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FULL PAPER

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Ni(II)-Adenine complex coated Fe_3O_4 nanoparticles as high reusable nanocatalyst for the synthesis of polyhydroquinoline derivatives and oxidation reactions

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In the present study, Fe_3O_4 nanoparticles were prepared via simple and versatile procedure. Then, a novel and green catalyst was synthesized by the immobilization of Ni on Fe_3O_4 nanoparticles coated with adenine. The activity of this nanostructure compound was examined for the oxidation of sulfides, oxidative coupling of thiols and synthesis of polyhydroquinolines. The prepared catalyst was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray Diffraction (XRD), thermal gravimetric analysis (TGA), and vibrating sample magnetometer (VSM) measurements. This organometallic catalyst was recovered by the assistance of an external magnetic field from the reaction mixture and reused for seven continuous cycles without noticeable change in its catalytic activity.

KEYWORDS
adenine, Fe_3O_4, polyhydroquinoline, sulfide, thiol

1 | INTRODUCTION

The target of science is recently shifted toward preserving environment, thus catalyst recovery and reusability are important properties in catalytic processes.[1,2] Homogeneous catalysts have complicated recovery process; therefore heterogeneous catalysts have been proposed as a primary solution in catalysis. In general, homogeneous catalysts can be easily recovered via surface grafting to heterogeneous supports, such as carbon, metal oxides, molecular sieves (SBA-15 and MCM-41), ionic liquids and polymers.[3–8] However, during the tedious recycling in these heterogeneous systems via filtration and the inevitable loss of solid in the recovery process, similar problems are encountered.[9–11] Nowadays, magnetic nanoparticles (MNPs) are considered as ideal supports for the heterogenization of homogeneous catalysts support because of their easy preparation and high surface area, high dispersion resulting in high catalyst loading capacity, outstanding stability, easy separation of the catalyst through an external magnet, and simple and inexpensive procedure.[12–20] In the last few years, several procedures including various magnetic catalysts have been reported for the synthesis of polyhydroquinoline derivatives and oxidation reactions.[21–23] Organic sulfoxides are vital in laboratory and are useful in chemical industries. Selective oxidation of sulfides to sulfoxides and sulfones under adjusted reaction has been the subject of various studies for the past two decades because it has extensive applications for production of organosulfurous compounds and some medicines.[24–27] Besides, polyhydroquinoline (PHQ) derivatives are important compounds because they have emerged as one of the most important classes of drugs for treatment of cardiovascular diseases. They are also geroprotective, bronchodilator and have the ability to modulate calcium channels.[28–32]

Although a few reagents and catalysts have recently been reported for these reactions,[33–37] there are major disadvantages of these methods such as long reaction times, operational costs and product purity, low product yields, difficulty in preparation and/or storage of reagents or catalysts, toxic chemicals and tedious workup. Hence, an environmentally benign process and development of new catalysts remains in great demand to overcome these drawbacks.

Adenine is a nucleobase, and used in synthesis of protein. This important organic compound as a chemical component of DNA and RNA is complementary to either thymine in DNA or uracil in RNA. Adenine and its derivatives have a variety of roles in the central and peripheral nervous systems and in the immune, anti-infection, cardiovascular, renal, musculo-skeletal systems, agonists and antagonists. These compounds have an important role to generate coordination complexes and polymers as natural multisided ligands.[38–45] In recent years, nickel compounds have been widely studied because of their potential applicability in biochemistry and industry. These compounds has been recognized as catalysts and widely utilized for the synthesis of polyhydroquinoline derivatives and oxidation reactions. Recently, there has been considerable effort in the ability of adenine to form complexes with nickel. [46–48] Therefore, our studies have been done on the synthesis of a magnetically recoverable nanocatalyst using complex formation of adenine with nickel.

In the current paper, we report the synthesis of a novel and magnetically separable nanocatalyst by the immobilization of a Ni complex onto Fe_3O_4, and successfully demonstrate its application as a heterogeneous catalyst in the oxidation of sulfides, oxidative coupling of thiols and synthesis of polyhydroquinolines.

2 | EXPERIMENTAL

2.1 | Materials

All reagents and solvents are commercially available from Sigma-Aldrich and Merck chemical companies and are used without further purification. The particle size and morphology were investigated by measuring SEM using FESEM-TESCAN MIRA3. VSM measurement was recorded by a Vibrating Sample Magnetometer (VSM) MDKFD. TGA was carried out on Shimadzu DTG-60 instrument. IR spectra were examined by KBr disc using a VRTEX 70 model BRUKER FT-IR spectrophotometer. Powder X-ray diffraction (XRD) measurements were investigated using Co Kα radiation (λ = 1.78897 Å nm) with operating at 40 keV, and a cathode current of 40 Ma. The content of Ni was investigated by inductively coupled plasma optical emission spectrometry (ICP-OES). Melting points were recorded by an Electrothermal 9100 apparatus. TEM analysis of the catalyst was recorded using Zeiss-EM10C transmission electron microscope.

2.2 | Preparation of the Fe_3O_4-adenine

Superparamagnetic nanoparticles (MNPs) were synthesized with chemical coprecipitation method and coated with 3-chloropropyltrimethoxysilane (CPTMS) by covalent bonds.[49,50] According to this method, 2.35 g of $FeCl_3.6H_2O$ and 0.86 g of $FeCl_2.4H_2O$ were dissolved in 40 ml deionized water under nitrogen gas with vigorous stirring at 80 °C. Then 5 ml of NH_4OH solution was injected into the reaction mixture and immediately black precipitate was formed. The black magnetite nanoparticles were separated by magnetic decantation, washed several times with deionized hot water and ethanol. Finally, MNPs were dried in vacuum at 60°C. To prepare Fe_3O_4-Cl, 1 g of MNPs powder was suspended in toluene (20 ml) and 1.5 ml of CPTMS was added into the reaction mixture. Then the mixture was refluxed for 24 h. Fe_3O_4-Cl was separated by an external magnet and washed with hexane and dried at room temperature. Finally, 1 g of Fe_3O_4-Cl powder and 3 ml of triethylamine were added in toluene (20 ml) then 0.27 g of adenine was added into the reaction mixture and refluxed for 48 h. The final product (Fe_3O_4-Adenine) was separated by an external magnet, washed with deionized water and ethanol several times and dried at room temperature.

2.3 | Preparation of the Ni(II) immobilized on Fe_3O_4-adenine

In this step, Fe_3O_4-Adenine was employed as support. Briefly, Fe_3O_4-Adenine (1 g) and $Ni(NO_3)_2.6H_2O$ (0.727 g) were mixed in 30 ml ethanol, and then the mixture was refluxed for 16 h. The nanosolid Fe_3O_4-Adenine-Ni was separated from the solution by an external magnet. Finally, the magnetic catalyst was washed with copious amounts of ethanol and dried under vacuum at room temperature.

2.4 | General procedure for the oxidation of sulfides

To a mixture of sulfide (1 mmol) and 33% H_2O_2 (0.5 mL), Fe_3O_4-Adenine-Ni (0.005 g) as catalyst was added; and then the mixture was stirred at room temperature under solvent-free condition and the progress of the reaction was monitored by TLC. Then, Fe_3O_4-Adenine-Ni catalyst was separated by an external magnet and the product was extracted with ethyl acetate, and then dried over anhydrous Na_2SO_4. Finally, the solvent was evaporated to obtain the pure products.

2.5 | General procedure for the oxidation of thiols to disulfides

Fe_3O_4-Adenine-Ni (0.005 g) was added to a mixture of sulfides (1 mmol) and H_2O_2 (0.5 ml) under solvent-free conditions with stirring at room temperature. After completion of the reaction (monitored using TLC), the catalyst was separated by applying an external magnet.

2.6 | General procedure for the synthesis of Polyhydroquinolines

Fe_3O_4-Adenine-Ni as catalyst (0.05 g) was added to a mixture of dimedone (1 mmol), aldehyde (1 mmol), ethyl acetoacetate (1 mmol), and ammonium acetate (1.2 mmol) in ethanol (2 ml) as solvent. Then the mixture was stirred for the appropriate time at 80°C, and the progress of the reaction was monitored by TLC. Finally, the catalyst was separated by an external magnet and solvent was evaporated. A crude solid was obtained and the pure product was prepared through crystallization from ethanol.

3 | RESULTS AND DISCUSSION

3.1 | Catalyst preparation

Scheme 1 illustrates the preparation of a novel magnetic nanoparticle catalyst. Fe_3O_4 nanoparticle was prepared according to our recently reported procedure.[51,52] Briefly, the surface of magnetic nanoparticles were coated using adenine ligand to achieve functionalized magnetic nanoparticles. Then, Fe_3O_4-Adenine-Ni nanocatalyst was prepared using stable interaction between the N7 atom of adenine and Ni^{2+}.[45]

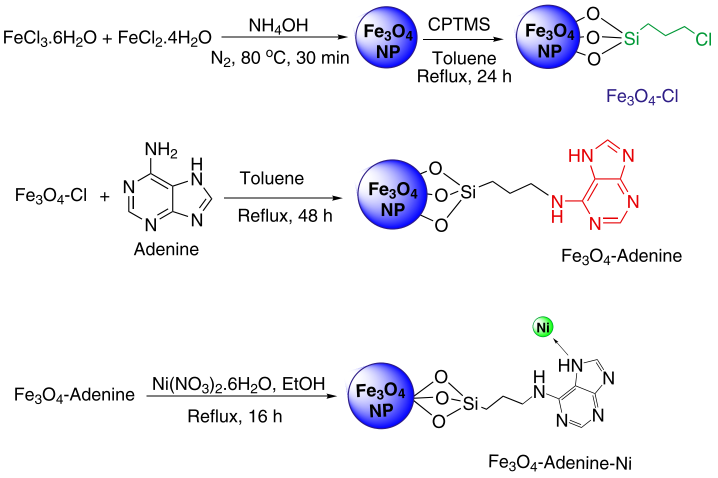
3.2 | Catalyst characterization

The morphology of the Fe_3O_4, Fe_3O_4-Adenine, Fe_3O_4-Adenine-Ni catalyst and recovered catalyst were obtained using scanning electron microscopy (SEM) technique. SEM images of these nanoparticles are given in Figure 1. As shown in this figure, the synthesized materials were formed with uniform nanometer-sized particles. It should be mentioned that the prepared samples were obtained with approximately spherical shape.

In order to observe the kinds of elements in Fe_3O_4-Adenine-Ni, the energy-dispersive X-ray spectroscopy (EDS) analysis of Fe_3O_4-Adenine-Ni was performed; which EDS patterns of this catalyst shows the presence of Fe, O, Si, N, C and Ni specie in the catalyst (Figure 2). Also, in order to determine the exact amount of Ni loaded on modified magnetic nanoparticles, ICP-OES analysis was performed and it was found to be 0.35 mmol g^{-1}.

Figure 3 shows TEM image of Fe_3O_4-Adenine-Ni nanocatalyst. This study showed particle size of approximately 10–30 nm for the synthesized catalyst.

Quantitative determination of the organic groups supported on the surface of Fe_3O_4 magnetic nanoparticles was investigated by thermo-gravimetric analysis (TGA) (Figure 4). The TGA curve shows a small amount of weight loss (about 2%) below 200 °C that is due to removal of hydroxyl groups and adsorbed solvents.[53] In the all samples, the first step of weight loss below 200 °C corresponds to the removal of the physically and chemically adsorbed solvents or surface hydroxyl groups, and the other weight loss in the range of 250–650 °C is related to the decomposition of the organic layers on the surface of Fe_3O_4 magnetic nanoparticles.[54] TGA curve of the Fe_3O_4-Adenine-Ni shows a weight loss of about 16% from 250 to 650 °C, resulting from the decomposition of immobilized organic spaces on the Fe_3O_4 surface. Meanwhile, weight loss of about 17% from 250 to 650 °C is observed for Fe_3O_4-Adenine.



SCHEME 1 Synthesis of Fe_3O_4-Adenine-Ni nanocatalyst

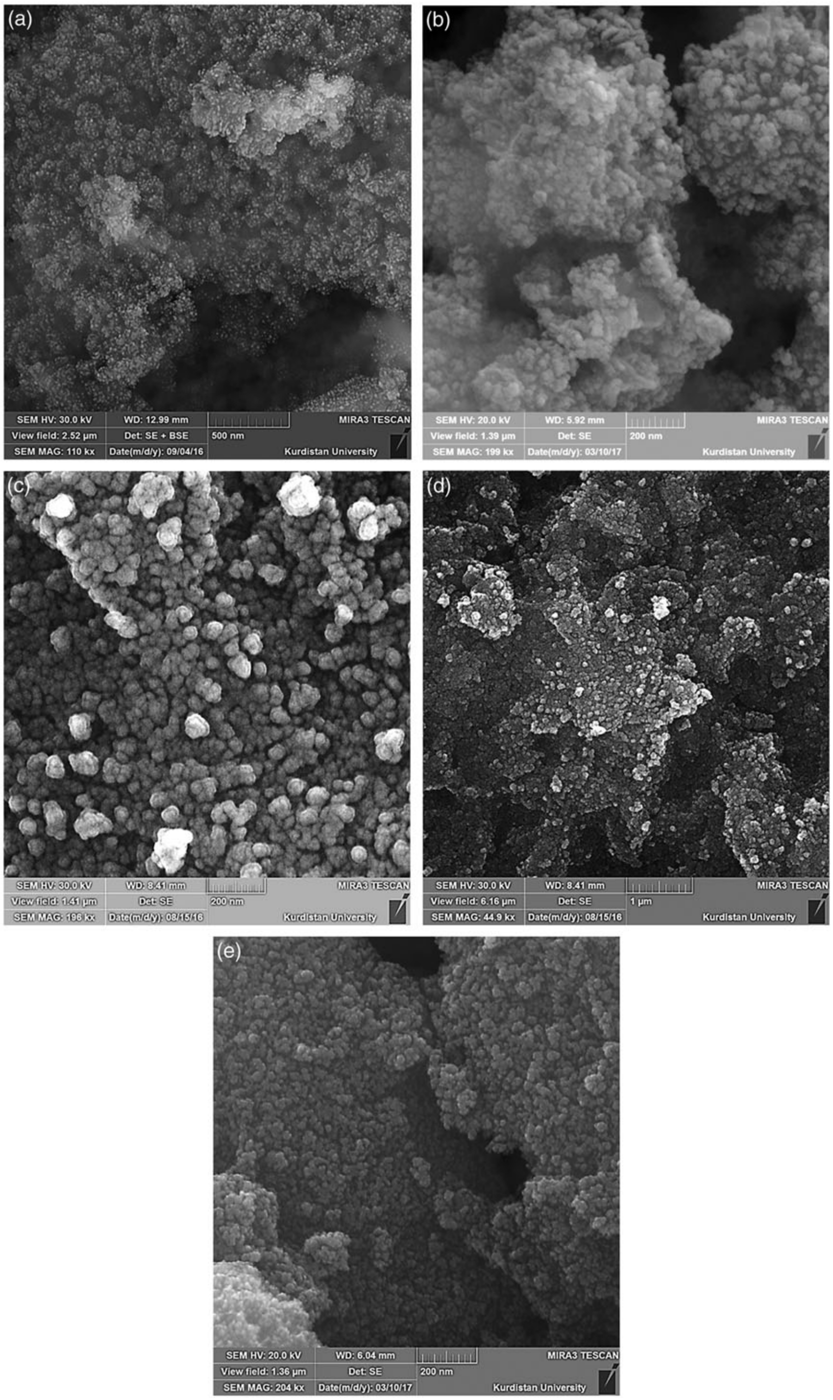


FIGURE 1 SEM images of Fe_3O_4 (a), Fe_3O_4-Adenine (b), Fe_3O_4-Adenine-Ni catalyst (c, d) at different magnifications and recovered Fe_3O_4-Adenine-Ni catalyst (e)

The X-ray diffraction analysis (XRD) pattern of Fe_3O_4-Adenine and Fe_3O_4-Adenine-Ni are shown in Figure 5 in which the Fe_3O_4 phase was identified by the peak positions of 2θ values at 35.69, 41.72, 51.05, 63.91, 67.94 and 74.83 which is in agreement with standard XRD pattern of Fe_3O_4 nanoparticles.[53] Also, the XRD pattern of catalyst shows that the Fe_3O_4 phase has not been changed during the modifications.

The magnetic property of Fe_3O_4-Adenine-Ni has been compared with bare Fe_3O_4 nanoparticles using vibrating sample magnetometer (VSM) technique (Figure 6). VSM measurements for Fe_3O_4 nanoparticles (77 emu g^{-1})[55] is higher than Fe_3O_4-Adenine-Ni (57.31 emu g^{-1}). Decrease in magnetic property of Fe_3O_4-Adenine-Ni is due to the grafting of organic layers and nickel complex on Fe_3O_4 nanoparticles.[56] On the basis of VSM results, the well grafting of organic layers including nickel complex on the Fe_3O_4 is verified.

FT-IR spectra for bare Fe_3O_4 nanoparticles, Fe_3O_4-Cl, Fe_3O_4-Adenine and Fe_3O_4-Adenine-Ni are shown in Figure 7. FT-IR spectrum of Fe_3O_4 nanoparticles (Spectrum a) shows a stretching vibration at 3401 and 579 cm

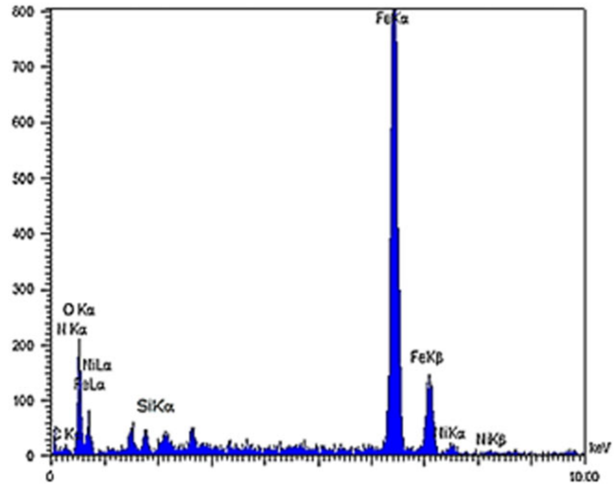


FIGURE 2 EDX spectrum of Fe_3O_4-Adenine-Ni

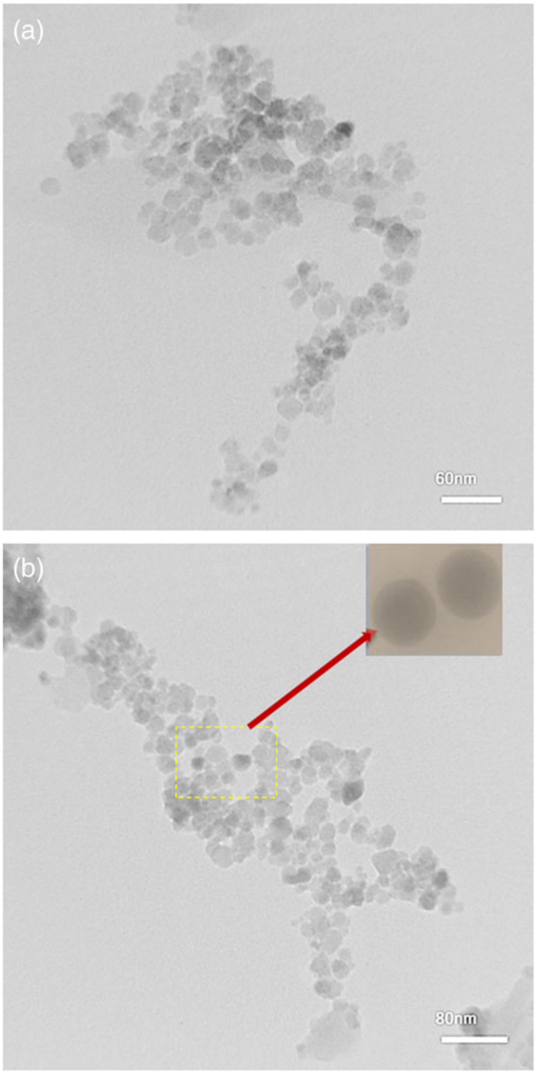


FIGURE 3 TEM images of Fe_3O_4-Adenine-Ni catalyst at different magnifications (a, b)

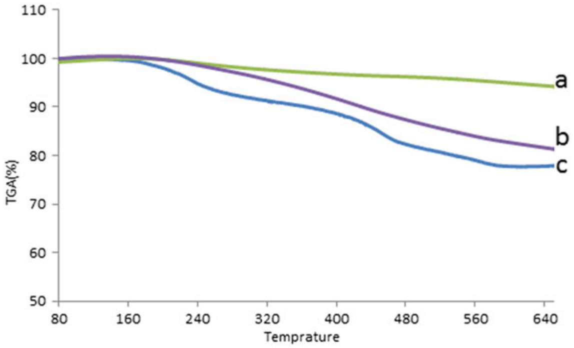


FIGURE 4 The TGA diagrams of Fe_3O_4 nanoparticles (a), Fe_3O_4-Adenine (b) and Fe_3O_4-Adenine-Ni (c)

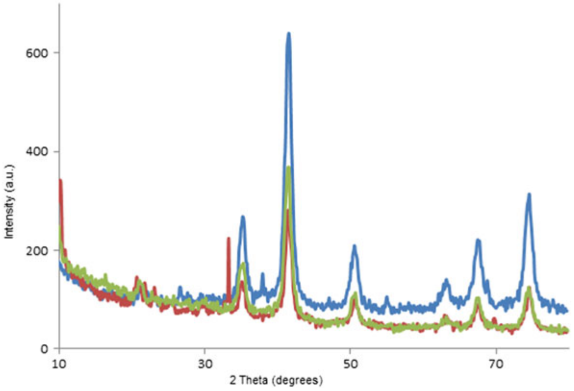


FIGURE 5 The XRD pattern of Fe_3O_4 (blue), Fe_3O_4-Adenine (red) and Fe_3O_4-Adenine-Ni catalyst (green)

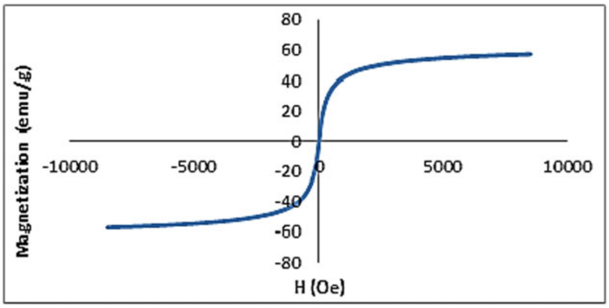


FIGURE 6 Magnetization curves for Fe_3O_4-Adenine-Ni at room temperature

$^{-1}$ which incorporates the contributions from both symmetrical and asymmetrical modes of the surface hydroxyl groups and Fe-O bonds of iron oxide, respectively.[57] In FT-IR spectra of Fe_3O_4-Cl (spectrum b), the presence of the anchored (3-choloropropyl) trimethoxysilane is identified by C–H stretching vibrations that appear at 2974 cm^{-1} and also O–Si stretching vibration modes that appear at 1009 and 1070 cm^{-1}.[58] In the FT-IR spectra of Fe_3O_4-Adenine (spectrum c), stretching vibrations of

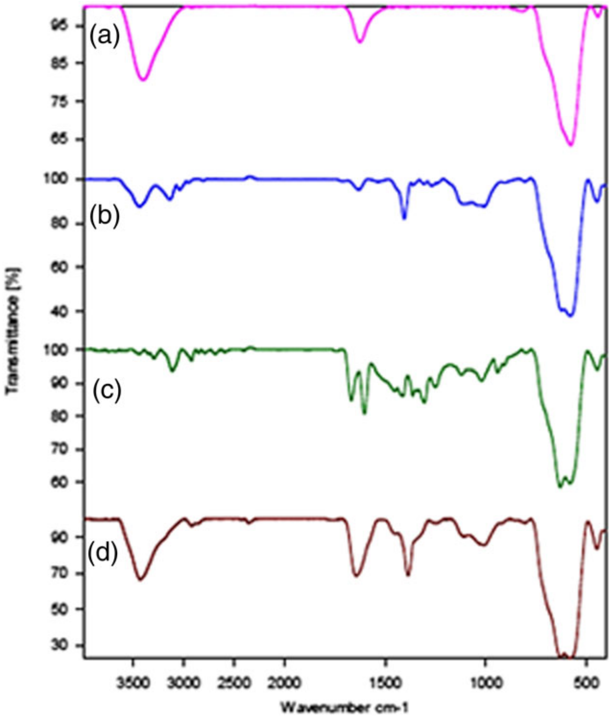
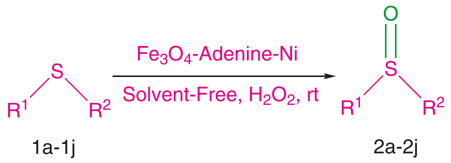
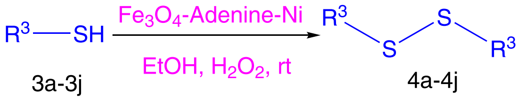


FIGURE 7 FT-IR spectrum for bare Fe_3O_4 nanoparticles (a), Fe_3O_4-Cl (b), Fe_3O_4-Adenine (c) and Fe_3O_4-Adenine-Ni (d)



SCHEME 2 Fe_3O_4-Adenine-Ni catalyzed the oxidation of sulfides to sulfoxides



SCHEME 3 Proposed mechanism for oxidation of sulfides in presence of Fe_3O_4-Adenine-Ni as catalyst

C = C and C = N has been identified by adsorption bands at 1306–1418 and 1603–1667 cm^{-1}. All of those bands reveal that the surface of Fe_3O_4 nanoparticles is successfully modified with organic layers.

3.3 | Catalytic studies

In this research, our studies were directed towards the outreach of practical and eco-friendly procedures for chemical synthesis.[59,60] We developed the preparation of a stable, recyclable and efficient Fe_3O_4-Adenine-Ni nanocatalyst. The catalytic activity of this nanocatalyst was examined with excellent activity in oxidation of sulfides to sulfoxides (Scheme 2), oxidative coupling of thiols into disulfides (Scheme 3) and synthesis of polyhydroquinoline derivatives (Scheme 6). In order to optimize the reaction conditions, methylphenylsulfoxide was prepared as a model compound in various solvents in the presence of different amount of catalyst and using different amount of hydrogen peroxide (H_2O_2). The results can be seen in Table 1. As shown in Table 1, the solvent-free condition in the presence of Fe_3O_4-Adenine-Ni (0.005 gr) and H_2O_2 (0.5 ml) at room temperature was found to be ideal reaction conditions for the conversion of methylphenylsulfide to the methylphenylsulfoxide.

In this study, a variety of sulfides with different functional groups were successfully employed to prepare the corresponding sulfoxides in high to excellent yields in a short reaction time. The results are shown in Table 2.

A plausible reaction mechanism for the oxidation of sulfides is shown in Scheme 4. The intermediate A is obtained by reaction of H_2O_2 with Fe_3O_4-Adenine-Ni, which is converted to active oxidant B. Then, nucleophilic attack of the sulfide on this intermediate (C_1) produces corresponding sulfoxide.[61]

In continuation of this research work, the catalytic activity of Ni-Adenine complex in comparison with Fe_3O_4-Adenine-Ni investigated for the conversion of

TABLE 1 Optimization of oxidation of sulfides to the corresponding sulfoxides using Fe_3O_4-adenine-Ni nanoparticles under various conditions

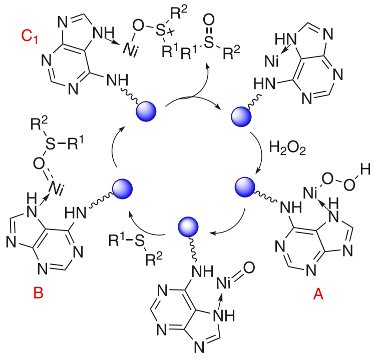
Entry	Solvent	H_2O_2	Catalyst (mg)	Time (min)	Yield (%)[a]
1	Solvent-Free	0.5	3	80	78
2	Solvent-Free	0.5	4	70	85
3	Solvent-Free	0.5	5	55	98
4	Solvent-Free	0.4	5	75	93
5	Ethanol	0.5	5	70	90
6	Ethyl acetate	0.5	5	85	88
7	Acetonitrile	0.5	5	95	83

[a] Isolated yields.

TABLE 2 Oxidation of sulfides to the sulfoxides in the presence of Fe_3O_4-Adenine-Ni

Entry	Substrate	Product	Time (min)	Yield (%)[a]	M.p. (°C)
1	Dipropylsulfide	2a	65	95	Oil
2	Diethylsulfide	2b	60	96	Oil
3	Dibenzylsulfide	2c	30	95	128–129
4	Benzylphenylsulfide	2d	90	97	115–117
5	Tetrahydrothiophene	2e	12	98	Oil
6	Dodecyl methylsulfide	2f	85	95	63–65
7	Methylphenylsulfide	2 g	55	98	Oil
8	Ethylphenylsulfide	2 h	65	94	Oil
9	2-(Methylthio)ethanol	2i	70	97	Oil
10	2-(Phenylthio)ethanol	2j	65	94	Oil

[a] Isolated yields.



SCHEME 4 Fe_3O_4-Adenine-Ni catalyzed the oxidative coupling of thiols into disulfides

methylphenylsulfide to the methylphenylsulfoxide under optimized conditions (Table 3). The results of this comparison show that the products were obtained in 97 and 98% yield in the presence of Ni-Adenine complex and Fe_3O_4-Adenine-Ni, respectively. Therefore to make an easily recoverable and efficient catalyst, the Ni-Adenine complex has been anchored on Fe_3O_4 nanoparticles. It should be mentioned that the Ni content of Ni-Adenine complex was found to be 0.65 mmol g^{-1}.

Also we examined the oxidative coupling of 4-methylbenzenethiol as a model substrate in various solvents and in the presence of different amount of Fe_3O_4-Adenine-Ni using different amount of hydrogen peroxide (H_2O_2) (Table 4). As shown in Table 4, Fe_3O_4-Adenine-Ni (0.005 g) in the presence of H_2O_2 (0.5 ml) in ethanol at room temperature was found to be the ideal reaction conditions for the oxidative coupling of 4-methylbenzenethiol.

As shown in Table 5, a wide range of thiols with different functional groups were converted to their corresponding products in the presence of Fe_3O_4-Adenine-Ni as catalyst in ethanol at room temperature. All products were prepared in the short reaction time and in good to excellent yields.

The proposed mechanism for this process using H_2O_2 as oxidant in the presence Fe_3O_4-Adenine-Ni catalyst is outlined in Scheme 5.[50]

We finally studied the synthesis of polyhydroquinoline derivatives. In order to optimize the reaction conditions, we examined the reaction of 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate (1.2 mmol) as a model reaction to synthesize the corresponding polyhydroquinoline. The effect of various parameters such as solvent, catalyst concentration and temperature was investigated for the model reaction. The reaction conditions for the one-pot synthesis of polyhydroquinoline derivatives were carried out for above mentioned reaction in EtOH, H_2O and PEG as solvents. As shown in Table 6, Fe_3O_4-Adenine-Ni is much more reactive in EtOH

TABLE 3 Effect of Ni-Adenine complex in comparison with Fe_3O_4-Adenine-Ni in oxidation of methylphenylsulfide as model compound under optimized conditions

Entry	Substrate	Catalyst	Time (min)	Yield (%)[a]
1	Methylphenylsulfide	Ni-Adenine complex	60	97
2	Methylphenylsulfide	Fe_3O_4-adenine-Ni	55	98 [this work]

[a] Isolated yields.

TABLE 4 Optimization of oxidative coupling of thiols into disulfides using Fe_3O_4-Adenine-Ni under various conditions

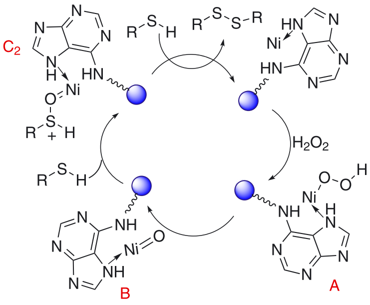
Entry	Solvent	H_2O_2	Catalyst (mg)	Time (min)	Yield (%)[a]
1	EtOH	0.5	3	85	78
2	EtOH	0.5	4	70	79
3	EtOH	0.5	5	70	97
4	EtOH	0.4	5	85	90
5	Solvent-free	0.5	5	75	96
6	Ethyl acetate	0.5	5	95	88
7	Acetonitrile	0.5	5	110	79

[a] Isolated yields.

TABLE 5 Oxidative coupling of thiols into disulfides using H_2O_2 in the presence of Fe_3O_4-adenine-Ni

Entry	Substrate	Product	Time (min)	Yield (%)[a]	M.p. (°C)
1	Phenylmethanethiol	4a	85	90	57–59
2	4-Methylbenzenethiol	4b	70	97	38–40
3	Naphthalene-2-thiol	4c	55	91	134–136
4	2-Mercaptobenzoic acid	4d	90	87	275–278
5	Benzo[d]thiazole-2-thiol	4e	48	96	174–175
6	2-Mercaptoethanol	4f	25	93	Oil
7	2-Mercaptoacetic acid	4 g	45	93	Oil
8	4-Bromothiophenol	4 h	80	95	88–90
9	Benzo[d]oxazole-2-thiol	4i	35	93	94–96
10	2-Mercaptopyridine	4j	70	87	55–57

[a] Isolated yields.

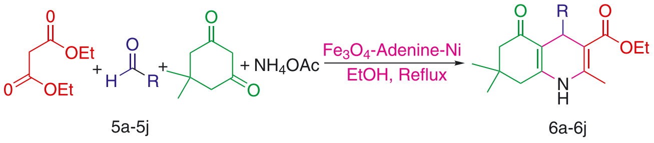


SCHEME 5 Proposed mechanism for oxidative coupling of thiols in presence of Fe_3O_4-Adenine-Ni as catalyst

compared with H_2O and PEG. Moreover, this reaction was optimized under the influence of different amounts of Fe_3O_4-Adenine-Ni as a reusable nanocatalyst in EtOH. We observed that the best results were obtained in EtOH in the presence of 50 mg of catalyst. The reaction temperature was also optimized and 80 °C was chosen as reaction temperature. The results of this study can be seen in Table 6.

Finally, a variety of aromatic and aliphatic aldehydes were employed to synthesis the corresponding polyhydroquinoline derivatives in high to excellent yields in a short time (Table 7 and Scheme 6).

A plausible reaction mechanism for the synthesis of polyhydroquinoline derivatives in the presence of Fe_3O_4-Adenine-Ni as catalyst is shown in Scheme 7. As shown in this scheme, the role of catalyst comes in the Knoevenagel coupling of aldehydes with active methylene compounds to produce an α, β-unsaturated compound and in the Michael addition of intermediates to obtain the polyhydroquinoline.[62]

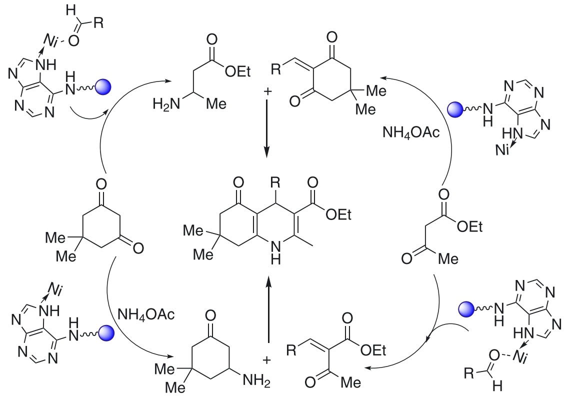


SCHEME 6 Fe_3O_4-Adenine-Ni catalyzed the one-pot synthesis of polyhydroquinoline derivatives

TABLE 6 Optimization of amount of catalyst, solvent and temperature for the synthesis of polyhydroquinolines via the condensation of 4-chlorobenzaldehyde (1 mmol), dimedon (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate (1.2 mmol) as a model reaction at 80 °C

Entry	Solvent	Catalyst (mg)	Temperature (°C)	Time (min)	Yield (%)[a]
1	EtOH	30	80	230	83
2	EtOH	40	80	165	87
3	EtOH	50	80	145	96
4	EtOH	50	40	195	91
5	PEG	50	80	350	83
6	H_2O	50	80	320	87

[a] Isolated yields.



SCHEME 7 The proposed mechanism of synthesis of polyhydroquinoline derivatives in presence of Fe_3O_4-Adenine-Ni as catalyst

3.4 | Recyclability of the catalyst

The reusability of magnetic catalysts is one of their noteworthy advantages, which makes them useful for environmental concerns and commercially applicable processes. In this study, the reusability of Fe_3O_4-Adenine-Ni catalyst was investigated after completion of the reaction. Fe_3O_4-Adenine-Ni catalyst could be easily separated using application of an external magnet then washed with ethanol and double distilled water. As shown in Figure 8, this catalyst was recycled and reused at least for seven consecutive cycles without considerable decrease of its catalytic activity. Since leaching of nickel from Fe_3O_4-Adenine-Ni is very negligible for these reactions, the catalytic activity has been slightly decreased. Also, in order to determine the exact amount of Ni loaded on modified magnetic nanoparticles for the conversion of methylphenylsulfide to the methylphenylsulfoxide at least for seven consecutive cycles, ICP-OES analysis was found to be 0.34 mmol g^{-1}.

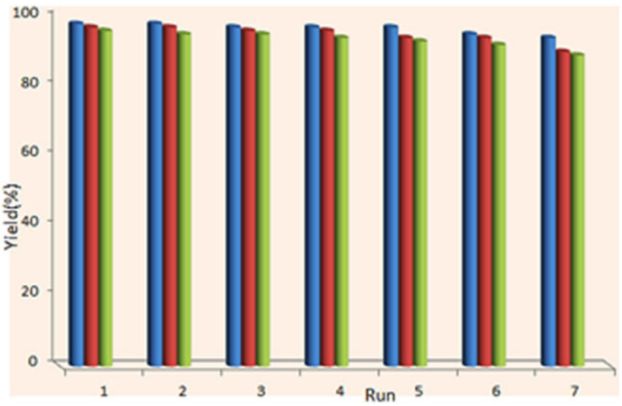


FIGURE 8 Reusability of Fe_3O_4-Adenine-Ni in the oxidation of methyl phenyl sulfide (blue column), coupling of 4-methylthiophenol (red column) and condensation of 4-chlorobenzaldehyde, dimedone, ethylacetoacetate and ammonium acetate (green column)

TABLE 7 Synthesis of various polyhydroquinolines in the presence of Fe_3O_4-Adenine-Ni (50 mg) under the standard reaction conditions

Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	M.p. (°C)
1	Benzaldehyde	6a	165	91	217–219
2	4-Bromobenzaldehyde	6b	205	95	251–253
3	4-Methylbenzaldehyde	6c	195	97	250–253
4	4-Chlorobenzaldehyde	6d	145	96	148–150
5	4-Fluorobenzaldehyde	6e	160	97	183–185
6	4-Methoxybenzaldehyde	6f	235	96	248–250
7	4-Hydroxybenzaldehyde	6 g	195	91	226–228
8	3-Nitrobenzaldehydel	6 h	210	93	176–179
9	3,4-Di(methoxy)benzaldehyde	6i	255	93	203–205
10	Isobutyraldehyde	6j	230	91	162–163

[a] Isolated yields.

TABLE 8 Comparison of Fe3O4-Adenine-Ni for the oxidation of methylphenylsulfide with previously reported procedure

Entry	Substrate	Catalyst	Time (min)	Yield (%)[a]
1	Methylphenylsulfide	Ni-salen-MCM-41	156	95 [63]
2	Methylphenylsulfide	$VO_2F(dmpz)_2$	300	95 [64]
3	Methylphenylsulfide	VO-2A3HP-MCM-41	120	96 [65]
4	Methylphenylsulfide	NBS	270	93[66]
5	Methylphenylsulfide	Zr-oxide@MCM-41	300	98 [67]
6	Methylphenylsulfide	DSA@MNPs	360	98 [68]
7	Methylphenylsulfide	Fe_3O_4-Adenine-Ni	55	98 [this work]

[a]Isolated yields.

3.5 | Comparison of the catalyst

In order to evaluate the efficiency of Fe_3O_4-Adenine-Ni nanocatalyst, we compared the results for the oxidation of sulfides in the presence of described catalyst with previously reported catalysts in the literature (Table 8). The results of this research project verified short reaction time and higher yield than the other catalysts. Furthermore, compared with other catalysts, ease of operation, simple and inexpensive procedure, easy separation of the catalyst through an external magnet, non-toxicity and low cost are several advantages of this organometallic catalyst.

4 | CONCLUSION

In summary, an environmentally friendly and novel Fe_3O_4-Adenine-Ni catalyst was prepared and its structure was characterized by FT-IR, TGA, EDS, ICP-OES, XRD and SEM. In addition, catalytic activity of this catalyst was probed for the synthesis of polyhydroquinoline compounds, sulfoxides and disulfides derivatives. Other significant features of this method include the use of a commercially available, waste-free process, cheap and chemically stabile reagents, short reaction time, operational simplicity, high efficiency under relatively mild conditions and use of ethanol as green solvent. This supported magnetic nanoparticle can be easily recovered with an external magnetic field and reused seven times before any considerable decrease in its catalytic activity.

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