Table 2).

Facility of catalyst recovery is very important parameter in performance of catalytic system. To obtain an insight into this issue, catalyst reusability experiments are carried out under the same reaction conditions. After the reaction is completed, $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} is easily separated with an external magnet from the reaction solution, the recovered catalyst is washed with ethanol, then dried and used in the next run. It is noteworthy that no significant change in the activity are observed for least 4 consecutive cycles which clearly demonstrates the stability and durability of the catalyst (Figure 6).

A possible mechanism for the synthesis of quinazolines over $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} NPs is presented (Scheme 4). The $Fe_3O_4@SiO_2$-$PrNH_2$-Fe^{3+} NPs acts as a Lewis acid, coordinates to the carbonyl groups and increases the electrophilicity of the carbonyl groups of 2-aminoaryl ketones and aldehydes. In the first step, the nucleophilic attack of the amine's substrate (1) on the activated carbonyl group of aldehyde (2), leads to an aldimine intermediate A. In the next step, condensation of the keto group of benzophenone in intermediate A with NH_4OAc (3), forms ketimine group in intermediate B. Then, the intermediate C is obtained *via* cyclization and transformation of hydrogen, which may render desired product (4) through aerial oxidation.

5 | CONCLUSION

Along this research line, we have developed a simple, inexpensive and robust protocol to immobilize iron on magnetite nanoparticles and its use as a real reusable heterogeneous catalyst for the synthesis of quinazoline derivatives *via* a one-pot three-component reaction of 2-aminoaryl ketones, aldehydes, and ammonium acetate under eco-friendly conditions. The advantages of this protocol includes avoiding the use of solvent, high yields, easy handling, short reaction time, simple experimental, and product purity. These together with the simple recovering of the catalyst make it a useful alternative for the scale-up for the synthesis of quinazoline derivatives.

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