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Synthesis and characterization of amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles: A heterogeneous, new and magnetically separable catalyst for the solvent-free synthesis of 2,4,5–trisubstituted imidazoles, benzo*[d]*imidazoles, benzo*[d]* oxazoles and azo-linked benzo*[d]*oxazoles

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Abstract

Amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles ($NiFe_2O_4$@SiO_2@amino glucose) were chemically synthesized and characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), energy dispersive X-ray analysis (EDX), vibrating sample magnetometer (VSM), Zetasizer and Fourier transform infrared spectroscopy (FT-IR) instruments. $NiFe_2O_4$@SiO_2@amino glucose supply an environmentally friendly procedure for the synthesis of 2,4,5-trisubstituted imidazoles through one-pot multicomponent condensation of benzil or benzoin, ammonium acetate with aryl aldehydes and for the synthesis of benzoxazoles using condensation reaction of 2-aminophenol with aryl aldehydes under solvent free condition. In the other study, this synthesized magnetically reusable catalyst was introduced as a new avenue for the synthesis of

benzo*[d]*imidazoles using the reaction between aryl aldehydes and 1,2-diaminobenzene. These compounds were obtained in high yields and short reaction times. The catalyst could be easily recovered and reused for five cycles with almost consistent activity. Synthesized compounds were characterized by their physical constant, comparison with authentic samples, FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis.

***Key Words*:** oxazoles, imidazoles, $NiFe_2O_4@SiO_2$@amino glucose, solvent free reaction

Introduction

The imidazole substructures were found in a large number of pharmacologically active compounds and natural products such as the hypnotic agent etomidate, amino acid histidine [1], the proton pump inhibitor omeprazole [2], the antiulcerative agent cimetidine [3], the benzodiazepine antagonist flumazenil [4], the fungicide ketoconazole [5], inhibitors of P38 MAP kinase [6], glucagon receptor antagonists [7], transforming growth factor b1 (TGF-b1) type 1 active receptor-like kinase (ALK5) [8], B-Raf kinase [9], cyclooxygenase-2 (COX-2) [10], biosynthesis of interleukin-1 (IL-1) [11], plants growth regulators [12], anti-bacterial [13], pesticide [14], therapeutic agents [15], antitumor [16], modulators of P-glycoprotein (P-gp)-mediated multidrug resistance (MDR) [17], and also CB1 cannabinoid receptor antagonists [18].

In 1882, Radziszewski and Japp [19, 20] reported the first synthesis of a highly substituted imidazole from a 1,2-dicarbonyl compound, aldehydes and ammonia. In addition, they can also be accessed by the cycloaddition reaction of mesoionic-1,3-oxazolium-5-olates with *N*-(arylmethylene)-benzene sulfonamides, [21] hetero-cope rearrangement, [22] four component condensation of aryl glyoxals, primary amines, carboxylic acids and isocyanides on Wang resin, [23] condensation of a 1,2-diketone with an aryl nitrile and primary amine under microwave

irradiation, [24] and reaction of *N*-(2-oxo)-amides with ammonium trifluoroacetate [25]. Another method for the synthesis of these compounds is the reaction of 1,2-phenylenediamine with aldehydes in the presence of acidic catalysts under various reaction conditions [26-34].

Benzoxazoles have been reported to release a wide range of biological activities as antitumor [35], antibacterial [36], antiviral [37], antibiotic [38], antifungal [39], antiulcer [40], antihistaminic [41], cyclooxygenase inhibiting [42], anticonvulsant [43], anti-inflammatory [44, 45], anti-tubercular [46], antiparasitics [47], hypoglycemic [48], herbicidal [49], antiallergic [50], antihelmintic and cytotoxic activity [51]. Benzoxazoles are structural isosteres of the nucleic bases adenine and guanine, that allow them to interact easily with polymers of living systems [52] and some of them have found applications as fluorescent whitening agents [53].

Two most common protocols for the synthesis of benzoxazoles are: (1) the direct condensation of 2-aminophenol with carboxylic acid or aldehyde under harsh conditions, such as in the presence of strong acid, high temperature [54] and (2) the oxidative cyclization of phenolic Schiff bases, using various oxidants [55-57].

Most of the repoted procedures for the synthesis of imidazoles and benzoxazoles have some serious defects, such as tedious work-up and purification, significant amounts of toxic waste materials, highly acidic conditions, long reaction time, occurrence of side reactions, low yields, use of expensive reagents or catalysts, low selectivity and high temperatures in refluxing or microwave condition. Therefore, development of easy, green, effective, high-yielding, and eco-friendly approaches using novel catalysts for the synthesis of imidazoles and benzoxazoles is an important research topic for organic chemists.

The main purpose of the present study was to synthesize magnetically separable $NiFe_2O_4$@SiO_2@amino glucose nanoparticles (NPs) as a reusable and efficient catalyst for the

green synthesis of 2,4,5-trisubstituted imidazoles and benzoxazoles using one-pot multicomponent condensation reactions.

2. Material and methods

2.1. Materials and instruments

All of the used chemicals were purchased from Merck (Darmstadt, Germany), Fluka (Buchs, Switzerland). All solvents used were dried and distilled according to standard procedures. Melting points were measured on an Electrothermal IA 9100 melting point apparatus (United Kingdom). FT-IR spectra were obtained in the range of 400-4000 cm^{-1} on a Shimadzu FT-IR 8600 spectrophotometer (Japan). ^{1}H and ^{13}C NMR spectra were determined on a Bruker 400 DRX Avance instrument (Germany) at 400 and 100 MHz. Elemental analyses were recorded on a Carlo-Erba EA1110CNNO-S analyser (Italy). X-ray powder diffraction (XRD) patterns of nanostructures were obtained using a Philips (Netherlands) Xpert diffractometer (CuK_{α}, radiation, λ=0.154056), at a scanning speed of 2°/min from 10° to 80° (2θ). Transmission electron microscopy (TEM) measurements were carried out on a Zeiss-EM10C-100 KV instrument (Germany). Energy dispersive X-ray spectroscopy (EDX) analysis was performed on a Sirius SD_scientific equipments (United Kingdom). Investigation of magnetic property of nanocatalyst was done using a vibrating sample magnetometer (VSM) from Meghnatis Daghigh Kavir company (model MDKB, Kashan, Iran). A strong magnet with 1.4 Tesla magnetic field was applied for the magnetic separation of nanocatalyst. A thermal analysis system from Polymer Laboratories Ltd (United Kingdom) was utilized to study the thermal stability of the synthesized nanocatalyst. The Zeta potential of the synthesized nanocatalyst was measured using

a Zetasizer instrument (Malvern, United Kingdom). Thin layer chromatography (TLC) was carried out with ethyl acetate: n-hexane 1:4 on TLC Silica gel 60 F□□□.

2.2. Synthesis of $NiFe_2O_4$ nanoparticles

The $NiFe_2O_4$ nanoparticles were prepared by the co-precipitation method. The starting materials were iron nitrate [$(Fe(NO_3)_3.9H_2O)$], nickel nitrate [$(Ni(NO_3)_2.6H_2O)$], polyethylene oxide (PEO) $[CH_2CH_2AOA]_n$ and hydrazine hydrate (N_2H_4-H_2O). In a typical synthesis, 0.2 M (20 mL) solution of iron nitrate and 0.1 M (20 mL) solution of nickel nitrate were prepared and vigorously mixed under stirring for 1 h at 80 °C. PEO was added into the solution as a capping agent. Here, 0.2 g of PEO capped $NiFe_2O_4$ composite was tagged as nanoparticles. Subsequently, 5 mL of hydrazine hydrate was added drop by drop into the solution and brown color precipitates were formed. Finally, the precipitates were separated by centrifugation and dried in oven for 4 h at 100 °C. The acquired substances were annealed for 10 h at 300 °C [58].

2.3. Synthesis of silica-coated $NiFe_2O_4$ magnetic nanoparticles ($NiFe_2O_4@SiO_2$ MNPs)

Typically, 500 mg of the $NiFe_2O_4$ nanoparticles were dispersed by ultrasonic vibration in a mixture of ethanol (20 mL), deionized water (3 mL) and 1 mL of 25 wt% concentrated aqueous ammonia solution for 20 min. Subsequently, 0.7 mL of tetraethylorthosilicate (TEOS) was added dropwise. After stirring for 12 h at room temperature under N_2 atmosphere, the products was collected from the solution using a magnet, and then washed several times with deionizied water and ethanol and dried at 25 °C under vacuum.

2.2. Synthesis of $NiFe_2O_4@SiO_2$-Cl MNPs

500 mg $NiFe_2O_4@SiO_2$ nanoparticles were dispersed into 50 mL toluene and sonicated for 20 min, followed by the addition of 0.5 mL (3-chloropropyl)trimethoxysilane (CPTES). Then, the mixture was refluxed at 110 °C with continuous stirring for 12 h under a nitrogen flow. The

resulting $NiFe_2O_4$@SiO_2-Cl MNPs were collected by magnetic separation followed by washing with toluene and ethanol several times and drying at 60 °C for 6 h.

2.3. Synthesis of $NiFe_2O_4$@SiO_2@amino glucose

500 mg $NiFe_2O_4$@SiO_2-Cl MNPs were dispersed into 50 ml of toluene and sonicated for 30 min, followed by the addition of 0.5 mL glucose amine. Then, the mixture was refluxed at 110 °C with continuous stirring for 12 h under a nitrogen gas flow. The resulting functionalized $NiFe_2O_4$@SiO_2@aminoglucose was collected by magnetic separation followed by washing with toluene and ethanol several times and drying at 80 °C for 8 h.

2.4. General procedure for preparation of trisubstituted imidazoles 4a-m

A mixture of aldehyde 1 (1.0 mmol), benzyl or benzoin 2 (1.0 mmol), NH_4OAc (1mmol) and 0.05 g $NiFe_2O_4$@SiO_2@aminoglucose were stirred at room temperature under solvent free condition for the required reaction time according to Table 3. After completion of the reaction, as indicated by TLC (TLC Silica gel 60 F_{254}, ethyl acetate: n-hexane 1: 4), the resulting mixture was diluted with hot ethanol (10 mL) and the catalyst was separated by the external magnet and washed with hot distilled water (5 mL) and ethanol (3 mL) two times. The filtrate was cooled down to room temperature and the precipitated crude products were collected and recrystallized from ethanol if necessary.

2.5. General procedure for preparation of benzo[d]imidazoles 6a-k

A mixture of aldehyde 1 (2.0 mmol), 1,2-diaminobenzene (1 mmol) and 0.05 g of $NiFe_2O_4$@SiO_2@aminoglucose were stirred at room temperature under solvent free condition for the required reaction time according to Table 4. After completion of the reaction, as indicated by TLC (TLC Silica gel 60 F□□□, ethyl acetate: n-hexane 1: 4), the resulting mixture was diluted with hot ethanol (10 mL) and the catalyst separated by the external magnet and washed with hot

distilled water (5 mL) and ethanol (3 mL) two times. The filtrate was cooled down to room temperature and the precipitated crude products were collected and recrystallized from ethanol if necessary.

2.6. General procedure for preparation of benzo[d]oxazoles 8a-k and 9a-d

A mixture of aldehyde 1 (1.0 mmol), 1,2-aminophenol (1 mmol) and 0.05 g of $NiFe_2O_4$@SiO_2@aminoglucose were stirred at room temperature under solvent free condition for the required reaction time according to Table 7 and 8. After completion of the reaction, as indicated by TLC (TLC Silica gel 60 F_{254}, ethyl acetate: n-hexane 1: 4), the resulting mixture was diluted with hot ethanol (10 mL) and the catalyst separated by the external magnet and washed with hot distilled water (5 mL) and ethanol (3 mL) two times. The filtrate was cooled down to room temperature and the precipitated crude product was recrystallized from ethanol if necessary.

2.5.1. 2,4,5-Triphenyl-1H-imidazole (4a)

m.p.: 269-271°C ; FT-IR (KBr) (vmax/cm^{-1}): 3365, 3046, 1666, 1651, 1496, 1396; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 7.05 (m, 2H), 7.13-7.24 (m, 2H), 7.31-7.39 (m, 2H), 7.43 (t, *J*= 8.0 Hz, 1H), 7.50 (t, *J*= 7.6 Hz, 2H), 7.74 (d, *J*= 6.4Hz, 2H), 7.91 (m, 2H), 8.00 (d, *J*= 5.2Hz, 2H); Anal calc. for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.12; H, 5.43, N, 9.45.

2.5.2. N,N-Dimethyl-4-(4,5-diphenyl-1H-imidazol-2-yl)benzenamine (4b)

m.p.: 238-240°C; FT-IR (KBr) (vmax/cm^{-1}): 3348, 3193, 1648, 1605, 1448, 1359; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 2.28 (s, 6H), 6.92 (d, *J*=7.4Hz, 2H), 7.15-7.22 (m, 2H), 7.32-7.38 (m, 2H), 7.40-7.46 (m, 2H), 7.50-7.52 (m, 2H), 7.53 (d, *J*= 7.6Hz, 2H), 7.69-7.88 (m, 2H); Anal Calc. for $C_{23}H_{21}N_3$: C, 81.38; H, 6.24; N, 12.38. Found: C, 81.36; H, 6.26, N, 12.38.

2.5.3. 4-(4,5-Diphenyl-1H-imidazol-2-yl)phenol (4c)

m.p.: 226-228°C; FT-IR (KBr) (vmax/cm^{-1}): 3344, 1658, 1517, 1449, 1402, 1289; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 6.91 (d, *J*= 8.2Hz, 2H), 6.92 (d, *J*= 6.4Hz, 2H), 7.13-7.24 (m, 2H), 7.32-7.38 (m, 2H), 7.40-7.51 (m, 2H), 7.53 (d, *J*= 8.2Hz, 2H), 7.69-7.88 (m, 2H), 9.07 (m, 1H), 10.12 (s, 1H) ppm; Anal Calc. for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.72; H, 5.13, N, 8.99.

2.5.4. 2-(4-Nitrophenyl)-4,5-diphenyl-1H-imidazole (4f)

m.p.: 223-225°C; FT-IR (KBr) (vmax/cm^{-1}): 3443, 3065, 1663, 1591, 1448, 1336, 1517, 1336; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 7.03-7.06 (m, 2H), 7.21-7.24 (m, 2H), 7.32-7.38 (m, 4H), 7.50-7.53 (m, 2H), 7.81 (d, *J*= 7.6Hz, 2H), 8.24 (d, *J*= 7.6Hz, 2H); Anal Calc. for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31. Found: C, 73.86; H, 4.48, N, 12.29.

2.5.5. 2-(4-Methoxyphenyl)-4,5-diphenyl-1H-imidazole (4g)

m.p.: 228-229°C ; FT-IR (KBr) (vmax/cm^{-1}): 3338, 1659, 1600, 1499, 1422, 1274; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 3.94 (s, 3H), 6.98 (d, *J*=7.6Hz, 2H), 7.04 (m, 2H), 7.13 (d, *J*= 8.8Hz, 2H), 7.32-7.38 (m, 2H), 7.55 (d, *J*= 7.6Hz, 2H), 7.87 (d, *J*= 6.8Hz, 2H), 8.00 (d, *J*= 8.4Hz, 2H) ; Anal Calc. for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58. Found: C, 80.95; H, 5.51, N, 8.54.

2.5.6. 2-(Furan-2-yl)-4,5-diphenyl-1H-imidazole (4k)

m.p.: 221-223°C; FT-IR (KBr) (vmax/cm^{-1}): 3325, 1621, 1543, 1472, 1259; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 7.12 (d, *J*= 7.6Hz, 2H), 7.17-7.23 (m, 2H), 7.31-7.38 (m, 2H), 8.06 (m,

2H), 7.92 (d, *J*= 7.2Hz, 1H), 7.90 (d, *J*= 7.8Hz, 2H), 7.56 (d, *J*= 7.4Hz, 2H) ppm. Anal Calc. for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N, 9.78. Found: C, 79.69; H, 4.95, N, 9.75.

2.5.7. 4-(4,5-Diphenyl-1H-imidazol-2-yl)pyridine (4l)

m.p.: 276-278 °C; FT-IR (KBr) (vmax/cm^{-1}): 3098, 2987, 1614, 1543, 1329, 1243; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 7.05-7.11 (m, 2H), 7.19-7.26 (m, 2H), 7.30-7.41 (m, 4H), 7.53-7.56 (m, 2H), 7.73 (d, *J*= 7.4Hz, 2H), 8.14 (d, *J*= 7.8Hz, 2H); Anal Calc. for $C_{20}H_{15}N_3$: C, 80.78; H, 5.08; N, 14.13. Found: C, 80.81; H, 5.11, N, 14.08.

2.5.8. 4,5-diphenyl-2-propyl-1H-imidazole (4m)

m.p.: 243-244 °C; FT-IR (KBr) (vmax/cm^{-1}): 3421, 1595, 1514, 1419, 1376, 1242; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 1.32 (t, *J*= 12.0Hz, 3H), 1.56-1.67 (m, 2H), 2.25 (t, *J*= 9.6Hz, 2H), 7.19 (d, *J*= 7.6Hz, 2H), 7.33-7.42 (m, 2H), 7.63 (d, *J*= 7.6Hz, 2H), 7.83 (d, *J*= 7.6Hz, 2H), 8.04 (m, 2H); Anal Calc. for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.41; H, 6.93, N, 10.67.

***2.6.1.1-Benzyl-2-phenyl-1H-benzo[d]imidazole (6a*)**

m.p.: 130-132°C ; FT-IR (KBr) (vmax/cm^{-1}): 3058, 2934, 1614, , 1547, 1434, 1321, 1145; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 5.76 (s, 2H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.29-7.45 (m, 3H), 7.50-7.68(m, 2H), 7.76-7.96 (m, 7H), 8.50 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C (ppm) 45.2, 111.6, 119.6, 121.6, 125.8, 127.8, 128.8, 128.9, 129.0, 129.7, 134.6, 135.8, 146.0, 149.5, 156.9; Anal Calc. for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.50; H, 5.69, N, 9.82.

2.6.2.4-(1-(4-(Dimethylamino)benzyl)-1H-benzo[d]imidazol-2-yl)-N,N-dimethyl benzenamine (6b)

m.p.: 252-254°C ; FT-IR (KBr) (vmax/cm^{-1}): 1609 , 1556, 1445 , 1376 , 1209, 1111 ; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 2.56 (s, 6H), 2.75 (s, 6H), 5.45 (s, 2H), 6.58-7.18 (m, 12H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C (ppm) 40.0, 41.5, 47.5, 110.9, 112.1, 112.9, 118.2, 119.1, 124.5, 124.6, 128.9, 130.5, 135.6, 145.7, 149.4, 154.4, 155.7; Anal Calc. for $C_{24}H_{26}N_4$: C, 77.80; H, 7.07; N, 15.12. Found: C, 77.78; H, 7.05, N, 15.14.

2.6.3.1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzo[d]imidazole (6c)

m.p.: 137-139°C ; FT-IR (KBr) (vmax/cm^{-1}): 1628 , 1279, 1406, 1095 ; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 5.61 (s, 2H), 7.20-7.25 (m, 3H), 7.30-7.40 (m, 1H), 7.52-7.61 (m, 4H), 7.69-7.76 (m, 2H), 8.20-8.23 (m, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C (ppm) 46.7, 110.6, 120.4, 122.4, 123.5, 126.5, 127.7, 128.6, 129.5, 130.1, 133.9, 133.2, 135.0, 135.7, 142.1, 152.1;Anal Calc. for $C_{20}H_{14}Cl_2N_2$: C, 68.00; H, 3.99; N, 7.93. Found: C, 68.02; H, 3.96, N, 7.91.

2.6.4.1-(4-Bromobenzyl)-2-(4-bromophenyl)-1H-benzo[d]imidazole (6d)

m.p.: 200-201°C ; FT-IR (KBr) (vmax/cm^{-1}): 3021, 1987, 1617, 1556, 1403 , 1076 ; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 5.54 (s, 2H), 7.21-7.37 (m, 2H), 7.44-7.47 (m, 2H), 7.62 (brs, 2H), 7.75 (brs, 2H), 7.89 (d, *J* = 8.3 Hz, 2H), 8.28 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C (ppm) 45.5, 118.2, 121.8, 123.8, 126.1, 127.3, 127.5, 128.9, 129.2, 131.2, 132.8, 134.5, 134.5, 135.2, 147.8, 154.1; Anal Calc. for $C_{20}H_{14}Br_2N_2$: C, 54.33; H, 3.19; N, 6.34. Found: C, 54.30; H, 3.17, N, 6.37.

2.6.5.1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (6e)

m.p.: 131-133°C ; FT-IR (KBr) (vmax/cm^{-1}): 1625, 1511, 1452 , 1410, 1246 ; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 3.77 (s, 3H), 3.92 (s, 3H), 5.47 (s, 2H), 6.75-7.86 (m, 12H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C (ppm) 45.8, 55.2, 55.5, 111.2, 114.4, 114.9, 116.2, 121.7, 122.0, 128.0, 128.7, 130.7, 135.9, 144.7, 154.4, 157.6, 159.6; Anal Calc. for $C_{23}H_{24}N_2O_3$: C, 73.38; H, 6.43; N, 7.44. Found: C, 73.41; H, 6.40, N, 7.45.

2.6.6. 1-(2-Chlorobenzyl)-2-(2-chlorophenyl)-1H-benzo[d]imidazole (6f)

m.p.: 154-155°C ; FT-IR (KBr) (vmax/cm^{-1}): 3017, 2936 , 1613 , 1562, 1447 , 1387 , 1221, 1057, 10438 ; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 5.43 (s, 2H), 6.51-7.94 (m, 12H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C (ppm) 45.9, 115.6, 122.4, 122.9, 125.6, 126.9, 127.3, 127.8, 129.1, 129.6, 129.7, 131.5, 131.9, 132.5, 133.9, 1343.5, 135.5, 137.9, 146.0, 155.8; Anal Calc. for $C_{20}H_{14}Cl_2N_2$: C, 68.00; H, 3.99; N, 7.93. Found: C, 68.03; H, 4.01, N, 7.93.

2.6.7. 2-((2-(2-Hydroxyphenyl)-1H-benzo[d]imidazol-1-yl)methyl)phenol (6g)

m.p.: 200-202°C ; FT-IR (KBr) (vmax/cm^{-1}): 1621,1514, 1472, 1418, 1241, 1159; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 5.53 (s, 2H), 6.21-7.28 (m, 12H), 9.52 (brs., 1H), 10.18 (s, br., 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C (ppm) 45.8, 110.2, 120.7, 121.7, 123.5, 125.7, 126.3, 127.4, 128.2, 129.0, 129.6, 130.5, 131.5, 132.8, 133.2, 133.8, 134.7, 135.0, 142.3, 151.2. Anal Calc. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.90; H, 5.12, N, 8.89.

2.6.8.1-(4-Nitrobenzyl)-2-(4-nitrophenyl)-1H-benzo[d]imidazole (6h)

m.p.: 117-119°C ; FT-IR (KBr) (vmax/cm^{-1}): 2975, 1612, 1535, 1344, 1222, 1108;^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 5.61 (s, 2H), 7.29-7.34 (m, 3H), 7.51 (brs, 1H), 7.64-7.66 (brs, 2H), 8.42 (d, *J* = 8.0 Hz, 2H), 8.49 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C

(ppm) 47.6, 112.4, 121.5, 122.0, 123.9, 124.6, 124.8, 125.9, 132.5, 135.2, 136.0, 141.0, 142.7, 149.0, 149.1, 155.0; Anal Calc. for $C_{20}H_{14}N_4O_4$: C, 64.17; H, 3.77; N, 14.97. Found: C, 64.18; H, 3.80, N, 14.94.

2.6.9. 1-(4-Hydroxybenzyl)-2-(4-hydroxyphenyl)-1H-benzo[d]imidazole (6i)

m.p.: 255°C ; FT-IR (KBr) (vmax/cm^{-1}): 1632, 1548, 1462, 1421, 1381, 1263, 1098. ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 5.44 (s, 2H), 7.28 (s, 2H), 6.67 (d, *J* = 8.2 Hz, 2H), 6.90 (t, *J* = 8.9 Hz, 4H), 7.56 (d, *J* = 8.0 Hz, 4H), 8.14 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C (ppm) 45.6, 111.6, 121.7, 122.7, 124.8, 125.3, 127.9, 128.2, 129.1, 131.5, 133.5, 133.9, 137.2, 137.8, 145.3, 153.8. Anal Calc. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.98; H, 5.05, N, 8.89.

2.6.10. 2-(2-Furyl)-1-(2-furylmethyl)-1H-benzimidazole (6j)

m.p.: 94-95°C ; FT-IR (KBr) (vmax/cm^{-1}): 3017, 2943, 1617, 1593, 1518, 1477 , 1335 , 1231 ; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 5.42 (s, 2H), 6.26-7.58 (m, 10H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C (ppm) 45.1, 111.7, 111.9, 113.4, 113.8, 113.9, 115.2, 119.3, 121.0, 123.3, 137.5, 142.9, 144.2, 144.5, 145.7, 151.2. Anal Calc. for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.73; H, 4.52; N, 10.58.

2.6.11. 2-(Pyridin-2-yl)-1-(pyridin-2-ylmethyl)-1H-benzo[d]imidazole (6k)

m.p.: 132-133°C ; °C; FT-IR (KBr) (vmax/cm^{-1}): 3012, 2978, 1578 , 1563, 1519, 1429 , 1316 ,1143 ; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H (ppm) 5.54 (s, 2H), 6.42–7.52 (m, 12H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C (ppm) 46.4, 110.5, 121.7, 123.6, 123.9, 124.8, 124.9, 125.9, 128.0,

128.9, 131.9, 132.6, 133.5, 134.2, 137.6, 146.3, 147.8, 149.0, 151.9; Anal Calc. for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.48; H, 4.93; N, 19.55.

2.7.1. 2-(4-Methoxyphenyl)benzo[d]oxazole (8b)

m.p.: 100-102°C ; FT-IR (KBr) (vmax/cm^{-1}): 3100, 2980, 1635, 1607, 1508, 1282; ^{1}HNMR (DMSO-d_6, 400 MHz): δ_H (ppm) 3.80 (s, 3H), 6.84 (t, *J*=7.4Hz, 2H), 7.10 (d, *J*= 7.9Hz,2H), 7.20 (t, *J*=7.4 Hz, 2H), 7.40 (d, *J*=7.5Hz, 2H) ; Anal Calc. for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22; Found: 74.63; H, 4.94; N, 6.21.

2.7.2. 4-(Benzo[d]oxazol-2-yl)phenol (8c)

m.p.: 98-99°C; FT-IR (KBr) (vmax/cm^{-1}): 3435, 3114, 1648, 1601, 1418, 1243; ^{1}HNMR (DMSO-d_6, 400 MHz): δ_H (ppm) 6.87 (t, *J*= 7.5Hz, 1H), 6.97 (d, *J*= 8.4Hz, 2H), 7.07 (8, *J*= 8.0Hz, 1H), 7.23 (t, *J*=7.7Hz, 1H), 7.37 (d, *J*= 7.7Hz, 1H), 7.75 (d, *J*= 8.4Hz, 2H); Anal Calc. for $C_{13}H_9NO_2$: C, 73.92; H, 4.29; N, 6.63; Found: C, 73.90; H, 4.30; N, 6.65.

2.7.3. 2-(Benzo[d]oxazol-2-yl)phenol (8e)

m.p.: 154-155 °C; FT-IR (KBr) (vmax/cm^{-1}): 3414, 3052, 1641, 1609, 1466, 1228; ^{1}HNMR (DMSO-d_6, 400 MHz): δ_H (ppm) 6.85 (t, *J*=7.1Hz, 1H), 6.91-6.98 (m, 1H), 7.10 (d, *J*= 7.9Hz, 1H), 7.15-7.26 (m, 1H), 7.40 (d, *J*= 7.3Hz, 1H), 7.48-7.53 (m, 1H), 7.59-7.73 (m, 1H), 7.87 (d, *J*= 7.7Hz, 1H) ; Anal Calc. for $C_{13}H_9NO_2$: C, 73.92; H, 4.29; N, 6.63; Found: C, 73.89; H, 4.32; N, 6.63.

2.7.4. 2-(3-Bromophenyl)benzo[d]oxazole (8f)

m.p.: 187-188 °C; FT-IR (KBr) (vmax/cm^{-1}): 1633, 1434, 1295, 1122; ^{1}HNMR (DMSO-d_6, 400 MHz): δ_H (ppm) 7.25-7.35 (m, 2H), 7.40-7.48 (m, 2H), 7.50-7.57 (m, 2H), 7.61-7.64 (m, 1H),

7.78 (d, *J*= 7.8Hz, 1H); cm^{-1}. Anal Calc. for $C_{13}H_8BrNO$: C, 56.96; H, 2.94; N, 5.11; Found: C, 56.98; H, 2.92; N, 5.09.

2.7.5. 2-(Pyridin-4-yl)benzo[d]oxazole (8j)

m.p.: 134-135°C; FT-IR (KBr) (vmax/cm^{-1}): 3012, 1605, 1463, 1272, 1125; ^{1}HNMR (DMSO-d_6, 400 MHz): δ_H (ppm) 7.32 (d, *J*= 8.0Hz, 1H), 7.37 (d, *J*= 7.8Hz, 1H), 7.45 (m, 1H), 7.53 (t, *J*= 8.0Hz,1H), 7.61 (d, *J*= 7.2Hz, 2H), 7.63 (d, *J*= 7.2Hz, 2H) ; Anal Calc. for $C_{12}H_8N_2O$: C, 73.46; H, 4.11; N, 14.28; Found: C, 73.44; H, 4.13; N, 14.30.

2.7.6. 2-Propylbenzo[d]oxazole (8k)

m.p.: 178-179 °C; FT-IR (KBr) (vmax/cm^{-1}): 3024, 2943, 1553, 1462, 1431, 1225; ^{1}HNMR (DMSO-d_6, 400 MHz): δ_H (ppm) 1.59 (t, 3H), 1.82-1.85 (m, 2H), 2.72 (t, 2H), 7.34 (d, *J*=8.0Hz, 1H), 7.40 (t, *J*= 7.2Hz, 1H), 7.44 (m, 1H), 7.54 (m, 1H); Anal Calc. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69; Found: C, 74.52; H, 6.90; N, 8.70.

2.7.7. 4-(2-Phenyldiazenyl)-2-(5-chlorobenzo[d]oxazol-2-yl)phenol (9a)

m.p. 246-248 °C; FT-IR (KBr) (vmax/cm^{-1}): 3344, 1678, 1612, 1449, 1234; ^{1}H NMR (400MHz, $CDCl_3$): δ_H (ppm) 7.27 (dd, *J* = 7.8 Hz, *J* = 2.1 Hz, 1H), 7.37 (t, *J* = 8.7 Hz, 1H), 7.42- 7.57 (m, 4H), 7.73 (d, *J* = 7.8Hz, 1H), 8.34- 8.43 (m, 2H), 8.63 (s, 2H), 8.97 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 104.6, 112.3, 119.1, 120.1, 120.7, 121.3, 126.8, 128.1, 128.9, 131.2, 131.7, 136.8, 145.2, 146.3, 151.5, 156.8, 175.3. Anal. Calcd. for $C_{19}H_{12}ClN_3O_2$: C, 65.24; H, 3.46; N, 12.01. Found: C, 65.21; H, 3.47; N, 12.02.

2.7.8. 4-(2-(2-Chloro-4-nitrophenyl)diazenyl)-2-(5-chlorobenzo[d]oxazol-2-yl)phenol (9b)

m.p. 241-242°C; FT-IR (KBr) (vmax/cm^{-1}): 3356, 1634, 1617, 1559, 1348, 1176; ^{1}H NMR (400MHz, $CDCl_3$): δ_H (ppm) 7.23 (t, *J* = 8. 8 Hz, 2H), 7.37-7-54 (m, 3H), 7.69 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 8.42 (dd, *J* = 7.6Hz, *J* = 1.2Hz, 1H), 8.69 (s, 1H), 8.91 (s, 1H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 115.1, 120.0, 121.9, 123.2, 123.6, 124.1, 124.9, 126.4, 127.1, 129.9, 131.1, 135.2, 139.8, 143.1, 145.7, 155.1, 159.0, 164.2, 175.0. Anal. Calcd. for $C_{19}H_{10}Cl_2N_4O_4$: C, 53.17; H, 2.35; N, 13.05. Found: C, 53.15; H, 2.32; N, 13.04.

2.7.9. 4-(2-(2-Nitrophenyl)diazenyl)-2-(5-chlorobenzo[d]oxazol-2-yl)phenol (8c)

m.p. 280- 282 °C; FT-IR (KBr) (vmax/cm^{-1}): 3357, 1679, 1628, 1604, 1533, 1341, 1126 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ_H (ppm) 7.5 (t, *J* = 8.5Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.69-7.79 (m, 3H), 7.89 (d, *J* = 7.8 Hz, 1H), 8.09 (t, *J* = 7.5Hz, 1H), 8.5 (s, 1H), 8.63 (s, 1H), 8.89 (t, *J* = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 111.7, 116.2, 119.1, 122.7, 128.0, 128.5, 128.9, 129.5, 129.9, 131.8, 132.0, 132.8, 135.3, 146.0, 148.2, 149.2, 155.1, 158.1, 165.3. Anal. Calcd. for $C_{19}H_{11}ClN_4O_4$: C, 57.81; H, 2.81; N, 14.19. Found: C, 57.82; H, 2.80; N, 14.22.

2.7.10. 4-(2-(2-Chlorophenyl)diazenyl)-2-(5-chlorobenzo[d]oxazol-2-yl)phenol (8d)

m.p. 238-240℃; FT-IR (KBr) (vmax/cm^{-1}): 3409, 1678, 1609, 1575, 1325, 1124 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ_H (ppm) 7.13 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.33-7.54 (m, 4H), 7.64 (d, *J* = 8.6 Hz, 1H), 8.06 (t, *J* = 8.4 Hz, 1H), 8.56 (s, 1H), 8.68 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 110.7, 119.9, 120.1, 124.2, 125.7, 128.1, 128.8, 129.1, 129.7, 130.1, 130.7, 130.8, 130.9, 136.5, 145.1, 155.8, 156.6, 159.5, 171.2. Anal. Calcd. for $C_{19}H_{11}Cl_2N_3O_2$: C, 59.39; H, 2.89; N, 10.94. Found: C, 59.41; H, 2.90; N, 10.92.

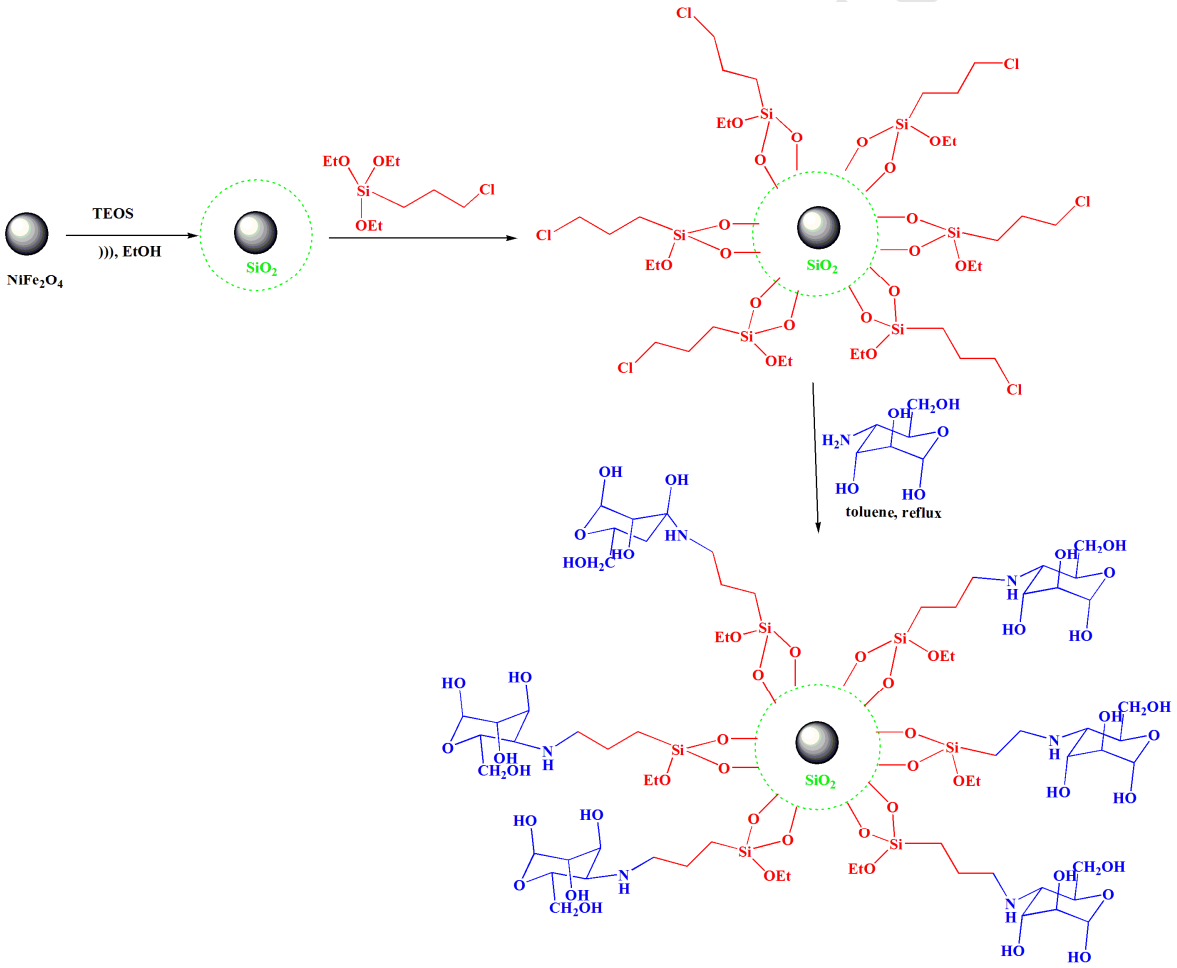
3. Results and Discussion

3.1 Synthesis and structural characterization of amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles ($NiFe_2O_4$@SiO_2@amino glucose) as catalyst

In continuation of our research for the green synthesis of organic compounds [59a-h], we describe here the use of acidic amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles

($NiFe_2O_4$@SiO_2@amino glucose) as a new, reusable and effective nanocatalyst for the synthesis of trisubstituted benzimidazoles, benzo[d]imidazoles and benzoxazoles.

As shown in Scheme 1, the $NiFe_2O_4$@SiO_2@amino glucose magnetic nanoparticles were synthesized in three steps from commercially available materials. $NiFe_2O_4$ NPs were coated by silica using a sol–gel process. The $NiFe_2O_4$@SiO_2 core-shell structures were then sequentially treated with 3-chloropropyltrimethoxysilane. Next, it was treated with aminoglucose to obtain the amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles.



Scheme 1. Stepwise synthesis pathway of $NiFe_2O_4$@SiO_2@glucoseamine

The FT-IR spectra of $NiFe_2O_4$, $NiFe_2O_4@SiO_2$ and $NiFe_2O_4@SiO_2$@amino glucose MNPs are shown in Figure 1. The absorption band in 594 cm^{-1} is related to the stretching vibration of the Fe–O bond of bare $NiFe_2O_4$ that was appeared in 590 cm^{-1} in the FT-IR spectrum of the $NiFe_2O_4@SiO_2$@amino glucose MNPs. The absorption bands of Si-O-Si vibrations in SiO_2 shell were appeared in 1045 and 1130 cm^{-1} in $NiFe_2O_4@SiO_2$ spectra that seemed at 1033, 1137 and 767 cm^{-1} in the spectrum of the $NiFe_2O_4@SiO_2$@amino glucose MNPs. Also, the peaks at 1645 and 3429 cm^{-1} (in the spectrum of the $NiFe_2O_4$) and at 1645 and 3423 cm^{-1} (in the spectrum of the $NiFe_2O_4@SiO_2$@amino glucose MNPs) are attributed to the stretching vibrations of the hydroxyl (–OH) groups on the surface of MNPs. The peaks in region 2950 and 3120 cm^{-1} refer to the stretching band of C-H aliphatic and NH stretching in $NiFe_2O_4@SiO_2$@amino glucose MNPs.

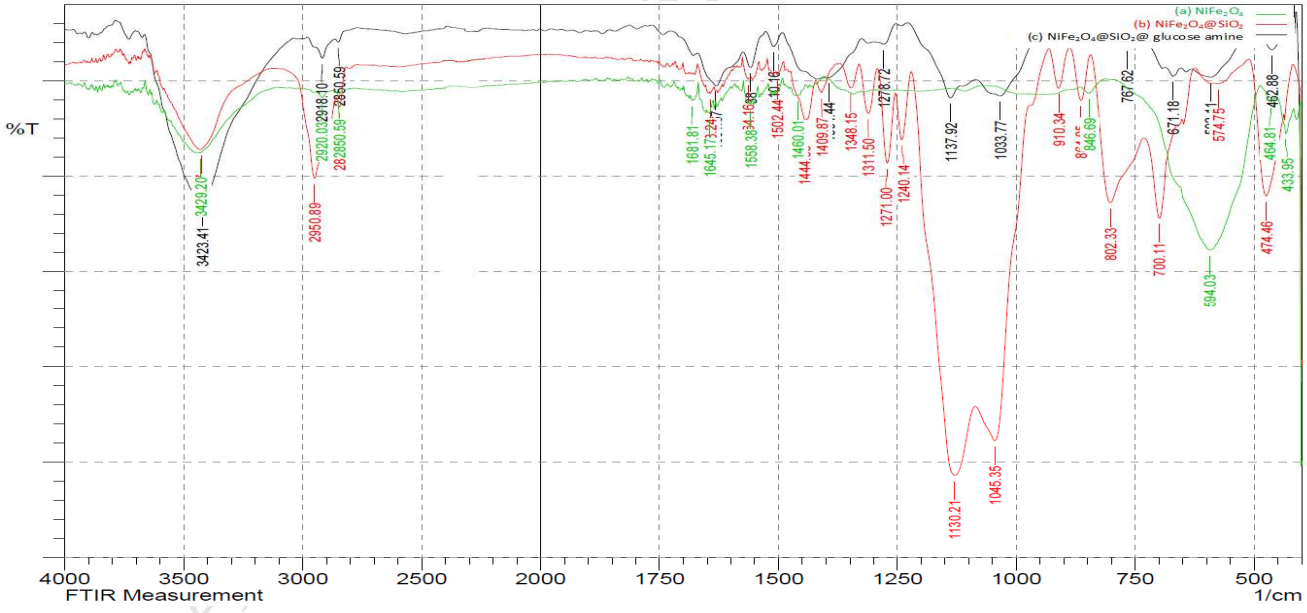


Figure 1. FT-IR spectra of (a) $NiFe_2O_4$, (b) $NiFe_2O_4@SiO_2$, (c) $NiFe_2O_4@SiO_2$@ aminoglucose MNPs

Next, the morphology and nanoparticle size of the synthesized magnetic catalyst were characterized by transmission electron microscope (TEM) (Figure 2). As shown in Figure 2, the

catalyst particles possess near spherical morphology with average diameter of about 20–40 nm. Furthermore, TEM images show some aggregation, which was illustrated the successful grafting of the polymer on to magnetic nanoparticles.

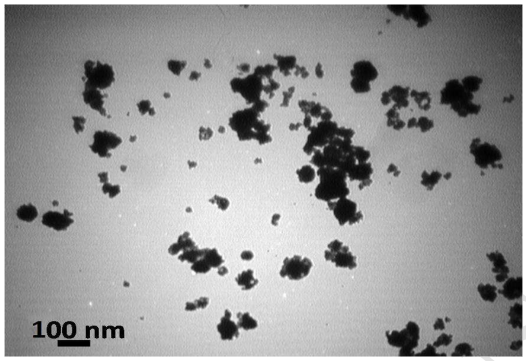


Figure 2. The TEM image of synthesized $NiFe_2O_4@SiO_2@$ aminoglucose

The structure of $NiFe_2O_4@SiO_2@$aminoglucose was also confirmed by XRD analysis. In Figure 3, the XRD patterns of $NiFe_2O_4@SiO_2@$aminoglucose MNPs and pure $NiFe_2O_4$ (from JCPDS No. 54-0964) are illustrated. The comparison of the XRD patterns indicated that both patterns exhibits peaks with 2θ at 30°,36°, 45°, 50°, 54°, 58° and 62° which are representative of the structure and broad peak in 10-30° is related to $NiFe_2O_4$ covered by SiO_2.

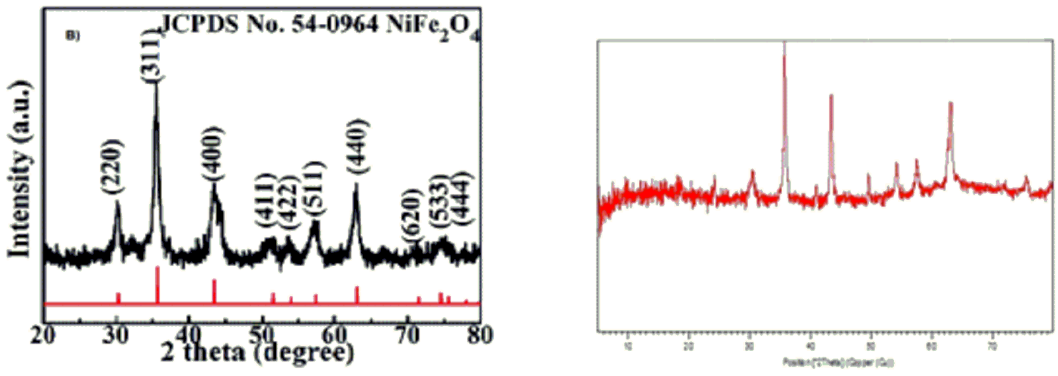


Figure 3. The XRD patterns of a) $NiFe_2O_4@SiO_2@$ aminoglucose and b) $NiFe_2O_4$

The results of energy dispersive X-ray spectroscopy (EDX) analysis of the synthesized $NiFe_2O_4$@SiO_2@aminoglucose MNPs (Figure 4) proved existence of Fe (30.17 w/w %), O (16.21 w/w %), Si (2.2 w/w %), N (0.45 w/w %), C (5.30 w/w %) and Ni (31.12 w/w %) atoms in the structure that confirms the presence of $NiFe_2O_4$ core in the structure of MNP.

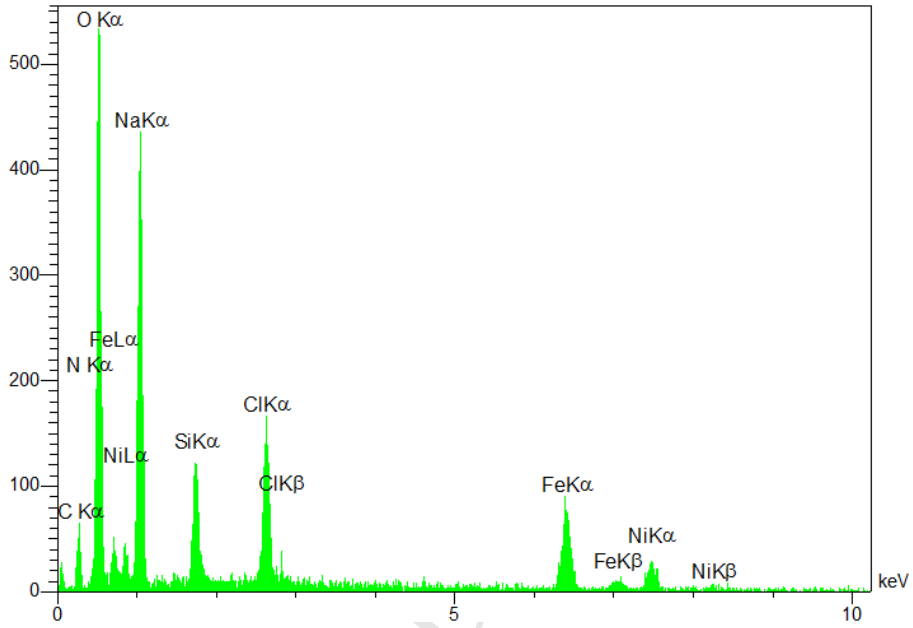


Figure 4. EDX results of the synthesized $NiFe_2O_4$@SiO_2@ aminoglucose MNPs

In order to investigate the thermal stability of the synthesized nanocatalyst, thermal gravimetric and derivative thermal gravimetric analysis (TGA and DTG) of the $NiFe_2O_4$@SiO_2@ aminoglucose MNPs were carried out from 50–700 °C at a heating rate of 10 °C min^{-1} under air atmosphere (Figure 5). The synthesized MNPs showed no weight losses at temperatures below 108.5 °C. Therefore, they are stable at working temperatures up to 108.5 ^{o}C. With increasing the temperature, a little weight losses observed with a maximum in 131.8 ^{o}C that could be due to the removal of physically adsorbed water molecules which were adsorbed during the synthesis of nanoparticles. Further increase in temperature causes more weight losses in different steps that

can be related to the desorption of the chemisorbed water on the MNPs surface and also, complete removal of aminoglucose groups from the MNPs.

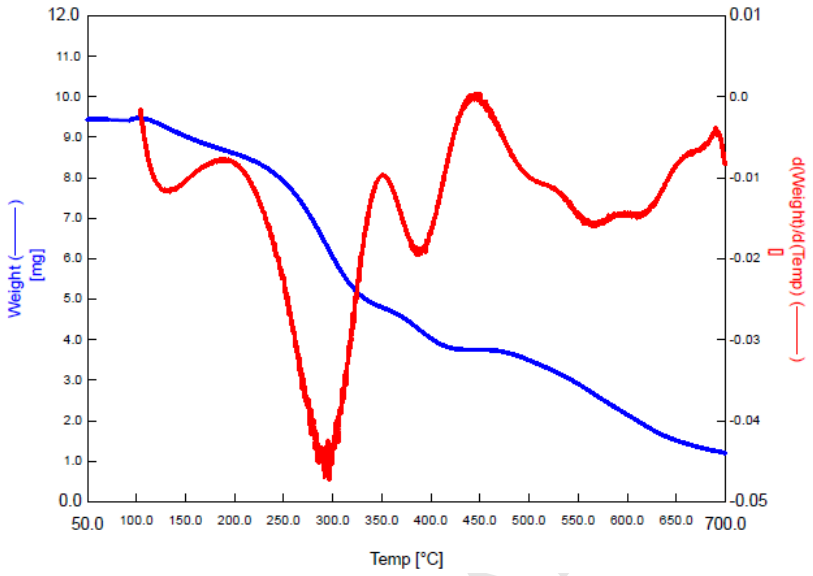


Figure 5. Thermogram of TGA (blue colour) and DTG (red colour) analysis of the synthesized $NiFe_2O_4$@SiO_2@ aminoglucose MNPs.

Figure 6 shows the hysteresis loop of the synthesized $NiFe_2O_4$@SiO_2@ aminoglucose MNPs. VSM measurements were carried out at room temperature by taking the solid sample on the tips of the vibrating rod and analyzing in an applied magnetic field sweeping from −20 to 20 kOe. The curve confirms the magnetic property of synthesized nanocatalyst that is in agreement with other studies [60].

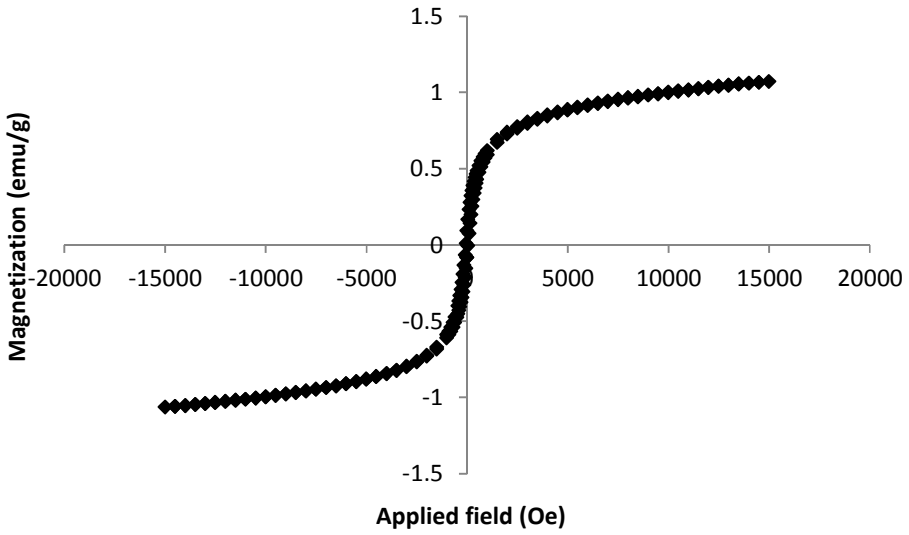


Figure 6. Vibrating scanning magnetometery (VSM) curve of the synthesized nanocatalyst

In order to investigate the surface charge of MNPs that influences their physical stability in solution, zeta potential values were measure using the Zetasizer instrument. Zeta potential values provide an indirect measurement of the net charge on the nanoparticle surface and often used as an indicator of dispersion stability. It value can be used as a criteria to determine particles tendency to aggregate in aqueous media. In the present study, the zeta potential and mobility were measured as -31.3 mv and -2.45 µmcm/Vs, respectively at 298 K with count rate of 94.4 kcps (Figure 7). The large zeta potential obtained in this study predicts a more stable dispersion of synthesized MNPs.

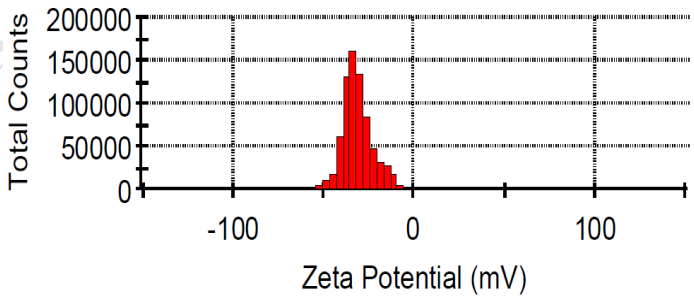
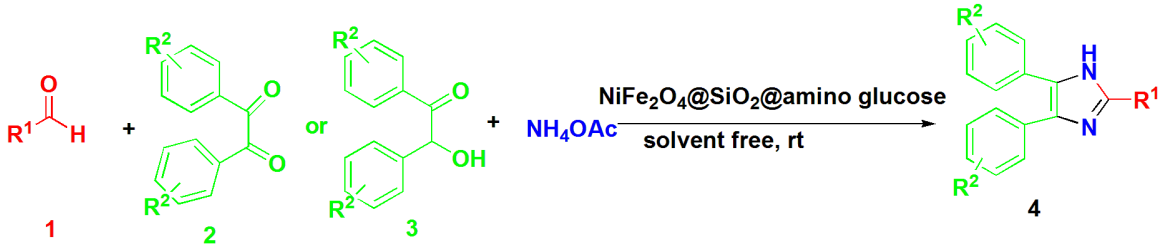


Figure 7. Statistics graph of zeta potential measurement

3.2. Catalytic studies

In order to evaluate the catalytic capability of the synthesized heterogeneous catalyst ($NiFe_2O_4$@SiO_2@ glucose amine) in organic reactions, we chose to examine its activity in a one-pot reaction for the synthesis of 2,4,5-triaryl-1*H*-imidazoles using the reaction between aldehyde **1**, 1,2-Diketone **2** or *α*-hydroxyketone **3** and ammonium acetate (Scheme 2).



Scheme 2. Synthesis of trisubstituted imidazoles using $NiFe_2O_4$@SiO_2@amino glucose

Initially, we observed that the reaction of 4-nitrobenzaldehyde with benzil and ammonium acetate in the presence of $NiFe_2O_4$@SiO_2@aminoglucose could be a suitable choice for the synthesis of trisubstituted imidazoles. This protocol proceeds fairly at room temperature to afford product **4f** in high yield. We have also carried out the sample reaction in the presence of $NiFe_2O_4$, $NiFe_2O_4$@SiO_2, SiO_2 or in the absence of catalyst. On the other hand, variables affecting on the reaction yields such as the type of solvent, the amount of catalyst, different temperatures, and solvent-free conditions were studied (Table 1). As shown in Table 1, the reaction under solvent-free conditions is more efficient.

Table 1. Screening the reaction parameters for the synthesis of trisubstituted imidazoles

entry	catalyst	Catalyst amount	Reaction condition	Time (min)	Yield (%)
1	-	-	Reflux in EtOH	720	trace
2	SiO_2	0.05 g	Stir, rt, EtOH	750	15
3	$NiFe_2O_4$	0.05g	Stir,rt, EtOH	720	24
4	$NiFe_2O_4$@SiO_2	0.05g	Stirr, rt, EtOH	300	53
5	$NiFe_2O_4$@SiO_2@ aminoglucose	0.05g	Stir, rt, EtOH	40	90
6	$NiFe_2O_4$@SiO_2@ aminoglucose	0.07g	Stir, rt, EtOH	40	87
7	$NiFe_2O_4$@SiO_2@ aminoglucose	0.03g	Stir, rt, EtOH	60	85
8	$NiFe_2O_4$@SiO_2@ aminoglucose	0.05g	Stir, rt, CH_3CN	60	76
9	$NiFe_2O_4$@SiO_2@ aminoglucose	0.05g	Stir, rt, H_2O	25	84
10	$NiFe_2O_4$@SiO_2@ aminoglucose	0.05g	Solvent free, rt	10	97
11	$NiFe_2O_4$@SiO_2@ aminoglucose	0.05g	Solvent free, 80°C	10	98

To present the efficiency and generality of the reaction, various aldehydes were reacted with benzil or benzoin and ammonium acetate in the presence of $NiFe_2O_4$@SiO_2@aminoglucose under solvent free condition. The results are summarized in Table 2.

Table 2. Synthesis of trisubstituted imidazoles

Entry	Aldehyde	Product	benzil		benzoin		Mp(°C)	
			Time (min)	Yield (%)[a,b]	Time (min)	Yield (%)[a,b]	Found	Reported
1	Benzaldehyde	**4a**	8	98	12	99	269-271	272-274 [61]
2	4-N,N-Dimethylbenzaldehyde	**4b**	11	93	15	96	238-240	-
3	4-Hydroxybenzaldehyde	**4c**	13	92	15	95	226-228	-
4	4-Chlorobenzaldehyde	**4d**	8	95	10	96	265-267	262-264 [61]
5	2-Chlorobenzaldehyde	**4e**	13	90	17	93	187-188	190-191 [61]
6	4-Nitrobenzaldehyde	**4f**	10	97	13	99	223-225	-
7	4-Methoxybenzaldehyde	**4g**	13	92	16	94	228-229	228-231 [61]
8	4-Bromobenzaldehyde	**4h**	10	94	13	97	257-259	263-265 [62]
9	4-Methylbenzaldehyde	**4i**	15	91	17	93	226-227	230-232 [62]
10	3-Nitrobenzaldehyde	**4j**	8	92	11	95	>300	>300 [62]
11	Furfural	**4k**	11	93	15	95	221-223	-
12	4-Pyridinecarbaldehyde	**4l**	11	92	13	96	276-278	-
13	Propanal	**4m**	15	90	18	93	243-244	-

[a]All the isolated products were characterized on the basis of their physical properties and IR, ^{1}H- spectra and elemental analysis and by direct comparison with authentic materials if there are; [b]Isolated yields

To check the efficiency of this method, the comparison between this method and some of previous reported methods for the synthesis of **4f** was carried out (Table 3).

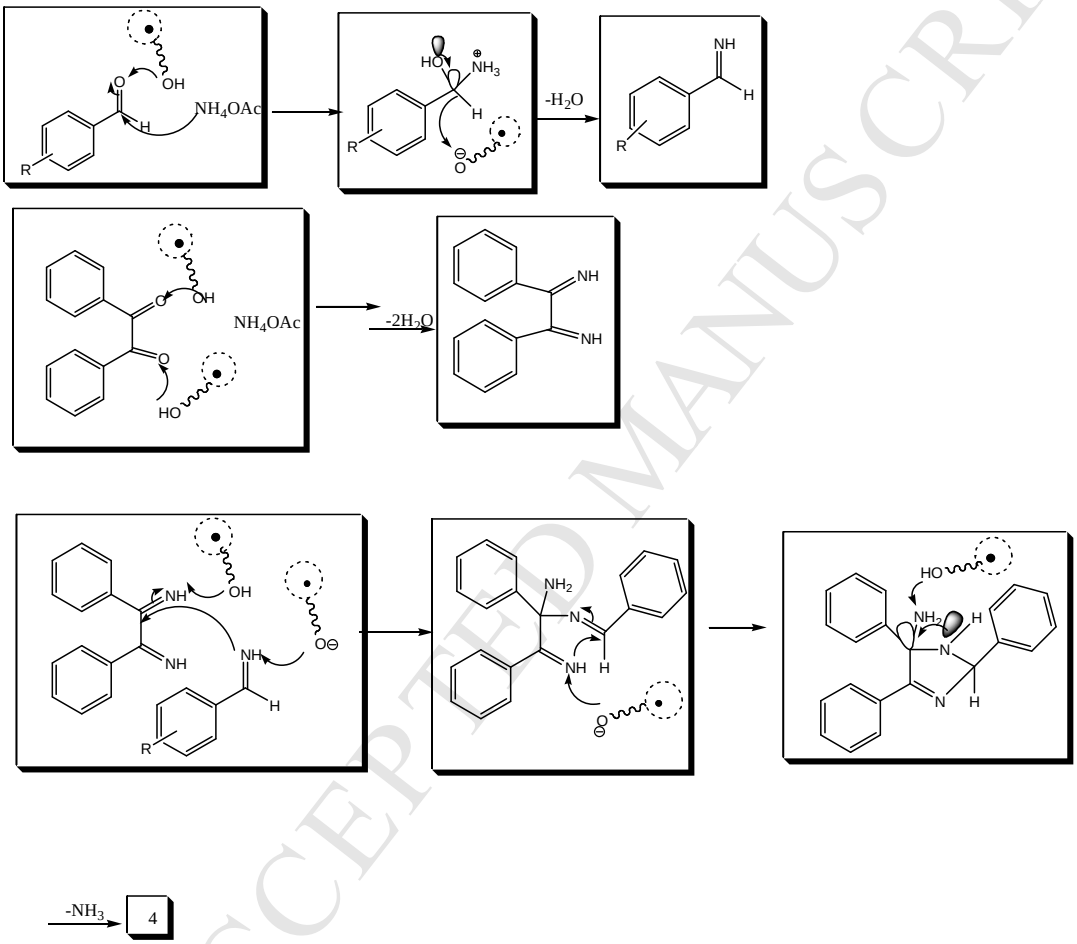
Table 3. Comparison of synthesis of compound **4f** in this method with some of previous reported methods

Catalyst	Condition	Time / min	Yield, %	Ref.
NBS	Heat, 120 °C	50	89	[63]
$ZrOCl_2.8H_2O$	Heat, 80 °C	30	97	[64]
$InCl_3.3H_2O$	Stir, rt	498	82	[65]
Fe_3O_4 nanoparticles	Stir, 80 °C	30	90	[66]
[Hmim]TFA	Heat, 80 °C	30	97	[67]
$NiFe_2O_4$@SiO_2@ aminoglucose	Solvent free, rt	10	97	This work

Anomeric effect has found its influential position in the field of chemistry and it can be defined as stereoelectronic stabilizing effect that favor the placement of electronegative substituents in the axial, rather than equatorial, position in a pyranoid ring system at C1 [68]. Recently, Zolfigol *et al.* have introduced a new mechanistic outlook for the oxidative aromatization of some heterocyclic compounds based on anomeric effect and present the term of "anomeric based oxidation (ABO)" as an explanation for the final step of aromatization mechanism [68-70]. In the proposed mechanism Described based of anomeric based oxidation (Scheme 3), initially aldehyde and benzil were activated by $NiFe_2O_4$@SiO_2@aminoglucose and converted to corresponding imine followed by nucleophilic attack of iminium species of aldehyde to the imine produced from benzil, intramolecular cyclization and departure of ammonia lead to product 4.

The recyclability and reusability of catalyst were studied in the model one-pot three-component reaction between 4-nitrobenzaldehyde, benzil and NH_4OAc. At the end of the reaction, the separated catalyst can be reused after being washed with warm EtOH and drying at 80 °C.

$NiFe_2O_4$@SiO_2@aminoglucose was used again for subsequent experiments under similar reaction conditions. The catalyst could be reused for the next cycle without any notable loss of its activity. Yields of the product decreased only slightly after reusing the catalyst five times (Figure 8).



Scheme 3. The proposed mechanism for the synthesis of trisubstituted imidazoles

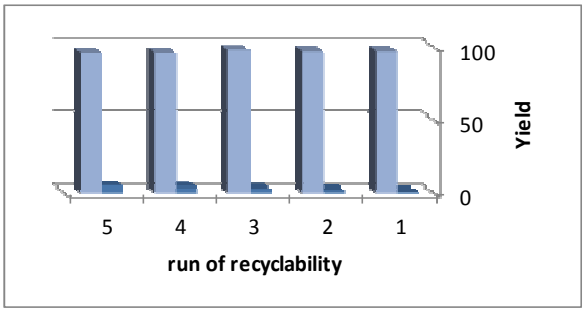


Figure 8. The recyclability of $NiFe_2O_4@SiO_2@$ glucose amine MNPs for the synthesis of tri-substituted benzimidazoles

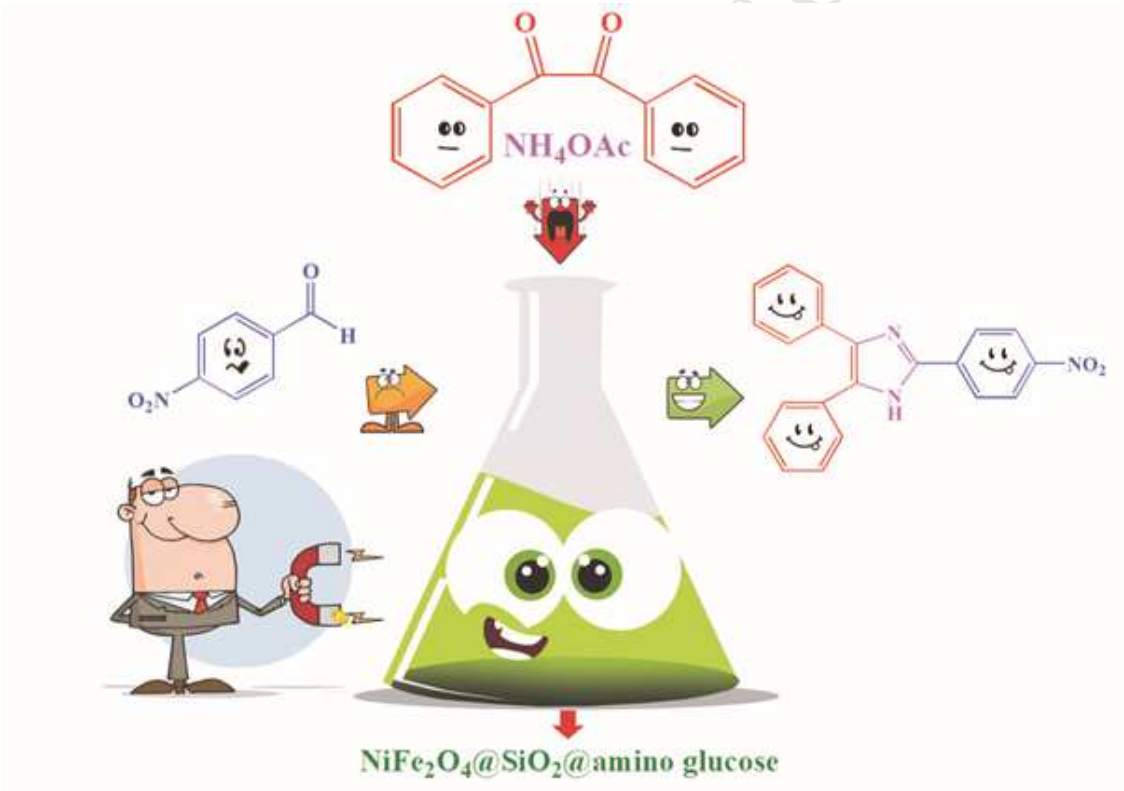
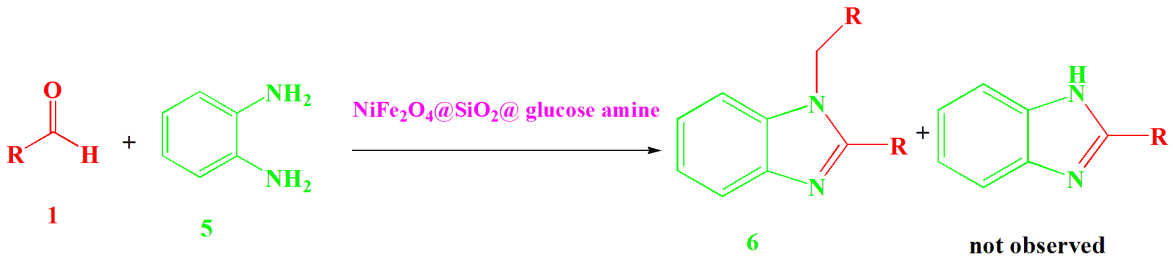


Figure 4. Representation of reaction and reusability of catalyst

As a part of our program, seeking at development $NiFe_2O_4$@SiO_2@glucose amine for the preparation of pharmaceutical and heterocyclic compounds, we check the efficiency of $NiFe_2O_4$@SiO_2@ aminoglucose for the synthesis of benzo[*d*]imidazole via two component reaction of aldehydes and 1,2- diaminobenzene under solvent free reaction (Scheme 4).



Scheme 4. Synthesis of benzo[d]oxazoles using $NiFe_2O_4$@SiO_2@ aminoglucose

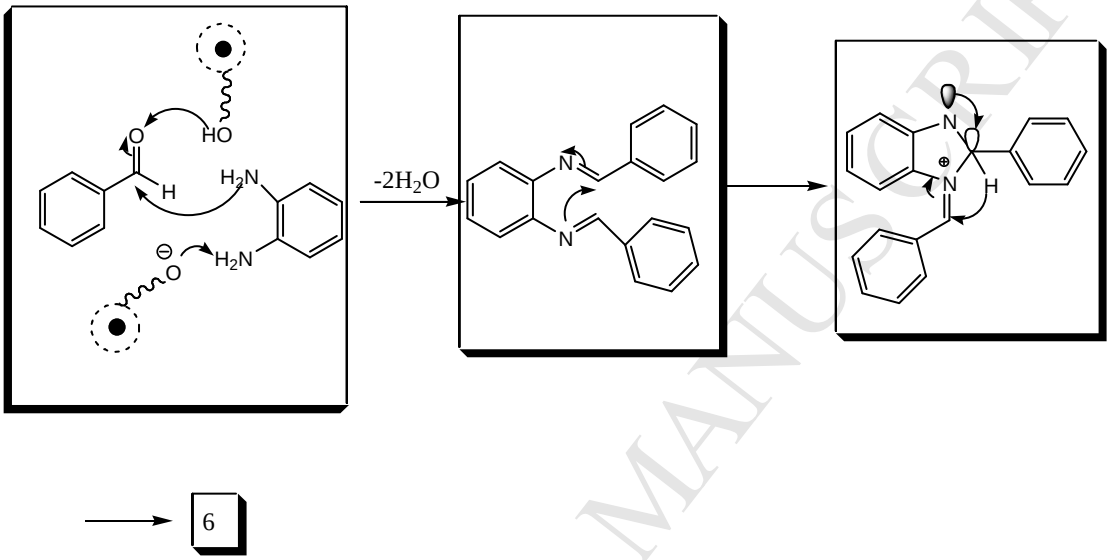
To present the efficiency and generality of the reaction, various aldehydes were reacted with 1,2-diaminobenzene in the presence of $NiFe_2O_4$@SiO_2@aminoglucose MNPs under solvent free condition. The results are summarized in Table 4.

Table 4. Synthesis of benzo*[d]*imidazoles using $NiFe_2O_4$@SiO_2@ aminoglucose

Entry	Aldehyde	Product	Time (min)	Yield (%)[a,b]	Mp (°C)	
					Found	Reported[59h]
1	Benzaldehyde	6a	5	98	130-132	132
2	4-N,N-Dimethylbenzaldehyde	6b	7	96	252-254	252
3	4-Chlorobenzaldehyde	6c	5	97	137-139	137
4	4-Bromobenzaldehyde	6d	5	98	200-201	196-198
5	4-Methoxybenzaldehyde	6e	7	95	131-133	131
6	2-Chlorobenzaldehyde	6f	9	93	154-155	155
7	2-Hydroxybenzaldehyde	6g	10	90	200-202	207-208
8	4-Nitrobenzaldehyde	6h	5	97	117-119	118
9	4-Hydroxybenzaldehyde	6i	10	94	255	253-254
10	Furfural	6j	7	95	94-95	96
11	2-Pyridincarbaldehyde	6k	7	96	132-133	130

[a] All products were characterized by their physical constant, comparison with authentic samples, IR, NMR spectroscopy and elemental analysis. [b] Yields based upon starting aldehyde

In the proposed mechanism, initially aldehyde and 1,2-diaminobenzene were activated by $NiFe_2O_4@SiO_2@$ glucose amine and converted to corresponding imine. Then, the diimine was activated by $NiFe_2O_4@SiO_2@$glucoseamine MNPs to iminium spiece followed by cyclization lead to final product (Scheme 5).



Scheme 5. Mechanistic pathway for the synthesis of benzo*[d]*imidazoles

To check the efficiency of this method, the comparison between this method and some of previous reported methods for the synthesis of **6a** was carried out (Table 5).

Table 5. Comparison of synthesis of compound 6a in this method with some of previous reported methods

Entry	Reagent	Condition	Time	Yield (%)	Ref.
1	silica sulfuric acid	rt	1.5 h	75	[71]
2	$RuCl_2(PPh_3)_3$	100 °C	20 h	90	[72]
3	AcOH, O_2	MW, 50°C	4 min	97	[73]
4	AcOH, O_2	Reflux, 80 °C	25 min	92	[74]

5	$NiFe_2O_4@SiO_2@$ aminoglucose	Solvent free, rt	5 min	98	this work

The recyclability and reusability of catalyst was studied in the model reaction between benzaldehyde and 1,2-diaminobenzene. The results are summarized in Figure 9.

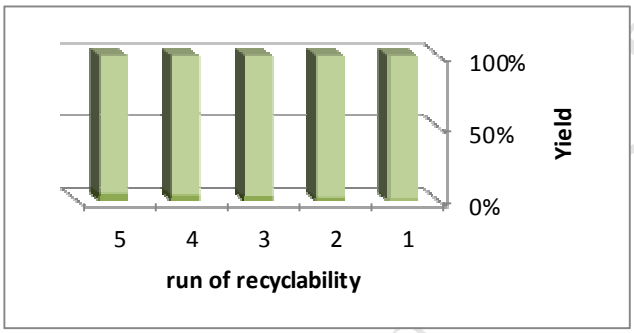
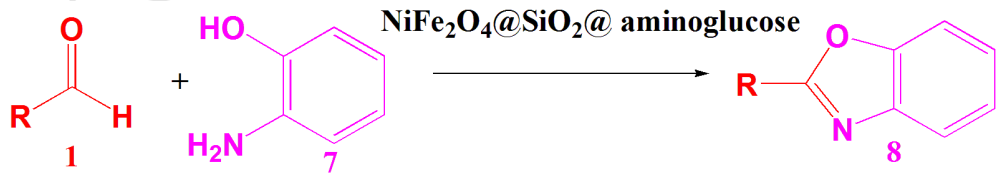


Figure 9. The recyclability of $NiFe_2O_4@SiO_2@$ glucoseamine for the synthesis of benzo[d]imidazoles

To extend the scope of our methodology, we carried out the condensation reaction of 1,2-aminophenol with various aryl aldehyde to synthesize benzoxazoles in the optimized reaction condition (Scheme 6, Table 7).



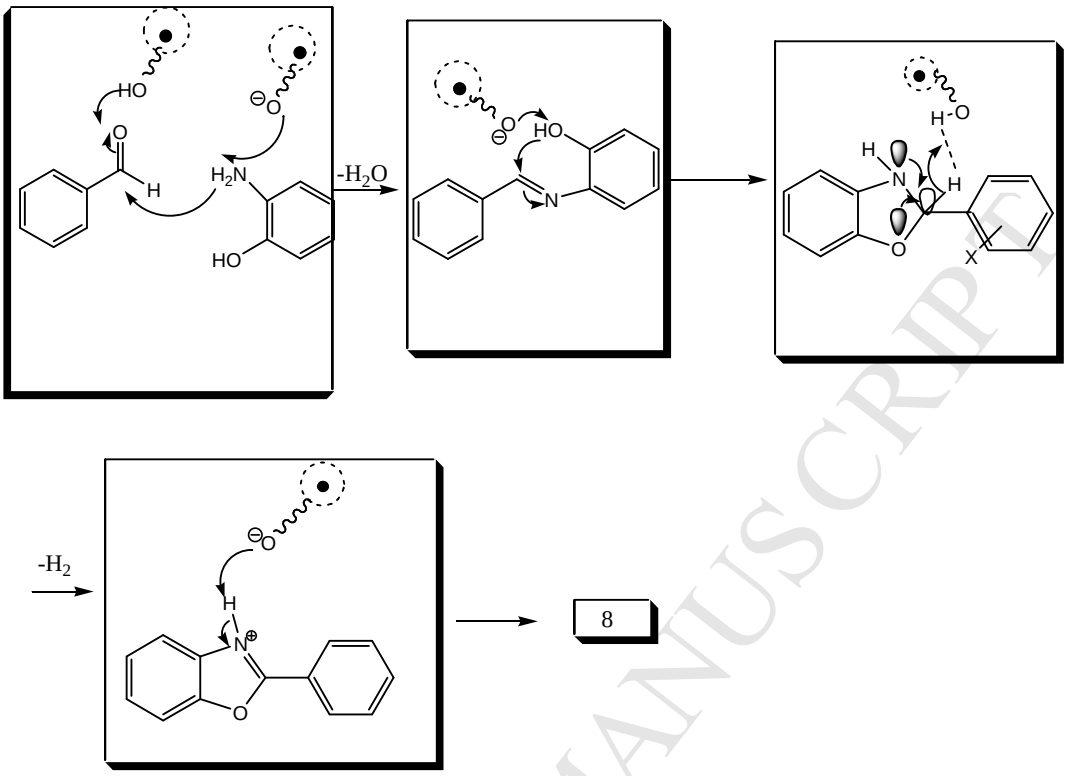
Scheme 6. Synthesis of benzoxazoles using $NiFe_2O_4@SiO_2@$ aminoglucose

Table 7. Synthesis of benzoxazoles

Entry	Aldehyde	Product	Time (min)	Yield (%)	Mp (°C)	
					Found	Reported
1	benzaldehyde	8a	10	95	103-105	102 [75]
2	4-methoxybenzaldehyde	8b	14	92	100-102	101 [75]
3	4-hydroxybenzaldehyde	8c	14	90	98-99	-
4	4-nitrobenzaldehyde	8d	8	98	265-266	266-268 [76]
5	2-hydroxybenzaldehyde	8e	16	89	154-155	-
6	3-bromobenzaldehyde	8f	8	96	187-188	-
7	4-bromobenzaldehyde	8g	8	98	157	157-158 [76]
8	4-chlorobenzaldehyde	8h	8	96	146-147	147 [75]
9	furfural	8i	13	93	90-92	89-90 [77]
10	4-pyridincarbaldehyde	8j	13	95	134-135	-
11	propanal	8k	16	89	178-179	-

[a]All the isolated products were characterized on the basis of their physical properties and IR, ^{1}H NMR spectral analysis and by direct comparison with authentic materials; [b]Isolated yields

In the mechanistically pathway, initially aldehyde was activated by $NiFe_2O_4$@SiO_2@ aminoglucose, 1 equivalence of 2-aminophenol was added to activated aldehyde. After dehydration, cyclization and oxidation, benzoxazole was produced (Scheme 7).



Scheme 7. Proposed mechanism for the synthesis of benzoxazoles

The recyclability and reusability of catalyst was studied in the model reaction between benzaldehyde and 1,2-diaminobenzene. The results are summarized in Figure 10.

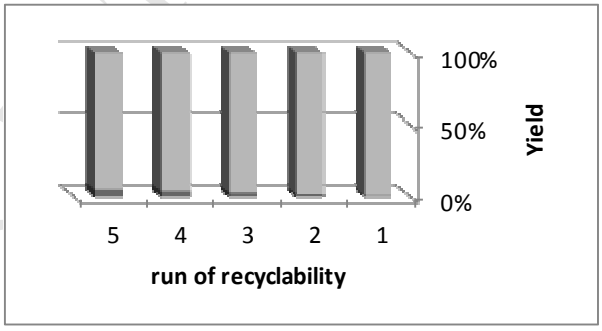


Figure 10. The recyclability of $NiFe_2O_4$@SiO_2@ aminoglucose fot the synthesis of benzoxazoles

To continuation of our study, we concentrated to synthesize a novel series of benzo[d]oxazoles bearing azo linkage, in the reported condition (Figure 10). The results are summarized in Table 8.

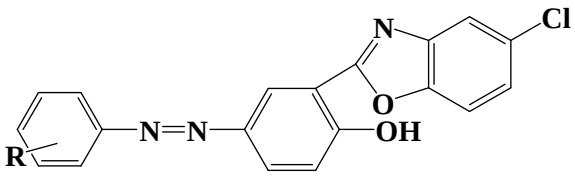


Figure 11. Azo-linked benzoxazoles

Table 8. synthesis of azo benzoxazoles using $NiFe_2O_4$@SiO_2@ aminoglucose

Entry	R	Product	Time (min)	Yield (%)[a]	Ref
1	H	9a	15	93	78
2	4-NO_2	9b	8	96	78
3	2-NO_2	9c	12	94	78
4	2-Cl	9d	12	92	78

[a]Isolated yields

CONCLUSION

In conclusion, we have investigated $NiFe_2O_4$@SiO_2@aminoglucose as a new, mild and efficient catalyst for the synthesis of trisubstituted imidazoles, benzo*[d]*imidazoles, oxazoles and azo-linked oxazoles. High yield, a simple work-up procedure, ease of separation and recyclability of the magnetic catalyst and waste reduction are some advantages of this method.

To the best of our knowledge, this is the first report on synthesis of $NiFe_2O_4$@SiO_2@aminoglucose and its application for the synthesis of benzimidazoles and benzoxazoles. Furthermore, this new avenue is cheap and environmentally benign. This novel concept is expected to use to development of more benign reactions.

Acknowledgements

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- The first synthesis of amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles was revealed.
- The first avenue for the synthesize of imidazole and oxazoles using $NiFe_2O_4$@SiO_2@amino glucose was described.
- The catalyst could be easily recovered and reused.
- Short reaction time and high yield were the other benefits of this avenue.