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Magnetic Chitosan-Supported Silver Nanoparticles: A Heterogeneous Catalyst for the Reduction of 4-Nitrophenol

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Abstract: Developing heterogeneous catalyst using chitosan (CS) and magnetic Fe_3O_4 as support has been remarkably attractive due to their availability, low cost and non-toxicity. In this work, a heterogeneous catalyst (denoted as Fe₃O₄@CS@MS@Ag) was fabricated by the deposition of silver nanoparticles on magnetic chitosan via an easy and facile modification of its surface with methyl salicylate (MS). The catalyst was characterized using Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), X-ray diffractometer (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). To the best of our knowledge, for the first time, CS decorated Fe₃O₄ (Fe₃O₄@CS) has shown the catalytic activity for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in presence of NaBH₄. Surface modified magnetic chitosan (Fe₃O₄@CS@MS) also acts as active catalyst towards the reduction of 4-NP. However, catalytic efficiency has increased fourfold when silver-nanoparticles-deposited magnetic chitosan (Fe₃O₄@CS@MS@Ag) used as our target catalyst. The catalyst was separated with external magnet after each cycle of catalytic reaction and reused effectively five times with almost 90% efficiency.

Keywords: chitosan; magnetic Fe₃O₄; silver nanoparticles; catalyst; 4-nitrophenol

1. Introduction

Many researchers are focusing on the development of sustainable materials by minimizing waste and pollution in the chemical synthesis. Literature survey reports that the catalyst used at least one step in more than 90% of industrial multi-step synthesis processes [1]. Generally, homogenous catalysts have some advantages such as easily dissolving in reaction media, active sites of catalysts are radially available for the substrates, monitoring real-life mechanistic study and good selectivity towards desired products [2]. However, heterogeneous catalysts are given priority over homogenous catalysts in the industrial application regarding the easy separation of the catalyst from the reaction mixtures and obtaining pure targeted products with minimal involvement of purification steps. Most of the heterogeneous catalysts are prepared based on inorganic carriers such as silica and mesoporous silica [3–5]. However, for effective designation of the heterogeneous catalyst, integrating nanomaterials are getting significant interest due to their unique physicochemical properties, high surface to volume ratio, highly active surface of atoms and large-scale application along with imaging, photonics, nanoelectronics, sensors, biomaterials and biomedicine [6–11]. Nanomaterials based heterogeneous catalysts have the benefit regarding recovery and reuse in green chemical synthesis processes. However, magnetic nanomaterials-based heterogeneous catalysts are superior over the other nanomaterials-based heterogeneous catalysts because of the us of external magnet rather than centrifuge or suction filtration or gravitational filtration for the



separation of catalyst from the reaction mixture. One of the most applicable magnetic nanomaterials is Fe₃O₄ because of its fundamental properties and wide application in various area of research such as medicine, sensors, high density magnetic recording media and catalysis [12,13]. An increased demand of using Fe₃O₄ in heterogeneous catalyst design has been prompted mainly due to its easy separation and requesing capability. The magnetic recovering property of Fe O. has been integrated in different catalytic

recycling capability. The magnetic recovering property of Fe_3O_4 has been integrated in different catalytic systems [14–16]. Recently, Shokouheimehr et al., reported magnetic nanomaterials based heterogeneous catalysts for different types of organic transformations such as reduction of aromatic nitro compounds, Suzuki-coupling, acetylation of phenols and tandem reactions [17–22]. However, Fe_3O_4 impregnated catalysts have been treated with different coating materials for increasing their biocompatibility and stability. Especially, the surface of Fe_3O_4 has been modified via introducing appropriate functionalizing agents or linkers. This strategy provides a scope for bringing additional functionalities to the surface of Fe_3O_4 such as introducing organic ligands or metal complexes parallel to displaying excellent thermal and chemical stability [23].

Amongst a plethora of functionalizing agents, biopolymers have been employed in many heterogeneous catalytic systems [24–27]. Using chitosan (CS) as catalyst support is very promising due to its low cost, non-toxicity and environmentally benign nature [28]. CS is a byproduct waste produced by the fishing industry and is the second most abundant structural polysaccharide after cellulose [29]. The wide use of the CS as catalyst support is mainly due to the presence of free primary and secondary hydroxyl as well as amine functional groups on its surface. This property opens up potential functionalization of the CS surface through activation of both electrophiles and nucleophiles via hydrogen bonding and lone pair interactions [30]. One of the easy and convenient modification of CS surface is the esterification of the amine functional group by direct reaction with carboxylic acid through the formation of amide functional group.

Every year around the world, a vast amount of organic waste is produced from the aromatic nitro compounds and their derivatives due to their wide application in the production of pesticides, herbicides, insecticides and synthetic dyes [31]. Among the aromatic nitro compounds, the nitrophenols are the most frequently found pollutants in industrial effluent. They have a huge adverse effect on the environment due to their difficult degradation process and are carcinogenic to living begins [32].

The United States Environmental Protection Agency (US-EPA) has rated nitrophenols as priority pollutants because of their perilous nature and recommended low concentration (10.0 ng/mL) in natural water bodies [33]. Therefore, catalytic reduction of nitrophenols is very important for pollution remediation. The reduction of 4-NP to 4-AP is one of the model reduction processes among nitrophenols derivatives that has attracted special attention in both academia and industrial research [34]. Noble metals such as Au, Ag, Pt and Pd are the active ingredients of the catalysts impregnated in their nanoforms which play a significant role in the catalytic reduction of 4-NP [35–49]. Compared to Au, Pt and Pd, using Ag in the design of environmentally benign heterogeneous catalysts is more convenient to address various economic and environmental issues [50–55]. For instance, Ag-deposited-on-silica coated magnetic Fe₃O₄ catalysts were used for the reduction of 4-NP to 4-AP [56,57] where silica was used as supportive matrix which helps in the dispersion of Ag nanoparticles during the catalysis process. However, the problem of using silica as catalyst support is the fragility in harsh acidic and alkaline media. On the other hand, CS shows the robustness compared to silica in these media. Recently, Xu et al. reported a Ag-decorated magnetic CS catalyst for the catalytic conversion of 4-NP to 4-AP where CS surface was modified using tween-80 as emulsifier and span-80 as surfactant and glutaraldehyde (GLA) as cross linker [58]. Despite this interest, no one to the best of our knowledge has reported the use of magnetic chitosan (Fe₃O₄@CS) as a heterogeneous catalyst for the reduction of 4-NP to 4-AP.

Herein, we successfully developed CS coated Fe_3O_4 ($Fe_3O_4@CS$) as a heterogeneous catalyst for the reduction of 4-NP to 4-AP using NaBH₄ solution. The surface of magnetic chitosan was modified by the reaction of the amine functional group of chitosan with methyl salicylate ($Fe_3O_4@CS@MS$). A variety of cleating molecules such as proline, amylase, glucoamylase, lipase, emulsifier, cross-linker and different aldehydes have been used for the modification of magnetic chitosan's surface so far [58–62]. However, we found methyl salicylate is more convenient compared to other chelating molecules or agent as it is cheap, non-toxic and extracted from many naturally available plants specially from wintergreens. Moreover, it is readily available even in most chemistry laboratories as common reagent. Then, magnetic chitosan was further modified by depositing silver nanoparticles on its surface to get our target heterogeneous catalyst (Fe₃O₄@CS@MS@Ag). All of these composite materials were investigated for the reduction of 4-NP. The sustainability of the catalyst was evaluated by separation of the catalyst with external magnet and reused in repeating catalytic cycles for the reduction of 4-NP under optimal conditions.

2. Results and Discussion

2.1. Characterization

In the Fourier transform infrared (FTIR) spectrum of the Fe₃O₄ (a), the characteristic stretching vibration of Fe-O has been observed at 545 cm⁻¹. This vibration was observed in all other spectra such as Fe₃O₄@CS (c), Fe₃O₄@CS@MS (d) and Fe₃O₄@CS@MS@Ag (e) except CS (b) indicating that all the prepared materials contain Fe₃O₄ (Figure 1). The C-O stretching vibration band of the CS (b) was observed at 1374 cm⁻¹ corresponding to the primary alcoholic group of the CS which was shifted to 1384 cm⁻¹ in magnetic chitosan Fe₃O₄@CS (Figure 1c), indicating the coating Fe₃O₄ with CS. The N-H bending vibration of CS (b) at 1644 cm⁻¹ shifted in magnetic CS (c) to 1640 cm⁻¹ and at surface modified magnetic CS (d) to 1636 cm⁻¹, respectively. Meanwhile, a broad peak around 3345 cm⁻¹ was attributed to -OH and -NH₂ stretching vibrations. The surface modified magnetic CS with methyl salicylate Fe₃O₄@CS@MS (d) exhibits an absorption band at 1733 cm⁻¹ which indicates the presence of carbonyl (C=O) group in the amide function moiety of the materials. No remarkable change was observed in the FTIR spectrum of the Fe₃O₄@CS@MS@Ag (e) after succeessful deposition of silver nanoparticles on the magnetic CS surface. This results imply that the silver nanoparticles have been deposited effectively on the modified magnetic CS surface via non chemical interaction.



Figure 1. FTIR spectra of (a) Fe₃O₄; (b) CS; (c) Fe₃O₄@CS; (d) Fe₃O₄@CS@MS and (e) Fe₃O₄@CS@MS@Ag.

Thermogravimetric analysis (TGA) was measured for all the prepared composite materials. It confirms the stepwise formation of the chitosan decorated Fe₃O₄, surface modified magnetic chitosan and deposition of silver nanoparticles on the magnetic chitosan surface. It also allows the determination of the stability, ratio of ingredients and organic moieties present in the composite materials. TGA plots for Fe₃O₄ (a), CS (b), Fe₃O₄@CS (c), Fe₃O₄@CS@MS (d) and Fe₃O₄@CS@MS@Ag (e) were recorded between 30 °C and 800 °C as shown in Figure 2 and evaluated by mass loss as a function of temperature. All the plots except Fe_3O_4 (a) resemble of pseudo-two step thermal decomposition. The first step of the thermal decomposition corresponds to the removal of physically absorbed water, and the second step is for the main mass loss related to the removing of organic moieties from the embedded chitosan part of the composite materials. The total mass losses for Fe₃O₄ (a), CS (b), Fe₃O₄@CS (c), Fe₃O₄@CS@MS (d) and Fe₃O₄@CS@MS@Ag (e) were 2.0%, 100.0%, 53.9%, 55.5% and 46.5%, respectively. These results showed a good agreement with theoretical calculation. For instance, Fe_3O_4 lost only 2% mass which was mainly due to the small amount of moisture present in the sample whereas CS lost 100% mass for its organic nature. The CS decorated Fe_3O_4 (c) lost 53.9% which is more than pure Fe_3O_4 and less than pure CS which is line with the theoretical concept. The surface modified magnetic chitosan Fe₃O₄@CS@MS (d) lost 55.5% which is slightly higher than magnetic CS due to the added salicylate group to the amine functional group. Noticeably, silver-nanoparticles-deposited magnetic chitosan $(Fe_3O_4@CS@MS@Ag (e) mass loss is relatively less than other prepared materials except Fe_3O_4, which$ indicates successful anchoring of nanoparticles on the surface. The amount of silver deposited on composite materials is 9.0% which has been estimated from the difference between the mass loss of Fe₃O₄@CS@MS (d) and Fe₃O₄@CS@MS@Ag (e), respectively. Furthermore, the amount of silver distributed on the magnetic CS surface is found 8.7% in the elemental composition of the catalyst (Figure S1 in ESI).



Figure 2. TGA thermogram of (a) Fe₃O₄; (b) CS; (c) Fe₃O₄@CS; (d) Fe₃O₄@CS@MS and (e) Fe₃O₄@CS@MS@Ag.

It confirms that silver nanoparticles have been deposited on the modified surface of magnetic CS successfully. After 575 °C, no significant mass loss was observed for all the prepared materials indicating

the stability of the materials at higher temperature. In the literature, it has been reported that amine group can absorb and reduce the metal ion directly into corresponding metal nanoparticles [59,63]. Therefore, amide and hydroxyl functional groups of Fe₃O₄@CS@MS provide suitable space for depositing silver nanoparticles on the modified surface.

The phase and purity of the catalyst $Fe_3O_4@CS@MS@Ag$ (e, above) was examined by X-ray diffractometer (XRD) analysis. For comparison, XRD spectrum of Fe₃O₄@CS@MS (d) (Figure 3, below) shows diffraction peaks corresponding to $2\theta = 30.0^\circ$, 35.4° , 42.5° , 53.5° , 56.8° and 63.0° respectively. These peaks are responsible for the magnetic Fe_3O_4 particles which is good fit with the literature reported result [57,64]. All of these peaks are present in our target catalyst Fe₃O₄@CS@MS@Ag (e) indicating the existence of Fe_3O_4 . The appearance of these peaks in both prepared composite materials confirms the coating of Fe₃O₄ with chitosan without any significant phase change. Moreover, chitosan did not destroy the crystal structure of Fe₃O₄. The face centered cubic structure of Fe₃O₄ in both Fe₃O₄@CS@MS and Fe₃O₄@CS@MS@Ag was confirmed by the JCPDS card NO 75-1609 [65]. Two characteristic diffraction peaks at $2\theta = 11.2^{\circ}$, 18.1° were observed for the effective coating of chitosan around the Fe₃O₄ crystal phase. The XRD pattern of both Fe₃O₄@CS@MS@Ag (e, above) and Fe₃O₄@CS@MS (d, below) indicated the presence of chitosan in both materials without induction of phase change. Furthermore, four characteristic peaks were observed in the XRD pattern of the Fe₃O₄@CS@MS@Ag (e, above) when $2\theta = 37.9^{\circ}, 44.1^{\circ}, 64.3^{\circ}$ and 77.3° respectively (Figure 3). The appearing of these peaks confirms the deposition of silver nanoparticles on the modified surface of the magnetic chitosan. These diffraction peaks are indexed to crystalline cubic phase of silver nanoparticles, which have a good agreement with the literature reported result [56]. However, few peaks at $2\theta = 22.1^{\circ}$, 27.8° , 31.0° , 33.7° and 47.0° were observed in our prepared target catalyst indicating the presence of impurity. These peaks might be responsible for excessive use of AgNO₃ during the deposition of silver nanoparticles on magnetic surface of the catalyst.



Figure 3. XRD pattern of Fe₃O₄@CS@MS (d, below) and Fe₃O₄@CS@MS@Ag (e, above).

After preparation and characterization of Fe₃O₄@CS@MS@Ag, the morphology of the surface of the catalyst was evaluated by scanning electron microscopy (SEM). For comparison, Figure 4a,b exhibits

the particle size of Fe_3O_4 which is relatively large (around 63 nm) due to the tendency of aggregation of nanoparticles by dipole–dipole interaction. Figure 4c shows the morphology and particle size of silver nanoparticles that deposited on the surface of catalyst $Fe_3O_4@CS@MS@Ag$ before the catalytic reaction. SEM image of the catalyst also shown in Figure 4d after the fifth catalytic cycle reduction of 4-NP confirms the presence of silver nanoparticles on catalyst surface. In both cases, particles size ranged between 112 and 241 nm.



Figure 4. SEM images of (**a**) Fe₃O₄; (**b**) Fe₃O₄ in different magnification; (**c**) catalyst Fe₃O₄@CS@MS@Ag before the reaction and (**d**) catalyst Fe₃O₄@CS@MS@Ag after fifth catalytic cycle of the reaction.

Energy dispersive X-ray spectroscopy (EDX) result was obtained from the SEM analysis of $Fe_3O_4@CS@MS@Ag$ which clearly shows the presence of silver nanoparticles in the catalyst. Figure S1 (in ESI) shows the EDX spectrum of the catalyst.

The elemental composition of the catalyst was found to be 8.7%, 16.3%, 34.4.0% and 37.0% for Ag, C, O and Fe, respectively. This result indicates that Fe_3O_4 was successfully covered with the CS, and silver nanoparticles have been deposited on its modified surface. In addition to that, Figure 5 exhibits the elemental mapping of the catalyst $Fe_3O_4@CS@MS@Ag$ before catalytic reaction and shows that silver nanoparticles have been distributed uniformly in the catalyst texture. For comparison, elemental mapping of the catalyst $Fe_3O_4@CS@MS@Ag$ was also recorded after the fifth cycle of catalytic reaction (Figure 6). It clearly proves that no significant chemical change happened to the catalyst even after the fifth cycle of the reaction.



Figure 5. Energy dispersive X-ray (EDX) mapping of the catalyst Fe₃O₄@CS@MS@Ag before the catalytic reaction.





Figure 6. Energy dispersive X-ray (EDX) mapping of the catalyst $Fe_3O_4@CS@MS@Ag$ after fifth catalytic cycle of the catalytic reaction.

2.2. Reduction of the 4-Nitrophenol (4-NP)

The prepared materials Fe₃O₄@CS, Fe₃O₄@CS@MS and Fe₃O₄@CS@MS@Ag were investigated for the catalytic reduction of the 4-NP to 4-AP in presence of aqueous NaBH₄ solution. Reduction of 4-NP was chosen as model reaction as this is only one product and its formation is easy to detect by measuring the absorbance at around 300 and 400 nm. Initially, a stock solution (10.0 mg /L) of 4-NP was prepared in water, and the light-yellow aqueous solution of 4-NP showed an absorption (λ_{max}) at 317 nm (Figure 7; — — violet color spectrum). When a freshly prepared NaBH₄ solution was added to the 4-NP solution, immediately the color of the reaction mixture changed from light yellow to bright yellow, and the position of absorption maximum (λ_{max}) shifted to 400 nm. This color change indicates the formation of nitrophenolate ions in presence of alkaline NaBH₄ solution (Figure 7; — — black color spectrum). The absorption (λ_{max}) remained unchanged over time (30 min) and even after adding an additional amount of NaBH₄ solution. It clearly proves that reduction of 4-NP does not proceed by using only NaBH₄ solution.



Figure 7. Optimization of catalytic reduction of 4-NP to 4-AP monitored by UV-Vis spectra of 4-NP only (— — violet line), in presence of NaBH₄ (– – – black line), NaBH₄ with Fe₃O₄ (— — red line) and NaBH₄ with 1.5 mg (1.2×10^{-6} mol Ag) of catalyst Fe₃O₄@CS@MS@Ag (— – blue line).

A control experiment was carried out by using the magnetic Fe_3O_4 on the aqueous solution of 4-NP and NaBH₄ mixture. No remarkable change was observed in Ultraviolet-Visible (UV-Vis) absorptions measurement, indicating Fe_3O_4 itself cannot catalyze the reaction (Figure 7; ------. However, when silver nanoparticles deposited surface modified magnetic chitosan catalyst Fe_3O_4 @CS@MS@Ag (1.5 mg; 1.2×10^{-6} mol Ag) was added to the aqueous solution of 4-NP and NaBH₄ mixture, immediately the color of the reaction mixture turned to very light yellow. This color change was estimated by UV-Vis absorption (Figure 7; ----- blue color spectrum), indicating the appearance of a new peak at 320 nm for the formation of 4-AP.

After getting this result in hand, the chitosan coated Fe_3O_4 was employed in the target reaction as catalyst; it showed catalytic activity towards the reduction of 4-NP to 4-AP, which is confirmed by the

blue shift of absorption (λ_{max}) from 400 nm to 320 nm (Figure 8; — — blue color spectrum). To the best of our knowledge, this is for the first-time the CS decorated Fe₃O₄ has shown catalytic activity for the reduction of 4-NP to 4-AP. The experiment was repeated for three times and every time the same result was reproduced. We speculate the reduction occurred via electron relaying mechanism from the donor BH₄⁻ to the acceptor 4-NP while both have been adsorbed on the surface of the catalyst. Hydrogen atom generated from hydride by transferring electron to magnetic chitosan surface and then attacking the substrate 4-NP and reducing it to 4-AP. During the reduction process, as concertation of NaBH₄ is relatively excessive compared to 4-NP, it has been considered that NaBH₄ concentration remains constant. Then, the surface modified magnetic CS by methyl salicylate Fe₃O₄@CS@MS was examined for the catalytic reduction of 4-NP in the presence of NaBH₄ solution (Figure 8; – – black color spectrum).



Figure 8. UV-Vis spectra for the reduction of 4-NP to 4-AP using 1.5 mg of each Fe₃O₄@CS (______ blue line), Fe₃O₄@CS@MS (_____ blue line) and Fe₃O₄@CS@MS@Ag (1.2×10^{-6} mol Ag) (______ red line) after 10 min.

A slight improved catalytic efficiency was found, compared to the CS decorated magnetic $Fe_3O_4@CS$. Finally, silver nanoparticles deposited magnetic chitosan $Fe_3O_4@CS@MS@Ag$ was investigated for the same catalytic reaction under optimal conditions. It showed the best catalytic efficiency for reduction of 4-NP to 4-AP while $Fe_3O_4@CS@MS@Ag$ was used as catalyst among three prepared materials that were investigated (Figure 8; ------ red color spectrum).

For further optimization for the catalyst loadings, we conducted the same catalytic reaction using different amount of catalysts such as Fe₃O₄@CS@MS@Ag and Fe₃O₄@CS respectively. In first case, we used 0.8 mg (6.5×10^{-7} mol Ag) of Fe₃O₄@CS@MS@Ag which is almost half of previous amount (1.5 mg; 1.2×10^{-6} mol Ag, in Figure 8) and later case we used 3.0 mg of Fe₃O₄@CS which is almost double of previous amount. In both cases, the absorption peak at 400 nm significantly decreases within 10 min and concomitant appearance of a new peak at 320 nm (Figure 9). It seems that silver nanoparticles deposited magnetic chitosan Fe₃O₄@CS@MS@Ag is fourfold effective catalyst than the chitosan decorated Fe₃O₄@CS for the reduction of 4-NP to 4-AP.



Figure 9. UV-Vis spectra for the reduction of 4-NP to 4-AP using 3.0 mg of Fe₃O₄@CS (— - - blue line) and 0.8 mg (6.5×10^{-7} mol Ag) of Fe₃O₄@CS@MS@Ag (------ red line) after 10 min.

Time dependent progress of the catalytic reduction reaction was monitored by adding 0.8 mg $(6.5 \times 10^{-7} \text{ mol Ag})$ of Fe₃O₄@CS@MS@Ag catalyst to 6.0 mL (10.0 mg/L) solution of 4-NP and 1.0 mL (1.0 mM) of freshly prepared NaBH₄ solution, as shown in Figure 10. At the beginning of reaction (0 min), absorption occurred at 400 nm indicating the presence of 4-nitrophenole ions only in the reaction mixture. During the progress of reaction, the intensity of absorptions at 400 nm decreased and appeared a new peak at 320 nm. The new absorption peak at 320 nm indicated the formation of 4-AP via the effective reduction of 4-NP. The absorption peak at 400 nm significantly decreased within 5 min, and simultaneously, the intensity of the new peak at 320 nm increased. Within 10 min of the reaction, the peak at 400 nm corresponding to the 4-nitrophemnole almost disappeared, and the peak at 317 nm was the prominent for 4-AP. This observation has close resemblance with the literature reported results [57,58].

In the reaction media, the concentration of 4-NP is directly proportional to the absorbance. Therefore, the ratio of absorbance at time t (A_t) to that at t = 0 (A_0) must be equal to the concentration ratio C_t/C_0 of 4-NP. Figure 11 shows the relationship C_t/C_0 versus time of the reaction and it was clearly observed that the reduction process follows the pseudo first order reaction kinetics. Furthermore, the appearance of an isosbestic point at 350 nm (Figure 10) is evident in one step reaction process. Most of the 4-NP converted to product 4-AP within 3 min of the reaction time and reaming conversion happened within 4–10 min of the progress of the reaction.



Figure 10. Monitoring the progress for the reduction of 4-NP to 4-AP using $0.8 \text{ mg} (6.5 \times 10^{-7} \text{ mol Ag})$ of Fe₃O₄@CS@MS@Ag as catalyst.



Figure 11. Relationship of C_t/C_0 versus time for the reduction of 4-NP to 4-AP using 0.8 mg (6.5×10^{-7} mol Ag) of Fe₃O₄@CS@MS@Ag as catalyst.

Recyclability and reusability of catalysts are two important parameters for designing sustainable and economically viable heterogeneous catalyst. Our silver nanoparticles deposited magnetic chitosan Fe₃O₄@CS@MS@Ag was investigated for repeated experiments through the reduction of 4-NP to 4-AP in presence of NaBH₄ solution. As our catalyst was cored with strong magnet Fe₃O₄, it was rapidly and conveniently collected from the reaction system with the help of an external magnet after each catalytic cycle. Figure 12 shows that the catalyst was successfully recycled and rescued for five times with efficiency of about 90%. Therefore, our prepared catalyst is a highly active catalyst for the reduction of 4-NP to 4-AP. That the activity of the catalyst gradually decreases might be due to the leaching of nanoparticles during washing of catalyst with water and ethanol.



Figure 12. Recycling efficiency of the catalyst Fe₃O₄@CS@MS@Ag for the reduction of 4-NP to 4-AP.

3. Materials and Methods

3.1. Reagents and Materials

Ferric chloride hexahydrate (FeCl₃·6H₂O; 98%), ferrous sulfate heptahydrate (FeSO₄·7H₂O; 99%), ammonium hydroxide (NH₄OH; 30–33%), ethanol (EtOH; 96%), chitosan (low molecular weight), sodium sulfate (Na₂SO₄; 99%), methyl salicylate (2-(HO)C₆H₄CO₂CH₃; 99%), silver nitrate (AgNO₃; 99.8%), sodium borohydride (NaBH₄; 99%) and 4-nitrophenol (C₆H₄OHNO₂; 99%) were purchased from Aldrich. All these chemicals were of analytical grade and used without any further purification. Double deionized water was used in all experimental procedures.

3.2. Synthesis of Magnetic Fe₃O₄

Magnetic Fe₃O₄ nanoparticles were synthesized with co-precipitation method adapting the literature procedure [66–68]. 6.0 g of FeCl₃·6H₂O and 4.1 g of FeSO₄·7H₂O were dissolved in 100.0 mL of deionized water, stirred and heated to 90 °C under nitrogen atmosphere for 20 min. 10.0 mL of 25% (m/v%) NH₄OH was added and the reaction mixture was stirred with heating for additional 30 min. Then, the reaction was stopped and cooled to room temperature. Finally, a black substance was collected by centrifugation and washed with excess amount of water until it was reached to neutral pH at 7.0.

3.3. Coating of Fe_3O_4 with Chitosan ($Fe_3O_4@CS$)

In a 500.0 mL round bottom flask, 1.0 g of CS was suspended in 100.0 mL acetic acid (2% w/v) under vigorous stirring using a mechanic stirrer for 1 h. Then, 500.0 mg of Fe₃O₄ and sodium sulfate

(20% w/v) were added to the CS slurry and was stirred for an extra hour. The magnetic CS was separated from the reaction mixture by an external permanent magnet and washed with ethanol (50.0 mL) and methanol (50.0 mL) for four times and finally dried under vacuum at 70 °C for 6 h.

3.4. Surface Modification of Magnetic Chitosan (Fe₃O₄@CS@MS)

The surface modification of magnetic CS was prepared by adding 1.5 g of Fe₃O₄@CS in 100.0 mL of ethanol following the literature procedure [69]. Then, the round bottom flask was charged with a condenser and mechanical stirrer following the addition of 6.5 mmol of methyl salicylate (MS) and refluxed for 24 h. The reaction mixture cooled down to room temperature and the surface modified magnetic chitosan (Fe₃O₄@CS@MS) was separated by external magnet and washed three times with ethanol (50.0 mL) and methanol (50.0 mL) to remove unreacted methyl salicylate. Finally, the product was dried in oven at 80 °C for 6 h.

3.5. Deposition of Silver Nanoparticles on Modified Magnetic Chitosan (Fe₃O₄@CS@MS@Ag)

AgNO₃ (4.3 mmol) was dissolved in 15.0 mL of ethanol and added to the suspension of Fe₃O₄@CS@MS (1.01 g in 20.0 mL of ethanol) and stirred at 60 °C for 18 h. The final product Fe₃O₄@CS@MS@Ag as brown solid materials were separated with external magnet and washed with ethanol (3×10.0 mL) to remove unreacted materials and finally dried in open air and oven at 80 °C for 4h. The final product was stored for further uses.

Overall synthetic procedure for the fabrication of the of the catalyst $Fe_3O_4@CS@MS@Ag$ has been depicted in Scheme 1.



Scheme 1. Synthetic procedure for the fabrication of the catalyst Fe₃O₄@CS@MS@Ag following the reaction conditions (**a**) solvent H₂O, heating 90 °C for 30 min, NH₃ (25%; m/v); (**b**) CH₃COOH (2%; w/v), Na₂SO₄ (20%; w/v), stirred at RT; (**c**) EtOH, methyl salicylate, reflux for 24 h and (**d**) EtOH, AgNO₃ (aq), stirred at 60 °C for 18 h.

3.6. Catalytic Reaction

The reduction of 4-NP was investigated by using $Fe_3O_4@CS$, $Fe_3O_4@CS@MS$ and $Fe_3O_4@CS@MS@Ag$ in the presence of reducing agent NaBH₄ in quartz cuvettes, and the reaction progress was monitored by UV-Vis spectroscopy. In optimal reaction condition, 1.0 mL of freshly prepared 1.0 mM NaBH₄ aqueous solution was added to 6.0 mL of (10.0 mg/L) 4-NP aqueous solution followed by the addition of 1.5 mg/0.8 mg of catalyst. Immediately after the addition of the catalyst, the reduction progress of reaction mixture was monitored by scanning UV-Vis spectra in the range 250–550 nm in every one-minute interval. The recyclability of the catalyst $Fe_3O_4@CS@MS@Ag$ was studied by separating the catalyst with external magnet and washed at least four times with ethanol and water and then used for next catalytic cycle.

3.7. Instrumentation

The thermogravimetric analysis (TGA) was performed using a thermo-balance instrument-type TGA-50, SHIMADZU, Japan. TGA analyses were performed in static air with a heating rate of 10 °C/min. FTIR spectra were recorded using an FTIR Bruker Platinum Spectrometer (Germany) fitted with an attenuated total reflection (ATR) unit, with single reflection geometry. X-ray diffraction (XRD) patterns were obtained using Bruker D8 Advance powder X-ray diffractometer (Germany) with CuK α radiation source. Maximum voltage: 40 kV and maximum Current: 40 mA. Scanning electron microscopy (SEM) images were recorded using TESCON VEGA3 (Brno-Kohoutovice, Czech Republic) XM variable pressure, accelerating voltage: max. 30k. For collecting SEM images, Sputter Coating System was used for preparing the sample. Quorum Technology Mini Sputter Coater, SC7620 (United Kingdom). Target: Gold/Palladium (80% & 20%); 57 mm $\emptyset \times 0.1$ mm thick, sputtering gas: argon, chamber pressure: 10^{-2} mbar, sputtering time: 120 s, plasma current: 18 mA, applied voltage: 1 kV, carbon fibre evaporation. Energy dispersive X-ray spectroscopy (EDX) was recorded using Oxford Instruments X-Max 50 EDS detector (LN2 free system). Resolution: 125 eV (United Kingdom). Ultraviolet-Visible (UV-Vis) absorbance was recorded using Spectrophotometer (UV-2510TS—Labomed, Los Angeles, CA, USA). The results were calculated from the averages of all sample readings and represented as Mean \pm SD. Calculations were made using Excel 2016.

4. Conclusions

In summary, we successfully coated magnetic Fe_3O_4 with chitosan (CS). This magnetic chitosan $Fe_3O_4@CS$ shows the catalytic efficiency for the reduction of 4-NP to 4-AP in the presence of NaBH₄ solution. To the best of our knowledge, this is the first example of using magnetic CS for the reduction of 4-NP. However, CS has great advantages in the modification of its surface by the reaction of amine functional group with safe and simple organic compound methyl salicylate to amide functional group which allows the support of metal interaction. We efficiently modified the surface of magnetic CS and deposited silver nanoparticles ($Fe_3O_4@CS@MS@Ag$), which reduced 4-NP to 4-AP four times more effectively than magnetic chitosan ($Fe_3O_4@CS$). Noticeably, this investigation represents the first example of the application of the functionalization of magnetic CS surface with methyl salicylate for preparing a magnetically separable silver-nanoparticles-based heterogeneous catalyst. Furthermore, the catalyst $Fe_3O_4@CS@MS@Ag$ was separated with external magnet from the reaction mixture and reused five times with almost 90% efficiency to the reduction of 4-NP to 4-AP. Finally, a practical and convenient heterogeneous catalyst has been developed from renewable resources and cheap materials.

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