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Synthesis and characterization of CoFe₂O₄@SiO₂@NH-NH₂-PCuW as an acidic nano catalyst for the synthesis of 1,4-benzodiazepines and a powerful dye remover

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Abstract

A novel magnetic heterogeneous nanocatalyst CoFe₂O₄@SiO₂@NH-NH₂-PCuW was synthesized and characterized. This powerful catalyst possesses Brønsted and Lewis acid properties. The presence of Cu enhances the acidity of this catalyst because of the increase in the electron deficiency of polyoxometalate. It was successfully applied for the easy and efficient one-pot synthesis of 1,4-benzodiazepine derivatives directly from dimedone, o-phenylenediamine, and an aromatic aldehyde under a solvent-free condition at 80°C. High yields in short reaction times, easy work-up, and environmental friendliness are some of the advantages of this protocol. Also, this nanocatalyst could conveniently be recovered by a magnetic field and reused several times without a significant loss of catalytic efficiency. The synthesized nanocatalyst CoFe₂O₄@SiO₂@NH-NH₂-PCuW also proved to be an excellent adsorbent for dye removal. These properties are related to the high surface area because of the nanostructure and high acidity due to the presence of Cu in polyoxometalate. Moreover, magnetic properties help better recovering of this adsorbent for dye removed from wastewater.

Keywords: aniline blue; benzodiazepine derivatives; dye removal; heterogeneous nanocatalyst; heteropoly acids; CoFe₂O₄ nanoparticles

1. Introduction

Benzodiazepine derivatives are a very valuable class of heterocyclic compounds that have attracted a great deal of attention because of their medicinal and biological properties such as antidepressive [1], antifungal [2], antiepileptic [3], analgesic [4], antibiotic [5], antibacterial [6], anticoagulant [7], analgesic [8], hepatitis C virus (HCV) NS5B inhibitors [9], and HIV-1 protease inhibiting (Fig. 1) [10]. In addition, Benzodiazepines exhibit potentially anxiolytic, antipsychotic, and anti-

anaphylactic activity [11]. Therefore, a variety of synthetic methods has been developed for the preparation of these compounds in the last decade. Several techniques have been reported for the preparation of benzodiazepines via the ophenylenediamine with α , β -unsaturated carbonyl, β -haloketones, and β -aminoketones in the presence of various acid catalysts. Many reagents have been reported for this condensation including trichlorotriazine (TCT) [12], Fe(ClO₄)₃. xH₂O [13], silica sulfuric acid (SSA) [14], Yb(OTf)₃ [15], Er(OTf)₃ [16], Sc(OTf)₃ [17], BF₃·Et₂O [18] and Sn(HPO₄)₂, H₂O under solvent-free condition [19] and MgO/POCl₃ [20], NaBH₄ [21], InBr₃ [22], *N*-bromosuccinimide (NBS) [23], and AcOH under microwave conditions [24]. Moreover, several methods have been reported for the synthesis of 4-substituted 1,5-benzodiazepine derivatives via the three-component condensation of *o*-phenylenediamine and dimedone with various aldehyde using Brønsted acid catalysts; e.g., HCl in ethanol [25], acetic acid in toluene [26], oxalic acid in water [27], H₂SO₄ in water [28], and acetic acid in ethanol [29]. To deal with weaknesses such as lengthy reaction time, low yields, environmental hazards, and non-recyclable catalysts, some improved methods have been reported, using Fe₃O₄@chitosan [30], ionic liquid [H-NMP][HSO₄] [31], Fe(OTs)₃/SiO₂ [32], La₂O₃ and La(OH)₃ [33], NiO-SiO₂ NCs [34] 'carbon catalysis' of GO [35], and Gr@TiO₂ NCs [36].

Fig. 1

Heteropoly acids (HPAs), particularly Keggin type, as strong heterogeneous acid catalysts have attracted much attention in recent decades because of their catalytic activity for acid-catalyzed reactions and their easy recyclability and reusability [37-40]. These catalysts have been used for dehydration of diols [41], rearrangement [42], Friedel-crafts alkylation [43], and the synthesis of antioxidants, vitamins, and biologically active substances [44]. Research has shown that immobilization of heteropoly acids on a suitable support can eliminate its homogenous drawbacks. However, supported HPAs have leaching problem. A strategy to deal with this problem is designing an organic-inorganic hybrid. Besides, using magnetic nanoparticles (MNPs) that can be easily separated from the reaction mixture using through a simple permanent magnet would be very helpful in this regard [45-49]. In continuation of our work using polyoxometalate as a catalyst, we report the synthesis of CoFe₂O₄@SiO₂@NH-NH₂-PCuW as a novel acidic ionic catalyst on MNPs. Also, for verifying the efficiency of the catalytic behavior of the catalyst, a controlled reaction was performed using dimedone, *o*-phenylenediamine, and an aromatic aldehyde for the synthesis of 1,4-benzodiazepine. Advantages of this catalyst according to green chemistry rules include using a low amount of catalyst via high yields over short reaction times, easy work-up, reusability of the nanocatalyst, and solvent-free conditions. The synthesized CoFe₂O₄@SiO₂@NH-NH₂-PCuW also showed a great potential as an adsorbent for dye removal.

2. Experimental

2.1. Material and instrumentation

All chemicals were purchased from Merck and Fluka Chemical Company and used without further purification. $H_5PW_{11}CuO_{39}$ was prepared according to literature [50].

FT-IR (Fourier transform infrared) spectra were recorded on a Perkin-Elmer (il74xb3gv5) spectrometer. ¹H NMR spectra were recorded on a Brucker spectrometer at 400 MHz with tetramethylsilane as an internal standard. X-ray diffraction (XRD) patterns of the synthesized samples were taken with a Philips X-ray diffractometer (model PW1840) over a 2 θ range from 10 to 80° using Cu K α radiation(λ = 1.54056 A°). The FESEM images were obtained using a Hitachi Japan S4160 scanning electron microscope .The magnetic properties of the fabricated CoFe₂O₄@SiO₂@NH-NH₂-PCuW composite as well as other samples were studied using vibrating sample magnetometer (VSM) of Meghnatis Daghigh Kavir Company. The TGA curve of the CoFe₂O₄@SiO₂@NH-NH₂-PCuW was recorded on a BAHR, SPA 503 at heating rates of 10 °C min⁻¹. The thermal behavior was studied by heating 1–3 mg of samples in aluminum-crimped pans under airflow, over the temperature range of 25–800 °C. Thermo gravimetric analyses (TGA) were performed using a TGA Q600 V20.9 Build 20 instrument.

Recording the spectra and the absorbance measurements were made by a Jenway UV–vis spectrophotometer model 6320 using quartz microcells with capacity of 350 μ L. A Metrohm 632 (Switzerland) pH-meter was used to measure pH with a combined glass electrode. A model BHG HERMLE centrifuge (Germany) was used for the phase separation.

2.2. Synthesis of CoFe₂O₄

Cobalt ferrite MNPs were prepared by a chemical co-precipitation method according to the literature reported by Maaz et al. with slight modifications [51]. $Fe(NO_3)_3 \cdot 9H_2O$ (0.01 mol) and $Co(NO_3)_2 \cdot 6H_2O$ (0.005 mol) were dissolved and mechanically stirred in 25 mL distilled water. A solution of NaOH (3M, 25 mL) was added dropwise to the salt solution under vigorous stirring until a pH level of 11-12 was reached. Then, 1g of Polyvinylpyrrolidone (PVP) as a surfactant was added and heated at 90 °C for 2 hours. The MNPs was separated by applying a permanent magnet and was washed several times with distilled water and ethanol and dried overnight at 80 °C.

2.3. Synthesis of CoFe₂O₄@SiO₂

Silica-coated CoFe₂O₄ MNPs was prepared through Stöber method, according to the reported method [52]. Obtained CoFe₂O₄ (1 g) was dispersed in a mixture of ethanol (40 mL), deionized water (10 mL), and concentrated ammonia aqueous solution (1 mL) by ultrasonication for 30 min. Subsequently, 0.4 mL of tetraethylorthosilicate (TEOS) was added dropwise and the mixture was continuously stirred at room temperature for 24 h. The silica coated MNPs was magnetically separated and washed with distilled water and ethanol (3 × 10 mL), and dried at 80 °C for 12h.

2.4. Synthesis of CoFe₂O₄@SiO₂-Cl

The obtained $CoFe_2O_4@SiO_2$ (0.7 g) was added to the solution of 3-chloropropyltrimethoxysilane (1mL) in dry toluene (100mL) and was refluxed for 48 h. After the reaction completion, $CoFe_2O_4@SiO_2$ -Cl MNPs were separated by a permanent magnet, washed with double-distilled water and ethanol (3 × 10 mL), and dried at 80 °C for 12h to give the $CoFe_2O_4@SiO_2$ -Cl.

2.5. Synthesis of CoFe₂O₄@SiO₂@N-NH

 $CoFe_2O_4@SiO_2-Cl (0.7 g)$ was dispersed in 70 mL of CH₃CN and ultrasonicated for 20 min. Then, 7mmol K₂CO₃ (0.967 g), 7mmol KI (1.162 g) and 10 mmol piperazine (0.861 g) were added and refluxed for 24 h. The solid was collected using a permanent magnet and washed with water/ethanol and dried at 80 °C for 12 h.

2.6. Synthesis of CoFe₂O₄@SiO₂@NH-NH₂-PCuW

For the preparation of diamine modified silica coated magnetite polyoxometalate nanoparticles, $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$ (1 g) and H_5PW_{11} CuO₃₉ (1 g) in 50 mL ethanol-water (80:20 ratio) was dispersed and stirred for 6 h. $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$ was separated by magnetic decantation, washed several times with water and dried at 80 °C for 4h.

2.7. General procedure for the synthesis of dibenzo [1, 4] diazepine derivatives

A mixture containing an aromatic aldehyde (1 mmol), dimedone (1 mmol, 0.140 g) and *o*-phenylenediamine (1 mmol, 0.108 g) was mixed with 0.02 g of the catalyst, and the mixture was stirred at 80 °C under solvent-free conditions for adequate time. After completion of the reaction, indicated by TLC (EtOAc/*n*-hexane), 5 mL CH₃CN was added and the catalyst was separated from the mixture using an external magnet. The solution was then concentrated under reduced pressure to obtain the product. The remaining solid product was recrystallized from aqueous ethanol to provide pure benzodiazepines.

11-(phenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H dibenzo[b,e][1,4]diazepin-1-one (4a). Yield: 98%; pale green solid, m.p = 251–252 °C; R_f = 0.131 (1:1 ethyl acetate/ n-hexane); ¹H NMR (DMSO 400 MHz): δ 1.03 (s, 3H, CH₃), 1.08 (s, 3H, CH₃), 2.08 (d, 1H, J = 16.0 Hz, CH₂), 2.20 (d, 1H, J = 15.6 Hz, CH₂), 2.58 (s, 2H, CH₂–C=O), 5.68 (d, 1H, J=5.6 Hz, C–H), 6.17 (d, 1H, J=6.0 Hz, N–H), 6.51 (d, 1H, J = 7.2 Hz, Ar), 6.54–6.61 (m, 2H, Ar), 6.90 (d, 1H, J = 7.2 Hz, Ar), 6.97-7.12 (m, 5H, Ar), 8.76(s, 1H, N–H); ¹³C NMR (400 MHz, DMSO-d₆): δ 27.8, 29.0, 33.2, 40.5, 49.9, 56.3, 110.6, 119.9, 120.4, 120.9, 123.1, 126.3, 127.7, 128.2, 131.4, 139, 145.2, 155.3, 192.6.

11-(4-methylphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H dibenzo[b,e][1,4]diazepin-1-one (4g). Yield: 92%; pale green solid, m.p = 227–229 °C; R_f = 0.129 (1:1 ethyl acetate/ n-hexane); ¹H NMR (DMSO 400 MHz): δ 1.03 (s, 3H, CH₃), 1.08 (s, 3H, CH₃), 2.06 (d, 1H, J = 16.0 Hz, CH₂), 2.13 (s, 3H, Me) 2.19 (d, 1H, J = 16 Hz, CH₂), 2.57 (s, 2H, CH₂–C=O), 5.64 (d, 1H, J=5.2 Hz, C–H), 6.12 (d, 1H, J=5.6 Hz, N–H), 6.50 (d, 1H, J = 7.2 Hz, Ar), 6.55–6.59 (m, 2H, Ar), 6.91-6.97

(m, 5H, Ar), 8.76(s, 1H, N–H); ¹³C NMR (400 MHz, DMSO-d₆): δ 20.95, 27.8, 29.0, 32.2, 44.5, 49.9, 56.0, 110.8, 119.9, 120.4, 121.0, 123.1, 127.7, 128.7, 131.5, 135.1, 139.1, 142.2, 155.1, 192.5.

11-(4-Chlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H dibenzo[b,e][1,4]diazepin-1-one (4d). Yield: 96%; pale green solid, m.p = 239–240 °C; R_f = 0.125 (1:1 ethyl acetate/ n-hexane); ¹H NMR (DMSO 400 MHz):): δ 1.02 (s, 3H, CH₃), 1.08 (s, 3H, CH₃), 2.08 (d, 1H, J = 16.0 Hz, CH₂), 2.19 (d, 1H, J = 16.0 Hz, CH₂), 2.58 (s, 2H, CH₂–C=O), 5.66 (d, 1H, J = 5.6 Hz, C–H), 6.19 (d, 1H, J=5.6 Hz, N–H), 6.51 (d, 1H, J = 7.2 Hz, Ar), 6.57–6.64 (m, 2H, Ar), 6.92 (d, 1H, J = 8.0 Hz, Ar), 7.07 (d, 2H, J = 8.4 Hz, Ar), 7.17 (d, J = 8.4 Hz, 2H, Ar), 8.82(s, 1H, N–H); ¹³C NMR (400 MHz, DMSO-d₆): δ 28.0, 28.8, 32.3, 44.5, 49.8, 55.9, 110.1, 120.3, 120.7, 121.1, 123.3, 128.1, 129.5, 130.1, 131.6, 138.8, 144.2, 155.4, 192.3. 11-(4-methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H dibenzo[b,e][1,4]diazepin-1-one (4J). Yield: 94%; pale cream solid, m.p = 250–252 °C; R_f = 0.127 (1:1 ethyl acetate/ n-hexane); IR (KBr, cm⁻¹): v 3352, 3282, 3015, 2955, 1587, 1382, 1512, 1383, 1426, 1279, 1062; ¹H NMR (DMSO 400 MHz): δ 1.03 (s, 3H, CH₃), 1.09 (s, 3H, CH₃), 2.10 (d, 1H, J = 16.0 Hz, CH₂), 2.20 (d, 1H, J = 16.0 Hz, CH₂), 2.61 (s, 2H, CH₂–C=O), 3.36 (s, 3H, Me), 5.72 (d, 1H, J=5.8 Hz, C–H), 6.32 (d, 1H, J=5.9 Hz, N–H), 6.52 (d, 1H, J = 8 Hz, Ar), 6.61–6.65 (m, 2H, Ar), 6.95 (d, 1H, J = 8.0 Hz, Ar), 7.24 (d, 2H, J = 8.6 Hz, Ar), 7.61 (d, J = 8.2 Hz, 2H, Ar), 8.90(s, 1H, N–H).

2.8. Adsorption porcedure for aniline blue (AB)

The adsorption experiments were performed by adding 12 mg of the adsorbent into a 100 mL beaker containing the dye solution (AB) at different initial concentrations. The mixture was stirred on a magnetic stirrer for 30 min. The solid adsorbent was separated by a permanent magnet and the supernatant solution was removed and its absorbance was measured at 589 nm. The equilibrium concentration of the dye was determined spectrophotometrically using a calibration graph constructed for the dye (A=0.0392x+0.0112). The amount of adsorbed dye at time (t) was calculated using the following equation: $q_i = (C_0 - C_1) V/W$

3. RESULTS AND DISCUSSION

3.1. Preparation and characterization of catalyst

The synthesis of Brønsted Lewis acidic catalyst with magnetic cores consists of three stages, shown in Schemes 1-3.

1) In the first step, cobalt ferrite MNPs are coated with a silica layer via a sol-gel method in ethanol. Organosilanes could be as a linker between the organic species and the inorganic core. Next, some of the chlorides in the linkers are replaced by nitrogen of piperazine (Scheme 1).

2) In the second step, H₅PW₁₁CuO₃₉ is synthesized according to the literature (Scheme 2)[50].

3) Finally, the diamine modified silica-coated magnetite and heteropoly acid obtained from steps 1 and 2 are mixed in an ethanol-water solvent and the main catalyst is prepared (Scheme 3).

Scheme 1

Scheme 2

Scheme 3

3.1.1. FT-IR spectroscopy

To characterize and confirm the formation of the catalyst, FT-IR spectra of $CoFe_2O_4$, $CoFe_2O_4$ @SiO₂, $CoFe_2O_4$ @SiO₂, $CoFe_2O_4$ @SiO₂, $CoFe_2O_4$ @SiO₂, $CoFe_2O_4$ @SiO₂@N-NH, $CoFe_2O_4$ @SiO₂@NH-NH₂-PCuW, and $H_3PW_{11}CuO_{39}$ were recorded (Fig. 2). In these spectra (Figs. 2a-d), two peaks appeared at 597 and 463 cm⁻¹ are indexed to Fe–O stretching vibration in the octahedral and tetrahedral sites of $CoFe_2O_4$, respectively [53]. The sharp band at 1092 cm⁻¹ and the weak band at 804 cm⁻¹ are attributed to symmetrical and asymmetrical stretching vibration the Si–O–Si bonds, suggesting the survival of a SiO₂ layer around the $CoFe_2O_4$ MNPs [54]. Observing peak with relatively low intensity at 1626 cm⁻¹ and a broad peak at the regions 3416 cm⁻¹ might be attributed to the OH groups of the surface of the adsorbed water bending and stretching vibrations [55]. Two weak absorption bands appeared at 2929 and 2853 cm⁻¹ are related to C–H stretching vibrations. These peaks confirm the presence of methylene and propyl-linked groups to nanoparticles (curve c and d). In addition, C-N stretching at 1370 cm⁻¹ is detected but the N-H stretching due to overlapping with the hydroxyl groups is not clearly realized. In spectrum d, the bands of Keggin appear at (1080 and 1050 cm⁻¹), 988, 888 and 808 cm⁺¹, which are indexed to the stretching vibrations of (P–O), (W=O), (W-O-W inter-octahedral), and (W-O-W intra-octahedral), respectively [56]. Compared to CoFe₂O₄@SiO₂@NH-NH₂-PCuW despite although the peaks at 1080 and 1050 cm⁻¹ overlap with Si–O–Si stretching vibration, but bands observed at 988, 888, and 808 cm⁻¹ indicated that H₃PW₁₁CuO₃₉ was anchored to CoFe₂O₄@SiO₂@NH-NH₂-PCuW successfully.

Fig. 2

3.1.2. X-ray diffraction (XRD) study

The XRD patterns of $CoFe_2O_4$, $CoFe_2O_4@SiO_2$, $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$, and $H_5PW_{11}CuO_{39}$ are shown in Fig. 3. The diffraction peaks at $2\Theta^\circ = 29.79$, 35.57, 42.73, 53.23, 57.07, and 62.45 correspond to pure $CoFe_2O_4$ phase (JCPDS PDF #221086) cubic spinel structure after coating and functionalization. However, there are no specific peaks of free $H_5PW_{11}CuO_{39}$ in the XRD spectrum of $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$.

Fig. 3

3.1.3. FESEM and EDX studies

 $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$ was recognized using EDX analysis, by which all the expected main elements including C, O, Si, P, Fe, Co, Cu, and W were detected. Based on these results, it can be stated that the catalyst consists of three-component and $H_5PW_{11}CuO_{39}$ was immobilized on the surface of the diamine functionalized $CoFe_2O_4$ MNPs (Fig. 4c)

3.1.4. Thermogravimetric analysis (TGA) study

The thermogravimetric analysis (TGA) was used to define the thermal stability and the presence of immobilized components on the surface of the MNPs. Fig. 5 presents three weight loss steps in the TGA curve of the $CoFe_2O_4@SiO_2@NH-NH_2$ -PCuW catalyst. The first weight loss (1.8%) at 120°C is related to the removal of adsorbed water moisture. The second weight loss (6.46%) from 183°C to 440°C is due to the decomposition of organic fractions coated on magnetic nanoparticles. The weight loss (7.60%) at about 440-780°C can be attributed to the decomposition of the $H_3PW_{11}CuO_{39}^{2-}$ structure. In addition, $CoFe_2O_4$ MNPs show excellent thermal stability at temperatures up to 800°C.

Fig. 5

3.1.5. The magnetic property study

Magnetic properties of MNPs were studied using vibrating sample magnetometry (VSM) at room temperature. Magnetization curves of prepared MNPs are shown in Fig. 6. The saturation magnetization (Ms) of $CoFe_2O_4$, $CoFe_2O_4@SiO_2$, and $CoFe_2O_4@SiO_2@PCuW$ are 71.88, 43.93, and 20.40 emu/g, respectively. Accordingly, when the nanoparticles are coated with silica and functionalized by heteropoly acid, the value of Ms is reduced. However, they could still be separated efficiently and easily from the solution media with an external magnetic.

Fig. 6

3.2. Evaluation of the catalytic activity of CoFe₂O₄@SiO₂@NH-NH₂-PCuW

To investigate the catalytic activity of $CoFe_2O_4@SiO_2@NH-NH_2$ -PCuW, the synthesis of benzodiazepine derivatives was studied. The reaction was optimized with respect to concentration, solvent, temperature, and reaction time. The reaction of *o*-phenylenediamine (1 mmol), dimedone (1 mmol), and 4-chlorobenzaldehyde (1 mmol) as a model reaction was carried out under various reaction conditions.

Initially, the reaction was performed without any catalyst, but it did not proceed even after a long time (Table 1; entries 1 and 2). The reaction was repeated in various solvents such as water, ethanol, ethanol-water, and CH_3CN and solvent-free conditions in the presence of the catalyst (Table 1; entries 3-12). It was found that solvent-free conditions are more suitable for this reaction. Then, the catalyst amount was optimized and the best result was obtained using 0.02 g of the catalyst in the absence of solvent at 80°C (Table 1, entry 9).

Table 1

In order to verify the efficiency of the catalyst, equimolar amounts of o-phenylenediamine 1, dimedone 2, and variety of aryl aldehydes 3 were reacted together in the presence of 20 mg nanocatalyst under a solvent-free condition at 80°C. A wide

range of meta-, para-, and ortho-substituted aromatic aldehydes including electron-donating and electron-withdrawing groups for the synthesis of dibenzo [1, 4] and diazepine derivatives were selected. The reaction proceeded with high speed and the corresponding products were isolated in excellent yields (Table 2, 4 a-k).

Table 2

A comparison of this work with other methods reported for the preparation of benzodiazepines is provided in Table 3. These results demonstrate that this protocol is superior to some of the previously reported methods in terms of the amount of used catalyst, yield, the reaction time, and the absence of volatile organic solvents. The higher efficiency of this catalyst can be attributed to the increase in the electron deficiency of POM due to the presence of Cu [60].

Table 3

3.3. Proposed reaction mechanism

Based on the results, a plausible mechanism is presented in Scheme 4 for the synthesis of benzodiazepine derivatives in the presence of MNPs as a catalyst. Initially, the addition of o-phenylenediamine 1 with dimedone 2 was assisted by the catalyst produced an imine intermediate 5. The carbonyl group of dimedone is activated by acidic sites of the catalyst. Then, the NH_2 group of o-phenylenediamine immediately reacts with this carbonyl group along with the elimination of H_2O , leading to imine intermediate 5. Moreover, the 1,3-hydrogen shift of imine 6 leads to the formation of tautomeric enamine 7. The amino group of enamine 7 attacks the activated carbonyl group of benzaldehyde derivatives 3 to form the intermediate imine 8. Finally, the seven-membered ring benzodiazepine 4 is obtained via intramolecular cyclization of imine 8.

Scheme 4

3.4. Recyclability of catalyst

The possibility of recycling and reusing the heterogeneous acidic catalyst of $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$ is one of the most important benefits compared to the homogeneous ones, which are economically and environmentally significant. After completion of the reaction, separation of the nanocatalyst takes place in a very short time using an external magnet. The MNPs were washed twice with 5 ml ethanol, dried at 100°C for 4 h, and used in the next run. This catalyst was reused for 6 times without any significant loss in its catalytic activity (Fig. 7).

3.5. Dye removal

3.5.1. Selective adsorption

The dye removal capability of the newly synthesized compound was also investigated. To test the adsorption behavior of different dyes by the synthesized $CoFe_2O_4@SiO_2@NH-NH_2$ -PCuW, three dyes of aniline blue (AB), sunset yellow (SY), and crystal violet (CV) were evaluated. The adsorption performance of the adsorbent for these dyes was investigated by recording the UV-Vis spectra. The adsorption spectra of the dyes before and after removal are presented in Fig. 8. According to the results, this absorbent shows very high selectivity to remove aniline blue with high efficiency (above 90%) in 20 min (Fig. 8a). However, the amount of other dye adsorption is lower than 10% (Figs. 8b and 8c) at a longer time (120 min). As shown in Fig. 9, the color of the aniline blue almost completely disappeared due to significant adsorption, and the color of the SY and CV dyes had no obvious change, indicating that the effect of adsorption is minor.

Fig. 8

Fig. 9

3.5.2. Effect of different variables

The effects of different parameters such as pH, adsorbent mass, and time on the adsorption of AB were investigated to find the optimum conditions. In this regard, pH is an important parameter for the removal of organic matter from aqueous solution. Because the surface charge of the adsorbent is affected by the pH of the solutions, optimizing the pH is important during the dye adsorption process. For this purpose, dye adsorption experiments were carried out in various pH values ranging from 2 to 6 for an initial concentration of 50 ppm and the adsorbent mass of 10 mg at room temperature (Fig. 10a). The results showed that with increasing pH in the range from 2 to 5.5, the removal percentage increases and then decreases. Therefore, optimum pH was considered to be 5.5 for the adsorption of AB.

The dependence of the dye adsorption on the amount of the adsorbent at room temperature and pH 5.5 was also studied. For this purpose, similar removal experiments were undertaken using various masses of the adsorbent (2-16 mg) in contact with the dye solution. The percentage of the dye adsorbed increased as the adsorbent mass was increased up to 12 mg and it was leveled off at higher amounts of the adsorbent (Fig.10b). Thus, the adsorbent mass of 12 mg was chosen for further experiments.

The effect of contact time on the removal of AB with initial concentrations of 50 and 100 mg/l was investigated within the time range of 0-40 min at room temperature (Fig. 10c). The contact time curves demonstrated that the highest amount of AB is adsorbed in the first 20 min and remains constant, thereafter. Therefore, 30 min was chosen as the optimum contact time.

Fig. 10

3.5.3. Adsorption equilibrium isotherms

Adsorption isotherm studies are important for the determination of the adsorption mechanism. Dye adsorption equilibrium isotherms in aqueous solution were investigated at pH 5.5 and room temperatures. Experimental data were evaluated using

Langmuir and Freundlich isotherms. Langmuir isotherm shows monolayer adsorption surface, assuming that all surface sites are energetically identical and the surface is homogeneous. Langmuir isotherm can be expressed as:

$$\frac{Ce}{qe} = \frac{ce}{qm} + \frac{1}{bqm}$$

Where C_e is the equilibrium concentration of the analyte on the adsorbent (mg/L), q_e is the amount of analyte adsorbed per unit mass of adsorbent at equilibrium concentration as mg/g, q_m (mg/g) is the maximum adsorption capacity, and b is Langmuir constant.

The Freundlich isotherm presents the adsorption at multilayer and energetically heterogeneous surfaces. It is an empirical equation suitable for a high and middle range of analyte concentration but not for low concentrations. The Freundlich isotherm is written as:

$$\ln q_e = \frac{1}{n} \ln ce + \ln k$$

Where q_e is the amount of dye adsorbed at equilibrium in mg/g, C_e is the analyte equilibrium concentration in mg/L, and *K* and *n* are Freundlich characteristic constants.

The corresponding parameters for both models for AB adsorption are shown in Table 4 and the model curves are demonstrated in Fig. 11. The results indicate that the Langmuir isotherm is a better fit for the adsorption behavior of the new adsorbent.

Table 4

Fig. 11

Conclusion

In this study, magnetic heterogeneous nanocatalyst $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$ was synthesized by the reaction of heteropoly acid $H_5PW_{11}CuO_{39}$ with diamine-modified silica coated MNPs and fully characterized by FT-IR, XRD, FESEM, EDX, TGA, and VSM techniques. More importantly, $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$ is a fundamentally heterogeneous Brønsted and Lewis acidic catalyst that can be recovered simply using an external magnetic. The efficiency of the nanocatalyst was verified in preparation of 1,4-benzodiazepine derivatives under solvent-free conditions. The benefits of this approach are high yield, short reaction times, and simple work-up procedure and green reaction conditions. In addition, the catalyst can be easily separated from the reaction mixture by a permanent magnet and reused several times without significant loss of catalytic activity. It was also found that the synthesized $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$ catalyst has a great ability for the aniline blue dye removal with an excellent adsorbent capacity (500 mg/g). Finally, the magnetic properties of this dye remover could accelerate the separation speed and enhancing the efficiency of wastewater treatment.

Conflicts of interest

There are no conflicts to declare.

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Figures and scheme captions

Fig. 1. HIV-1 protease inhibiting (I, II) and HCV NS5B inhibitor (III, IV)

Fig. 2. FT-IR spectra of $CoFe_2O_4(a)$, $CoFe_2O_4@SiO_2(b)$, $CoFe_2O_4@SiO_2@N-NH$ (c), $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$ (d) and $H_5PW_{11}CuO_{39}$ (e).

Fig. 3. XRD patterns of CoFe₂O₄ (a), CoFe₂O₄@SiO₂@NH-NH₂-PCuW (c) and H₅PW₁₁CuO₃₉ (d).

Fig. 4. (a), (b) SEM images of $CoFe_2O_4@SiO_2@NH-NH_2$ -PW at the scale 100 µm and 500 nm respectively and (c) the EDX spectrum proves the elemental composition

Fig. 5. TGA Curves of CoFe₂O₄@SiO₂@NH-NH₂-PCuW

Fig. 6. Hysteresis loops of CoFe₂O₄ (a), CoFe₂O₄@SiO₂@N-NH (b) and CoFe₂O₄@SiO₂@NH-NH₂-PCuW

Fig. 7. Reusability of the $CoFe_2O_4@SiO_2@NH-NH_2$ -PCuW nanocatalyst

Fig. 8 The selective adsorption of $CoFe_2O_4@SiO_2@NH-NH_2$ -PCuW for aniline blue

Fig. 9. Pictures of AB-SY-CY before (a) and after (b) adsorbed the three dyes

Fig. 10. Effect of pH (a), mass of adsorbent (b) and contact time (c) on AB removal at 25 °C

Fig. 11. Langmuir transformation (a) and freunlich (b) of equilibrium adsorption isotherms of AB

Scheme 1. Pathways for preparation of CoFe₂O₄@SiO₂@N-NH (step1)

Scheme 2. Pathways for the preparation of H₅PW₁₁CuO₃₉ (step 2)

Scheme 3. Pathways for the preparation of CoFe₂O₄@SiO₂@NH-NH₂-PCuW (step 3)

Scheme 4. Proposed mechanism for the formation of benzodiazepines

CCE

Table 1. Optimization of reaction conditions^a



^a o-Phenylenediamine (1 mmol), dimedone (1 mmol) and 4-chlorobenzaldehyde (1 mmol) in the presence of catalyst in solvent free condition

^b Isolated yield of the pure product.



Table 2. Synthesis of benzodiazepine derivatives**4a-k** in the presence of $CoFe_2O_4@SiO_2@NH-NH_2$ -PCuW under solventfree condition^a



∖ 4j



^a o-Phenylenediamine (1 mmol), dimedone (1 mmol) and, (1 mmol) and nanocatalyst 20 mg at 80 °C in solvent free condition

:	^a o-Phenylenediamine (1 mmol), dimedone (1 mmol) and, (1 mmol) and nanocatalyst 20 mg at 80 °C in solvent free
	condition
I	^b Isolated yield of the pure product.
	^e decomposition point
Table	3. Comparison of efficiency of CoFe ₂ O ₄ @SiO ₂ -N-NH-PCuW with some various catalysts in the synthesis of dibenzo [1, 4] diazepine
deriva	tives

Entry	Catalyst and conditions	product	Time (min)	Yield	Ref
				(%)	
1	oxalic acid (40 mol%)/water/100 °C	4d	120	94	[27]
2	Fe ₃ O ₄ @chitosan (0.03 g) /ethanol/r.t	4d	120	91	[30]
3	Fe(OTs) ₃ /SiO ₂ (100 mg)/solventfree/80 °C	4d	5	96	[32]
4	ZnS nanoparticles (0.01 g) /ethanol/80 °C	4d	10	85	[58]
5	Gr@TiO ₂ NCs (0.14g)/ethanol /20 °C	4a	79	92	[36]
6	TiO ₂ NPs(0.14 g) /ethanol /20 °C	4a	100	75	[36]
7	Irradiation/70 °C NiO-SiO2 NCs (0.05 g)/ethanol- Microwave	4d	10	98	[34]
8	Cu/GA/Fe ₃ O ₄ @SiO ₂ (100 mg)/ethanol/60 °C	4d	30	95	[59]
9	GO nanosheet (15 mg) /water/70 °C	4a	20	90	[35]
10	[H-NMP][HSO ₄](10 mol%)/solvent free/100 °C	4d	15	85	[31]
11	La ₂ O ₃ (0.01 eq)/water/60 °C	4d	216	84	[33]
12	La(OH) ₃ (0.01 eq)/water/60 °C	4d	240	81	[33]
13	CoFe ₂ O ₄ @SiO ₂ @NH-NH ₂ -PCuW(20mg)/solvent free/80 °C	4a/4d	10/15	98/96	This work

Table 4. Parameters of the Langmuirand Freundlich model

Model	Paran	neter	
	$q_m(mg.g^{-1})$	500	
Langmuir	b(L.mg ⁻¹)	0.1227	
	\mathbb{R}^2	0.9973	
	k	76.3326	
Freundlich	n	1.8242	
	R^2	0.9869	
			6
		ph -	
		OW	
		, O nh	
		, C nh	
6			

In this study, magnetic heterogeneous nanocatalyst $CoFe_2O_4@SiO_2@NH-NH_2-PCuW$ was synthesized. This Brønsted and Lewis acidic catalyst was successfully applied for the easy and efficient one pot synthesis of 1,4-benzodiazepine derivatives. It was also found that the synthesized catalyst has a great ability for the aniline blue dye removal.

HaPW11CuOa ACCEPTED

















(a)





Accention







1) 11 Na₂WO₄ + Na₂HPO₄ + 17 H⁺ → Na₇PW₁₁O₃₉ + 9H₂O

With Contract of the second se 2) $Na_7PW_{11}O_{39} \xrightarrow{1)CuSO_4} K_5PW_{11}CuO_{39} \xrightarrow{resins(H^+)} H_5PW_{11}CuO_{39}$



