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Synthesis of copper (II)-supported magnetic nanoparticle and study of its catalytic activity for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones

Arash Ghorbani-Choghamarani*, Masoomeh Norouzi.

Department of Chemistry, Faculty of Science, Ilam University, P.O. Box 69315516, Ilam, Iran

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ABSTRACT

A magnetic nanoparticle supported efficiently catalyzes for condensation 2-aminobenzamide with aldehydes to afford the corresponding 2,3-dihydroquinazolin-4(1H)-one derivatives successfully in high yield. The reactions were carried out in ethanol under reflux conditions. The protocol proves to be efficient and versatile benign in terms of very easy work-up and reused seven times without significant loss of catalytic activity. The heterogeneous catalyst was characterized by FT-IR spectroscopy, thermogravimetric (TGA) analysis, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscope (TEM).

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1. Introduction

In recent years, the design of efficient and recoverable catalysts has become an important issue for reasons of economic and environmental impact. One strategy has focused on combining the advantages of different types of catalyst; for example the high activity and selectivity of homogeneous species with the ease of separation and recycling of heterogeneous catalysts [1]. Nanoparticles have emerged as efficient alternative support materials for homogeneous catalyst immobilization [2,3]. These nanoparticles, because of their high surface area and unique magnetic properties, have a broad range of potential uses in disciplines, including physics, biomedicine, biotechnology, material science and catalysis support applications [4–6]. In this regard, the use of magnetic nanoparticles (MNPs) supported catalyst has been efficiently employed as heterogeneous catalysts. The main advantage of a catalytic system based on magnetic nanoparticles is that the nanoparticles can be efficiently isolated from the product solution through a simple magnetic separation process after completing the reactions [7]. Additionally, the MNP-supported catalysts also show high dispersion and reactivity with a high degree of chemical stability. By utilizing these advantages of magnetic nanoparticles over other supporting materials, various catalysts and ligands have been immobilized on these particles [8]. The various types of transition metal-catalyzed reactions using catalytic sites grafted on MNPs that have emerged recently include olefin hydroformylation [9], alcohol hydrogenation [10], olefin hydrogenation [11], asymmetric hydrogenation [12], aldol reaction [13], Suzuki and Heck reactions [14,15], Sonogashira and Carbonylative Sonogashira reactions [16], Knoevenagel condensation [17], ring-closing metathesis [18], cycloaddition reaction [19], and as supports for biocatalysts [20].

Over the past decade, the synthesis of heterocyclic compounds has become the cornerstone of synthetic organic chemistry as a result of a wide variety of their application in medicinal and pharmaceutical chemistry [21]. 2,3-Dihydroquinazolin-4(1H)-ones, an important class of heterocyclic compounds influence numerous cellular processes [22]. These exhibit a wide range of biological activities, such as antitumor, antibiotic, antidefibrillatory, antipyretic, analgesic, antihypertonic, diuretic, antihistamine, antidepressant, and vasodilating behaviour [23]. Furthermore, quinazolinone skeleton is frequently found in various natural products. Some examples include the anticancer compound trimetrexate, the sedative methaqualone, the alpha adrenergic receptor antagonist such as doxazosin and the antihypertensive agent ketanserin [24].

Several strategies for their synthesis were already developed: condensation of anthranilamide with an aldehyde or ketone using p-toluenesulfonic acid as a catalyst [25]; desulfurization of

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* Corresponding author. Tel.: +98 841 2227022; fax: +98 841 2227022.
E-mail addresses: a.ghorbani@mail.ilam.ac.ir, arashghch58@yahoo.com (A. Ghorbani-Choghamarani).

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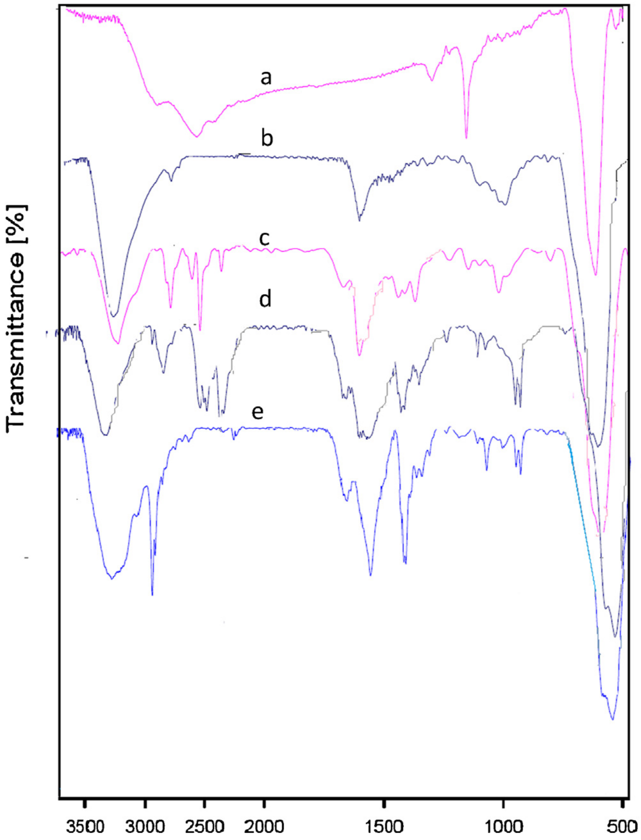


Fig. 1. FT-IR spectra of Fe_3O_4 nanoparticles (a), amino-functionalized (b), MNP-acryloxyl (c), MNP-TEDETA (d), and $CuCl_2/Fe_3O_4$-TEDETA (e).

2-thioxo-4(3H)-quinazolinones [26]; reaction of isatoic anhydride with Schiff-bases [27]; one-step conversion of 2-nitrobenzamides to 2,3-dihydro-4(1H)-quinazolinones [28]; condensation of anthranilamide with benzil [29]; two-step synthesis starting from isatoic anhydride and amines, then annulated with ketones [30]; a one-pot three-component condensation of isatoic anhydride, aldehydes and amines [31]. More attractive and convenient method for synthesis of such significant heterocycles is three-component condensation of isatoic anhydride, aldehydes, and amines.

The catalysts reported for the above stated one-pot procedure include inorganic catalysts like aluminium tris(dihydrogen phosphate) [32], silica sulfuric acid [33], magnetic Fe_3O_4 particles [34], reaction media like acidic ionic liquid [35] and Brønsted acid [36]. Some of these methodologies involve strongly acidic conditions, toxic catalysts, hazardous organic solvents and long reaction times. Thus, there is a need for a non-acidic and novel catalyst that could overcome the above drawbacks.

Here, we report the magnetic nanoparticle-supported copper (II) as a catalyst for synthesis of 2,3-dihydroquinazolin-4(1H)-ones derivatives. The magnetic catalyst could be readily separated from the media by simple magnetic decantation, and could be reused without significant degradation in activity and minimize the environmental damages.

2. Experimental

2.1. Materials

Chemicals were purchased from Fisher and Merck. The reagents and solvents used in this work were obtained from Sigma-Aldrich, Fluka or Merck and used without further purification. Nanostructures were characterized using a Holland Philips X·pert X-ray powder diffraction (XRD) diffractometer (Co Kα, radiation = 0.154056 nm), at a scanning speed of 2° min^{-1} from 10° to 100°. The particle size and morphology were investigated by a JEOL JEM-2010 scanning electron microscopy (SEM), on an accelerating voltage of 200 kV. The infrared spectra (IR) of samples were recorded in KBr disks using a NICOLET impact 410 spectrometer. The thermogravimetric analysis (TGA) curves are recorded using a PL-STA 1500 device manufactured by Thermal Sciences. The particle size and morphology were investigated by a Zeiss-EM10C transmission electron microscope (TEM) on an accelerating voltage of 80 kV.

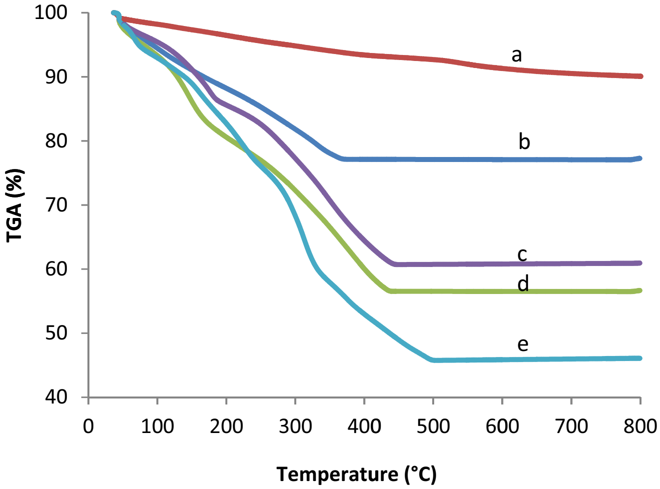


Fig. 2. TGA curves of Fe_3O_4 (a), amino-functionalized (b), MNP-acryloxyl (c), MNP-TEDETA (d), and $CuCl_2/Fe_3O_4$-TEDETA (e).

The 1H and 13C spectra were measured using a Bruker Avance III 400.

2.2. Preparation of the magnetic Fe_3O_4-nanoparticles (MNPs)

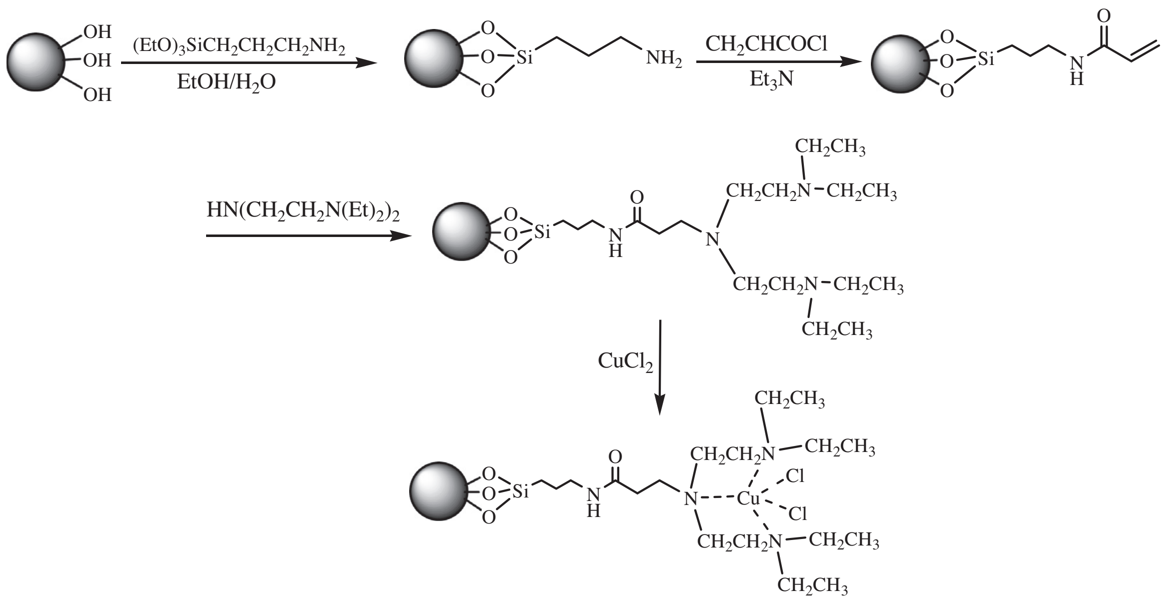
The mixture of $FeCl_3·6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2·4H_2O$ (2.147 g, 0.0108 mol) were dissolved in 100 mL of deionized water in a three-necked bottom (250 mL) under N_2 atmosphere. After that, under rapid mechanical stirring, 10 mL of NH_3 was added into the solution within 30 min with vigorous mechanical stirring. After being rapidly stirred for 30 min, the resultant black dispersion was heated to 80 °C for 30 min. The black precipitate formed was isolated by magnetic decantation, washed with double-distilled water until neutrality, and further washed twice with ethanol and dried at 80 °C in vacuum.

2.3. Preparation of Fe_3O_4-(3-aminopropyl)-trimethoxysilane

The obtained magnetic nanoparticles (MNPs) powder (1.5 g) was dispersed in a mixture of ethanol and water (250 mL, 1:1 by volume) and solution by sonication for 30 min. Then 3-aminopropyl (triethoxy) silane (99%, 3 mL) was added to the mixture. After mechanical stirring under N_2 atmosphere at room temperature for 8 h. The settled product was redispersed in ethanol by sonication. The final the product was washed with copious amounts of deionized water and ethanol by magnetic decantation, and dried under vacuum at room temperature overnight.

2.4. Preparation of Fe_3O_4-TEDETA

The amino-functionalized MNPs (1 g) were dispersed in dry CH_2Cl_2 (3 mL) by ultrasonic bath for 10 min, and the flask was cooled in an ice-water bath. Triethylamine (3.2 mL) was added



Scheme 1. Synthesis of $CuCl_2/Fe_3O_4$-TEDETA.

and stirred for 30 min. Subsequently, acryloyl chloride (0.8 mL, 9.84 mmol) was added drop wise over a period of 30 min at room temperature. The mixture was stirred at room temperature for 48 h. Then, the as prepared functionalized MNPs nanoparticles were separated by magnetic decantation and washed three times with acetone and deionized water to remove the unattached substrates. The resulting product was dispersed in methanol (10.0 mL), and stirred with *N,N,N″,N″*-tetraethyldiethylenetriamine (TEDETA) (1.0 mL, 3.8 mmol) at room temperature for 1 week. The solids were separated by a magnetic field and washed with acetone. The resulting product was dried under vacuum for 12 h.

2.5. Magnetic nanoparticle-supported catalyst $CuCl_2/Fe_3O_4$-TEDETA

The Fe_3O_4-TEDETA (0.2864 g), was added to the round-bottom flask containing a solution of $CuCl_2$ anhydrous (0.134 g, 1 mmol) in ethanol (280 mL). The mixture was then stirred vigorously at room temperature for 5 h. The solid was separated by magnetic decantation. The magnetic catalyst was washed with copious amounts of ethanol and dried under vacuum at room temperature.

2.6. Catalytic studies

2.6.1. General synthesis for the preparation of 2,3-dihydroquinazolin-4(1H)-ones

A mixture of aldehydes **1** (1 mmol), 2-aminobenzamide **2** (1 mmol) and $CuCl_2/Fe_3O_4$-TEDETA (5 mg) in ethanol (10 mL) was stirred and heated at 80 °C. Reaction progress was monitored by TLC (acetone:n-hexane, 2:8). After the TLC indicates the disappearance of starting materials, the reaction was cooled to room temperature. The catalyst was separated by an external magnet and reused as such for the next experiment. The filtrate was evaporated to remove solvent, the resultant solid was then washed with ethanol to obtain pure 2,3-dihydroquinazolin-4(1H)-ones in 95–98% yields.

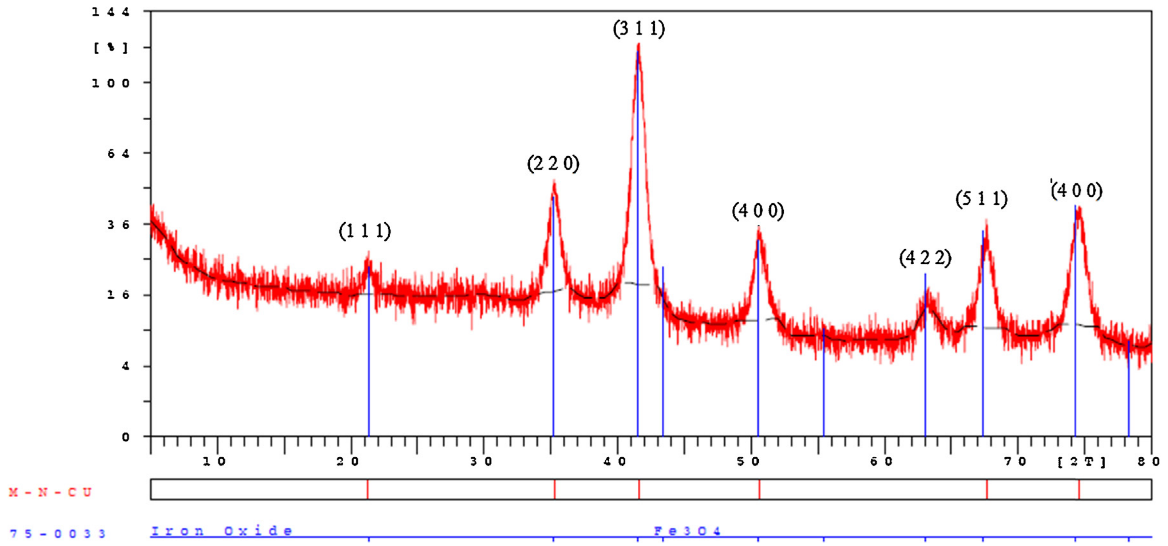


Fig. 3. XRD patterns $CuCl_2/Fe_3O_4$-TEDETA.

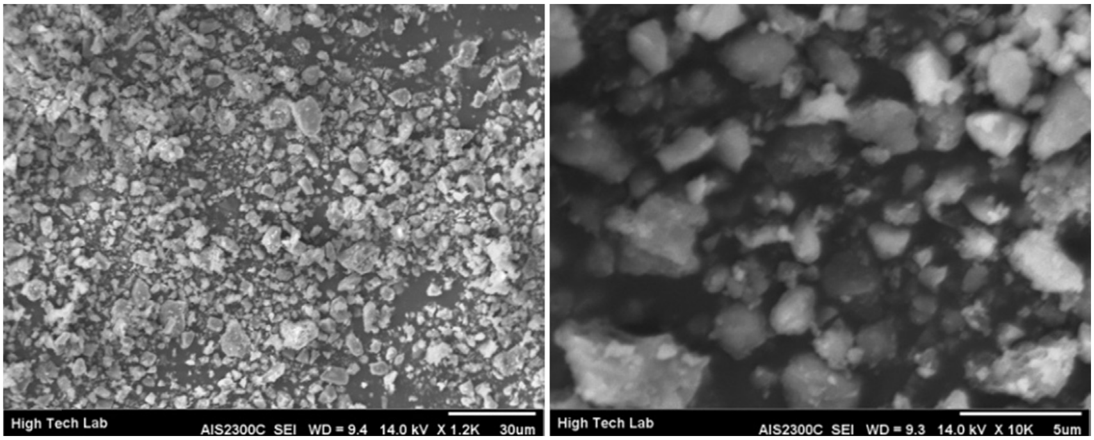


Fig. 4. SEM images of $CuCl_2/Fe_3O_4$-TEDETA at different magnification.

2.7. *Spectral data for new compounds*

2.7.1. *2-(4-Ethoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (**3g**)*

White solid, m.p. 161–162 °C, ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.98$ (brs, 1H), 7.6 (d, $J = 6$ Hz, 2H), 7.34 (s, 1H), 7.26 (d, $J = 2$ Hz, 1H), 6.87–7.03 (m, 3H), 6.65 (d, $J = 5.6$ Hz, 1H), 5.87 (s, 1H), 5.75 (s, 1H), 4.12 (*t*, $J = 4$ Hz, 2H) 1.45 (q, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.4$, 148.9, 147.5, 131.5, 129.9, 120.7, 116.8, 116.0, 115.7, 69.8, 64. 8, 15.9; IR (KBr): $\bar{V}$ = 3300, 3060, 3000, 2930, 1666, 1650, 1610, 1487, 1387 cm^{-1}.

2.7.2. *2-(2-hydroxy-4-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (**3j**)*

White solid, m.p. 262–263 °C, ^{1}H NMR (400 MHz, DMSO): $\delta = 9.35$ (s, 1H), 7.68 (d, $J = 6.8$ Hz, 1H), 7.57 (s, 1H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.14 (s, 1H), 6.98 (s, 1H), 6.67 (d, $J = 8$ Hz, 2H), 6.36 (s, 1H), 6.28 (d, $J = 6$ Hz, 1H), 5.96 (s, 1H), 3.68 (s, 3H) ppm; IR (KBr): $\bar{V}$ = 3389, 3223, 2924, 1643, 1614, 1505, 1451, 1394, 1247, 754 cm^{-1}.

2.7.3. *2,2′-(1,2-phenylene)bis(2,3-dihydroquinazolin-4(1H)-one) (**12l**)*

White solid, m.p. 272–273 °C, ^{1}H NMR (400 MHz, DMSO): $\delta = 7.87$ (d, $J = 8.4$ Hz, 4H), 7.64 (s, 2H), 7.46 (s, 2H), 7.32 (d, $J = 6$ Hz, 2H), 7.15 (s, 2H), 6.69 (s, 3H), 6.63 (s, 2H), 5.75 (s, 2H) ppm; IR (KBr): $\bar{V}$ = 3299, 3248, 3181, 2961, 2831, 1698, 1639, 1808, 1515, 1481, 1297, 1151, 742 cm^{-1}.

3. Results and discussion

3.1. *Catalyst synthesis and characterization*

Magnetic nanoparticles (MNPs) were prepared by coprecipitation from Fe^{2+} and Fe^{3+} using NH_3 solution. Then, the 3-aminopropyltriethoxysilane added was adsorbed onto the surface of the Fe_3O_4 nanoparticles and form coordination bond with hydroxyl group, obtained amino-coated Fe_3O_4 nanoparticles. The reaction of amino groups with acryloyl chloride led to acryloxyl groups-functionalized magnetic Fe_3O_4 nanoparticles. Subsequent, the (TEDETA)-functioned magnetic nanoparticles were prepared by the Michael reaction of the acryloxyl groups with tetraethyldiethylenetriamine (TEDETA). Ultimately, the complexes $CuCl_2/Fe_3O_4$-TEDETA were prepared by reactions of copper (II) chloride with the individual ligands MNP-TEDETA ethanol. Scheme 1 illustrates the detail synthetic procedure for functioned Fe_3O_4 nanoparticles.

The prepared catalyst was characterized by FT-IR spectroscopy, the thermo gravimetric analysis (TGA), the X-ray diffraction (XRD),

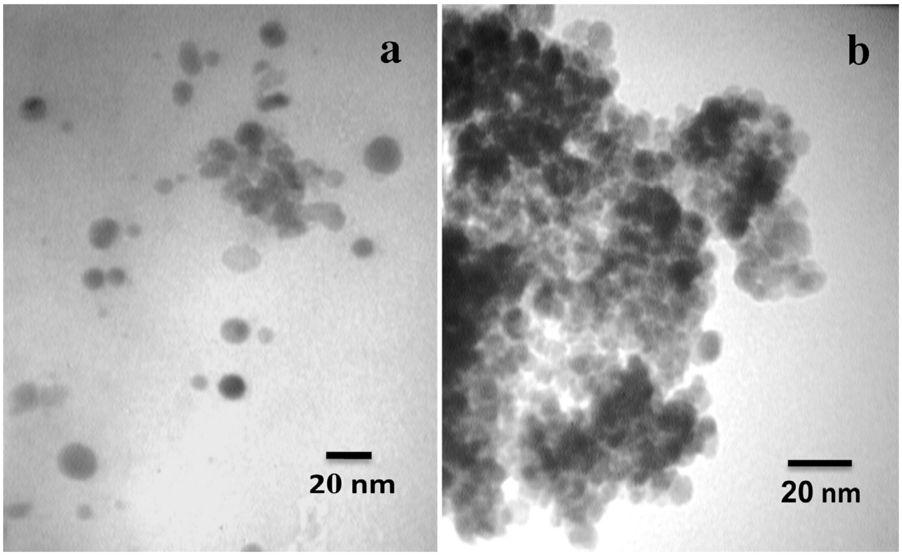


Fig. 5. TEM images of $CuCl_2/Fe_3O_4$-TEDETA at (a) 63,000 and (b) 125,000 magnification.

scanning electron microscopy (SEM) and transmission electron microscope (TEM).

FTIR spectroscopy (Fig. 1a–e) represents the IR spectra obtained for Fe_3O_4 nanoparticles, amino-functionalized, MNP-acryloxyl, MNP-TEDETA and $CuCl_2/Fe_3O_4$-TEDETA respectively. The strong absorption at 580 cm^{-1} was characteristic of the Fe–O stretching vibration but for Fe_3O_4 nanoparticles at 572 cm^{-1} as a blue shift, due to the size reduction. The broad feature at 3500–3000 cm^{-1} for MNP corresponds to the absorption of –OH stretching of hydroxyl groups. The amino-functional groups of Fe_3O_4 and the corresponding infrared absorption frequency are shown in Fig. 1b. The spectra display a number of absorption peaks, indicating the 3-aminopropyl (triethoxy) silane. The absorption around at 1111 and 1001 cm^{-1} corresponds to Si–O stretching vibration. The FT-IR spectroscopic analysis indicated broad band at 3394 cm^{-1}, representing bonded $-NH_2$ groups. The band observed at about 2922–2854 cm^{-1} could be assigned to the aliphatic C–H group.

The spectrum of Fe_3O_4-acryloxyl (Fig. 1c) at wave number 1710 cm^{-1} is observed, which due to the carbonyl stretch of carboxyl. The trough at 1642 cm^{-1} represents the C═C stretching mode conjugate with the C═O (amide 1 band). The peak observed at 3020 cm^{-1} corresponds to the secondary amide group. The peak observed at 1245 and 1164 cm^{-1} could be assigned to C–N stretching and C–O stretching of ether groups, respectively.

When comparing the two spectra in Fig. 1c and d, Fig. 1d shows that there were various functional groups detected on the surface of Fe_3O_4-TEDETA. There are some peaks that were shifted, disappeared and new peaks were produced. Significant band decrease of functional group on the Fe_3O_4-TEDETA were detected at bands 1701 and 1155, which corresponded to the bonded C═O stretching and –C–C– groups, respectively. These two significant bands in the spectrum indicate the possible involvement of those functional groups on the surface of Fe_3O_4-TEDETA process. Thus, it seems that this type of functional group is likely to participate in metal binding. Fig. 1e shows the FTIR spectrum after adsorption of Cu (II) ions onto Fe_3O_4-TEDETA.

To obtain more quantitative information about extent of functionalization and contents of $CuCl_2/Fe_3O_4$-TEDETA, the thermo gravimetric analysis (TGA) was performed and the profiles obtained are exhibited in Fig. 2. The profile of MNPs showed a minute weight loss of about 126 °C owing to the removal of physically adsorbed solvent and surface hydroxyl groups (Fig. 2a). In addition, there is a weight loss of about 3.5% displayed for MNPs in the temperature range of between 200 and 474 °C is attributed to dehydration of the surface –OH group. From the TG data (Fig. 2b–e), we calculate that the organic chemicals concentration sin samples **a**mino-functionalized, MNP-acryloxyl and MNP-TEDETA are 11.0, 23.79 and 28.94 wt% respectively. While $CuCl_2$/MNPs-TEDETA exhibited a weight loss of 36.08% in the temperature range from 200 to 488 °C due to the thermal decomposition of the functionalized groups, which indicates the amount of functionalized grafted to MNP_S was 36.08 wt% (Fig. 2e).

The $CuCl_2/Fe_3O_4$-TEDETA catalyst was characterized using various methods. X-ray diffraction (XRD) of the bare MNP displayed patterns consistent with the patterns of spinel ferrites described in the literature (Fig. 3). A series of characteristic peaks in pattern A at (2θ= 21.2°, 35.2°, 41.5°, 50.6°, 63.1°, 67.5° and 74.4°), marked by their indices ((1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0)), agree with the standard Fe_3O_4 XRD spectrum [37]. This revealed that the surface modification and conjugation of the Fe_3O_4 nanoparticles do not lead to their phase change. The sample show very broad peaks, indicating the ultra-fine nature and small crystallite size of the particles.

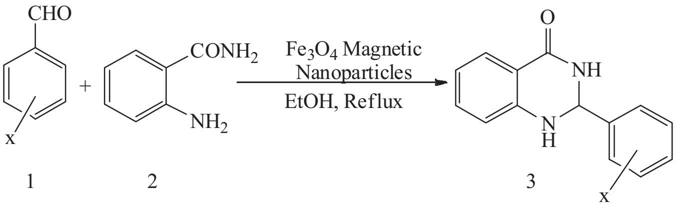
SEM images of $CuCl_2/Fe_3O_4$-TEDETA at different magnification are shown in Fig. 4. According to Fig. 4, the $CuCl_2/Fe_3O_4$-TEDETA exhibited a cluster of aggregated spherical particles with an average size 25 nm in diameter. The surface morphology of the supported TEDETA was practically identical to that of molecular sieves supports and was composed of relatively well formed, spherical particles having rather uniform coating of the organic layers.

Morphology of synthesized of $CuCl_2/Fe_3O_4$-TEDETA nanoparticles were investigated by TEM and few micrographs along with the size distribution diagram obtained thereof are presented in Fig. 5. Particles are observed to have spherical morphology from Fig. 5. Average particle size is estimated at 19 nm from the TEM micrographs (Fig. 5). This is an indication of nearly single crystalline character of $CuCl_2/Fe_3O_4$-TEDETA nanoparticles. These nanoparticles consist of irregular $CuCl_2/Fe_3O_4$-TEDETA and have a narrows size distribution (mostly between 10 and 19 nm) with an average diameter of 25 nm, much smaller than the sizes obtained from the SEM measurements.

3.2. *Catalytic studies*

As a part of our ongoing project devoted towards the development of a practical synthesis of biologically interesting heterocyclic molecules [38–42], herein we had the opportunity to further explore the catalytic activity of $CuCl_2/Fe_3O_4$-TEDETA in the synthesis of 2,3-dihydroquinazolin-4(1H)-ones derivatives, *via* one-pot and the condensation reaction of 2-aminobenzamide with aldehydes in ethanol under reflux conditions to excellent yields (Scheme 2).

In order to establish the optimum conditions, for our initial screening experiments, the optimal catalyst loading were examined. The synthesis of 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one **3a** was used as a model. A mixture of 4-chlorobenzaldehyde **1a** (1 mmol), and 2-aminobenzamide **1** (1 mmol) reaction in the absence of any catalyst and observed that there was no formation of product after 12 h. To improve the yield and optimize the reaction conditions, the same reaction was carried out in the presence of a catalytic amount of $CuCl/Fe_3O_4$-TEDETA under similar conditions. Surprisingly, a significant improvement was observed and the yield of **3a** was dramatically increased to 23% after stirring; the mixture was stirred for only 45 min (Table 1, Entry 2). An increase in the quantity of $CuCl/Fe_3O_4$-TEDETA from 1 to 5 mg increased the product yield slightly from 23% to 98% (Table 1, Entry 3). Using more than 5 mg $CuCl/Fe_3O_4$-TEDETA has less effect on the yield and time of the reaction.



Scheme 2. Synthesis of 2,3-dihydroquinazolin-4(1H)-ones.

Table 1
Optimization of the amount of $CuCl/Fe_3O_4$-TEDETA.[a]

Entry	Catalyst (mg)	Yield[b] (%)
1	–	Trace[c]
2	1	23
3	3	50
4	5	98
5	8	98

[a] Reaction conditions: 4-chlorobenzaldehyde (1 mmol), 2-aminobenzamide (1 mmol) and ethanol (10 mL) at reflux temperature.

[b] Isolated yields.

[c] Reaction proceeds in the absence of the catalyst.

Table 2
Synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives.

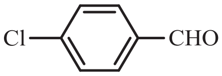
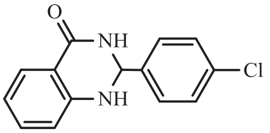
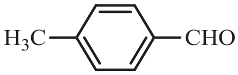
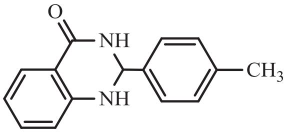
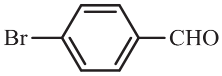
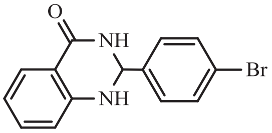
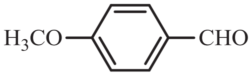
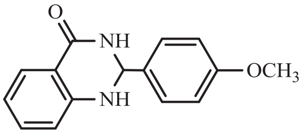
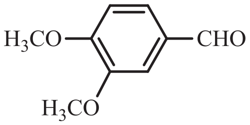
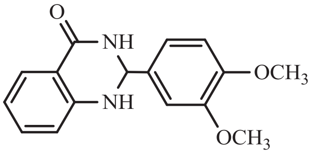
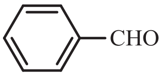
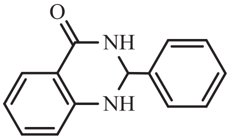
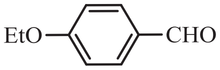
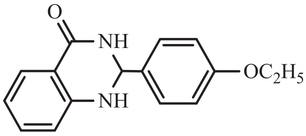
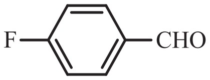
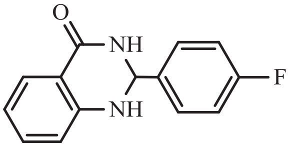
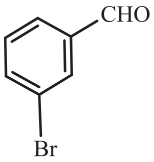
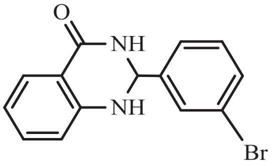
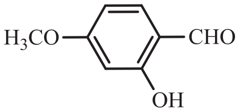
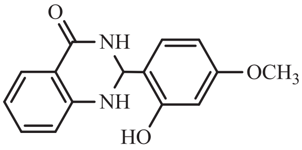
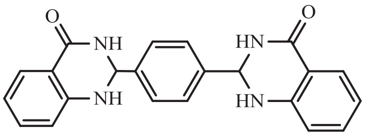
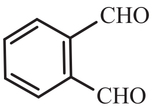
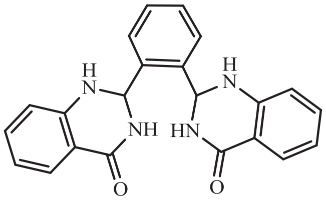
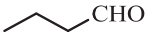
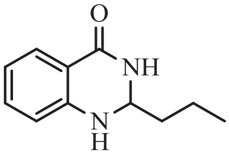
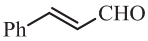
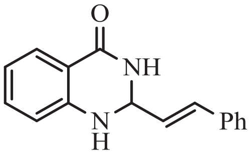
Entry	Compound	Aldehyde (1)	Product (3)	Time (min)	Yield[b] (%)	Mp (°C) [Ref.]
1	**A**			45	98	202–203 [24]
2	**B**			60	95	225–226 [31]
3	**C**			55	98	197–200 [34]
4	**D**			25	97	182–183 [31]
5	**E**			30	96	211–212 [24]
6	**F**			30	97	223–224 [24]
7	**G**			40	97	167–168
8	**H**			20	96	192–193 [34]
9	**I**			50	94	184–185 [36]
10	**J**			40	97	262–263
11	**K**			100	98	244–245 [34]

Table 2 (*Continued*)

Entry	Compound	Aldehyde (1)	Product (3)	Time (min)	Yield[b] (%)	Mp (°C) [Ref.]
12	**L**			70	97	272–273
13	**M**			30	95	157–159 [23]
14	**N**			45	96	209–210 [23]

[a] Reaction conditions: aldehyde (1 mmol), 2-aminobenzamide (1 mmol), catalyst (5 mg) and ethanol solvent (10 mL) at reflux temperature.

[b] Isolated yields.

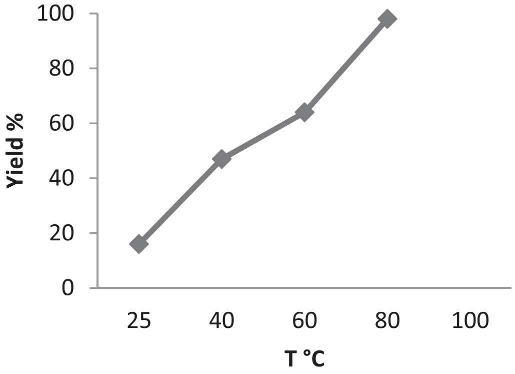


Fig. 6. Effect of temperature in the preparation of 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one.

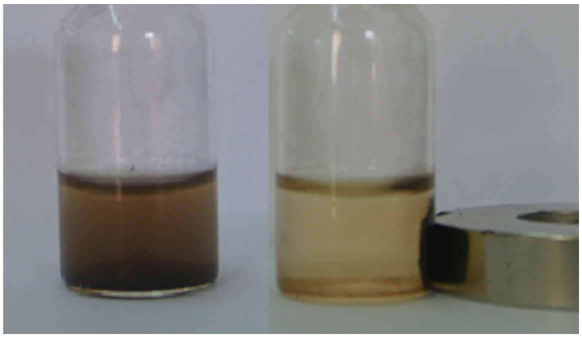


Fig. 7. CuCl/Fe_3O_4-TEDETA in the reaction mixture (a) and its recovery using an external magnet (b).

In the next step, the effect of temperature was investigated by carrying out the model reaction in the presence of CuCl/Fe_3O_4-TEDETA (5 mg) at room temperature (25 °C), 40, 60 and 80 °C. It was observed that the yield was increased as the reaction temperature was raised (Fig. 6).

Based on above observations, we conducted the same reactions using 2-aminobenzamide, variety of different substituted aldehydes **1a–n** in the presence of 5 mg of CuCl/Fe_3O_4-TEDETA under similar conditions. As expected, satisfactory results were observed, and the results are summarized in Table 2. It is shown that in general a wide range of aldehydes could react with 2-aminobenzamide smoothly and give **3a–n** in good to excellent yields (Table 2, entries 1–12). It is also notable that the electronic property of the aromatic ring of aldehydes has some effects on the rate of the condensation process. The use of aliphatic aldehydes derivative, such as butyraldehyde and cinnamaldehyde also afforded the desired products in excellent yield (Table 2, entries 13 and 14).

After completion of the reaction, the reaction solution was then easily removed from the reaction vessel by decantation while the magnet held the magnetic nanoparticles inside the vessel. The magnetic catalyst was washed with ethanol and water (Fig. 7).

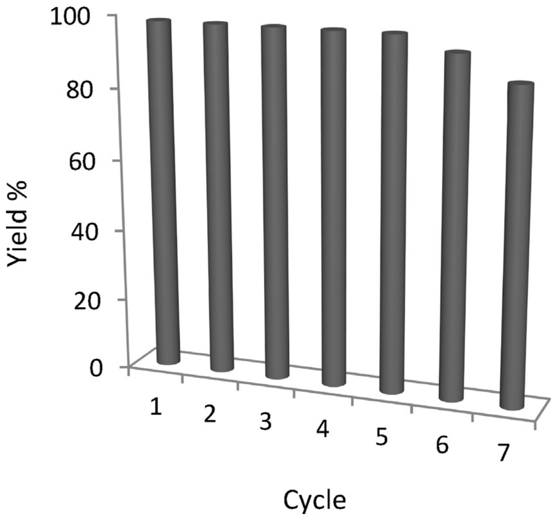


Fig. 8. Reuse of the nanocatalyst for conversion of 4-chloroaldehyde to the corresponding 2,3-dihydroquinazolin-4(1H)-ones.

3.3. *Recyclability of the catalyst*

Reusability of the catalyst was studied through a condensation reaction of 4-chlorobenzaldehyde with 2-aminobenzamide. The reaction was carried out under specified reaction conditions using 5 mg CuCl/Fe_3O_4-TEDETA as the catalyst. After completion of the reaction, nanoparticles were magnetically separated. The deposited catalyst was washed with ethanol 3–4 times to confirm the complete removal of any organic residuals; the activated catalyst was then redispersed in the desired solvent for further catalytic reaction cycles. The same process was repeated after each reaction cycle to isolate and reuse the catalyst. The reaction proceeded smoothly with a yield of 98–87% (Fig. 8). This result indicates that the activity of the catalyst was not much affected on recycling.

4. Conclusions

In conclusion, $CuCl_2/Fe_3O_4$-TEDETA complex can function as a heterogeneous catalyst for synthesis of 2,3-dihydroquinazolin-4(1H)-ones. The large surface area of magnetic nanoparticle made complex a good catalyst. Due to its operational simplicity, generality and efficacy, this material is applicable to the synthesis of a variety of organic compounds. It is important to mention that the morphology of $CuCl_2/Fe_3O_4$-TEDETA does not change after reaction which is the key factor for its reusable property. Importantly, the current $CuCl_2/Fe_3O_4$-TEDETA catalyst offers the great advantage that it can be recovered and introduced in further catalytic cycles with similar catalytic efficiency and/or activity.

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