

# Biosynthesized gold nanoparticles supported on magnetic chitosan matrix as catalyst for reduction of 4-nitrophenol

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## Graphical abstract



## Abstract

The design and environmentally-safe synthesis of magnetically recoverable solid-supported metal nanoparticles with remarkable stability and catalytic performance have significant industrial importance. In the present study, we have developed an inexpensive bioinspired approach for assembling gold nanoparticles (AuNPs) in magnetic chitosan network under green, mild and scalable condition. AuNPs were well loaded on the surface of the magnetic support due to the presence of hydroxyl (-OH) and amino (-NH<sub>2</sub>) groups in chitosan molecules that provided the driving force for the complexation reaction with the Au(III) ions. Reduction of the Au(III) to Au(0) was achieved by using *Melicope ptelefolia* aqueous leaf extract. The synthesized magnetic chitosan supported biosynthesized Au nanocatalyst was characterized using Fourier Transform Infrared (FT-IR), Carbon, Hydrogen and Nitrogen (CHN), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and Atomic Absorption Spectroscopy (AAS) analyses. FTIR spectrum of magnetic chitosan showed peaks at 1570 cm<sup>-1</sup>, which indicate for N-H bending vibration and at 577 cm<sup>-1</sup> which designates the Fe-O bond. CHN analytical data further supported the coating of chitosan onto the magnetite. TEM analysis showed an amorphous layer around the magnetite core, proving the coating of chitosan on the magnetite surface and the average particle size of AuNPs calculated was 7.34 ± 2.19 nm. XRD analysis showed six characteristics peaks for magnetite, corresponding to lattice planes (220), (311), (400), (422), (511) and (440) in both the magnetite and magnetic chitosan samples (JCPDS file, PDF No. 65-3107). Meanwhile, XRD analysis of catalyst showed characteristic peaks of AuNPs at 2θ (38.21°, 44.38°, 62.2°, 77.32° and 80.76°), which correspond to (111), (200), (220), (311) and (222) lattice planes (JCPDS file, PDF No.04-0784). AAS analysis showed the loading of AuNPs as 5.4%. The rate constant achieved for the reduction of 4-nitrophenol to 4-aminophenol in the presence of hydrazine hydrate using 10 mg of catalyst was 0.0046 s<sup>-1</sup>. The magnetic chitosan supported AuNPs is effective as catalyst for the reduction of 4-nitrophenol.

**Keywords:** [Magnetic chitosan, Gold nanoparticles, Biosynthesis, *Melicope ptelefolia*, 4-nitrophenol]

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## INTRODUCTION

Nanomaterials are receiving a considerable amount of attention from different fields of science because of their unique properties in which they differ from those of bulk materials. Among various metal nanoparticles, gold exhibits a significant potential of application in different areas like medical science, catalysis and drug delivery [1].

The most common method used for the synthesis of Au is the chemical reduction of Au(III) ions solution by using chemical reducing agent such as sodium borohydride (NaBH<sub>4</sub>) and citrate but such reducing agents are toxic and hazardous [2]. Due to these problems, there is a need to develop environmental friendly process for gold nanoparticles (AuNPs) production that does not involve toxic chemicals in the synthesis process. Among different biological systems employed for AuNPs synthesis, plants extract has several advantages as compared to fungi and bacteria, as it is easily available, non-toxic and eliminate the use of complicated techniques for cell cultures [3].

*Melicope ptelefolia* is a plant species belonging to the family Rutaceae. It is a medicinal and widely grown plant in Malaysia and is locally known as 'Tenggek Burung'. It is a popular salad and consumed raw by the Malay community. Leaves of this plant have its own benefits such as to revitalize the body and to release tension. In addition, its leaves have been reported to help in controlling and reducing high blood pressure and *diabetes mellitus* if consumed regularly [4]. This plant can be used as a reducing agent in this research due to the presence of biomolecules in its leaf extract. These biomolecules are responsible to reduce metal ions to form metal atom [5]. As in [6], *Hygrophila spinosa* aqueous leaf extract has been used as reducing agent for HAuCl<sub>4</sub> to obtain gold nanoparticles in order to apply in pharmaceutical industry.

Chitosan (CS), a derivative biopolymer obtained from the deacetylation of chitin, occurs naturally and abundantly from the exoskeletons of insects, crustaceans' shells and fungi cellular walls. Chitosan is one of the bioabsorbable and non-toxic polymers, which is processed in different biofunctionalities. Recently, chitosan, which is used as an adsorbent, is attracting a lot of attention due to its hydroxyl

and amino functional groups that show high potential for adsorption of metal ions [7].

Magnetic separation technique has some advantages, such as high efficiency and cost-effectiveness. In this regard, magnetite ( $\text{Fe}_3\text{O}_4$ ) has been widely used as magnetic material due to its excellent magnetic properties, chemical stability and biocompatibility. Thus, by using  $\text{Fe}_3\text{O}_4$  as the main support, the catalyst can be easily separated from the reaction media with the aid of an external magnet, leading to fast and efficient recovery route [8].

4-nitrophenol is a common organic waste water pollutant which is widely used in the preparation of pesticides, explosives and pharmaceutical industries. This compound poses significant health risk due to its carcinogenic activities. On the other hand, 4-aminophenol is an important intermediate for the production of pharmaceuticals substances, photographic materials and rubber materials [9].

In the present study, we have developed an inexpensive bioinspired approach for decorating small gold nanoparticles (AuNPs) in a magnetic chitosan network using *Melicope ptelefolia* leaf extract under green, mild and scalable condition. Preparation of magnetic chitosan matrix is significant due to prevent agglomeration between metal-metal atoms after being reduced. Structural features as well as catalytic performance of the prepared hybrid nanocomposite have been investigated in the reduction of 4-nitrophenol to 4-aminophenol.

## EXPERIMENTAL

### Materials

All glasswares were washed thoroughly with deionised water and dried overnight in the oven before being used for experiment. Deionised water was used throughout this study. Commercial grade solvents were distilled before being used. All chemicals were obtained commercially from Sigma-Aldrich and were used as received without further purifications. *Melicope ptelefolia* (Tenggek Burung) leaves were purchased from a local market in Johor Bahru.

### Synthesis of magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles

$\text{Fe}_3\text{O}_4$  was prepared according to literature method with some modifications [8]. A mixture of iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) (2.7 g, 10 mmol) and iron(II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) (1.0 g, 5 mmol) was dissolved in deionised water (130 mL) under  $\text{N}_2$  flow. Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) (11 mL, 28% v/v) was added under rapid mechanical stirring (700 rpm). The resultant solution was heated to 60 °C and stirred for 1 h under  $\text{N}_2$  flow. The reaction mixture was let to cool at room temperature before washing it using deionised water twice. The product formed was collected by using external magnet and redispersed in trisodium citrate (200 mL, 0.3 M). Then, the solution was further heated at 80 °C for 1 hr. The precipitate formed ( $\text{Fe}_3\text{O}_4$ ) was collected by using external magnet and washed with acetone. The product was kept in a desiccator for further reaction.

### Synthesis of magnetic chitosan ( $\text{Fe}_3\text{O}_4$ -CS) nanoparticles

Magnetic chitosan ( $\text{Fe}_3\text{O}_4$ -CS) was prepared following the method as reported with some modifications [9].  $\text{Fe}_3\text{O}_4$  (0.5 g) was dispersed in deionised water (150 mL) while chitosan (75%-85% deacetylated) flakes (0.25 g) were dissolved separately in acetic acid (70 mL, 2 wt%) with continuous stirring. Both solutions were mixed under vigorous stirring for 1 h. Then, the resultant solution was transferred quickly into a beaker. The product obtained was collected by using external magnet, washed with acetone and kept in a desiccator for further use.

### Preparation of *Melicope ptelefolia* leaf extracts solution

Fresh *Melicope ptelefolia* leaves were washed thoroughly with deionised water to remove any dust or impurities and dried at room temperature for 1-2 weeks. The dried leaves were ground into powder using an electrical blender. *Melicope ptelefolia* leaf powder (4 g) was extracted with deionised water (200 mL) in a Soxhlet apparatus for 8 h. The resultant leaf extract was transferred into a porcelain crucible and slowly heated to remove the solvent. The dried, powdered solid obtained was kept in a vacuum desiccator for further use. A 10 % w/v

leaf extract solution was prepared by dissolving 10 mg of dried powder in 100 mL deionised water.

### Immobilization of Au(III) ions onto $\text{Fe}_3\text{O}_4$ -CS nanoparticles

Tetrachloroauric(III) acid ( $\text{HAuCl}_4$ ) (0.3 mM, 25 mL) was mixed with  $\text{Fe}_3\text{O}_4$ -CS (30 mg) in a centrifuge tube. The mixture was shaken mechanically (480 rpm) for about 24 h at room temperature. The product ( $\text{Fe}_3\text{O}_4$ -CS-Au(III)) was collected by an external magnet, washed with deionised water and allowed to dry. The separated solution was analyzed by Atomic Absorption Spectroscopy (AAS).

### Bioreduction of immobilized Au(III) to Au(0) nanoparticles using *Melicope ptelefolia* leaf extract

$\text{Fe}_3\text{O}_4$ -CS-Au(III) obtained from the previous reaction was directly treated with *Melicope ptelefolia* leaf extract solution (12 mL, 10% w/v). The mixture was shaken for 2 h at room temperature. The final product ( $\text{Fe}_3\text{O}_4$ -CS-AuNPs) was collected using an external magnet, washed with deionised water and dried in the desiccator for further use.

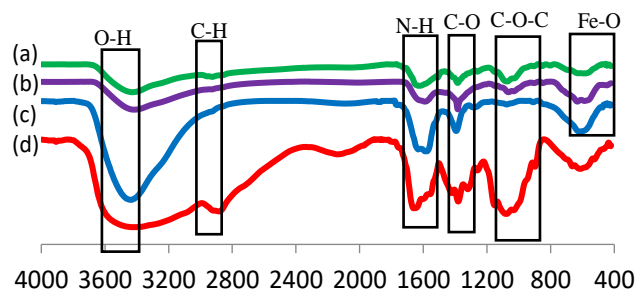
### Catalytic reduction of 4-nitrophenol to 4-aminophenol

Catalytic reduction of 4-nitrophenol was performed following literature method [10]. Hydrazine hydrate (0.375 mM, 1.6 mL) was added into 4-nitrophenol (0.125 mM, 1.6 mL). Then, the  $\text{Fe}_3\text{O}_4$ -CS-AuNPs (10 mg) catalyst was added into the reaction mixture with stirring. The UV-vis absorption spectrum of the reaction mixture was recorded with time to monitor the change in absorption intensity of the reaction mixture in the scanning range of 200-500 nm.

## RESULTS AND DISCUSSION

$\text{Fe}_3\text{O}_4$ -CS-AuNPs was synthesised via a simple and inexpensive method by the immobilisation of AuNPs on the magnetic chitosan support using *Melicope ptelefolia* leaf extract in this work. The leaf extract acted as a reducing and stabilizing agent in the preparation of AuNPs on the surface of the magnetic chitosan. The presence of biomolecules such as *p*-*O*-geranylcoumaric acid and 2,4,6-trihydroxy-3-farnesylgeranylacetophenone in the *Melicope ptelefolia* leaf extract are believed to be responsible in the reduction of Au(III) to Au(0) [11].

FTIR spectroscopic analysis was carried out to identify functional groups presented in CS,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ -CS and  $\text{Fe}_3\text{O}_4$ -CS-AuNPs. The FTIR spectra of the samples were as presented in Figure 1.



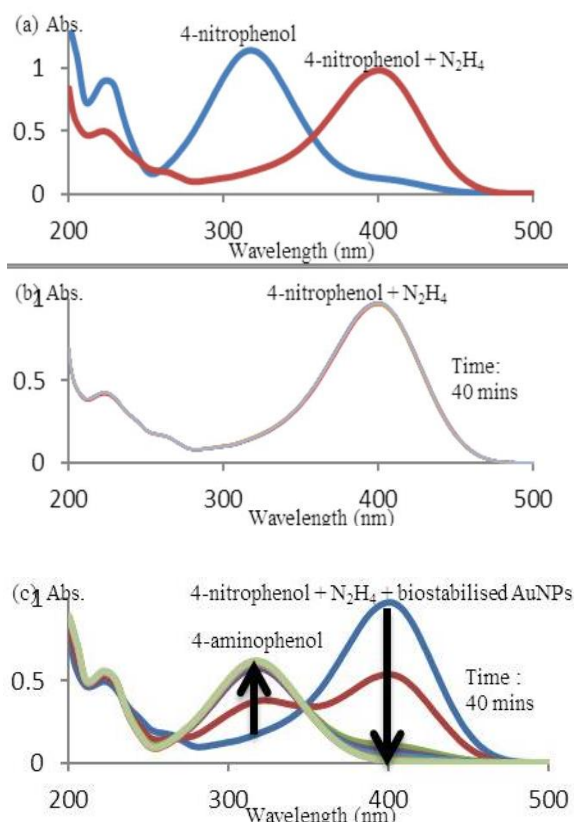
**Figure 1** FTIR absorption spectra of (a)  $\text{Fe}_3\text{O}_4$ -CS, (b)  $\text{Fe}_3\text{O}_4$ -CS-AuNPs, (c)  $\text{Fe}_3\text{O}_4$  and (d) CS.

Absorption bands at 3401  $\text{cm}^{-1}$  and 3370  $\text{cm}^{-1}$  observed in the IR spectrum of magnetite and magnetic chitosan are indicative of OH group. The presence of an OH band in the magnetite spectrum may be due to trace of water during its preparation. The appearance of characteristic bands at 591  $\text{cm}^{-1}$  and 580  $\text{cm}^{-1}$  in the IR spectrum of magnetite and magnetic chitosan is due to Fe-O bond. The FTIR spectrum of chitosan was characterized by the following absorption bands; the (NH) of backbone polymer arose around 1650  $\text{cm}^{-1}$ , (C-O) of primary alcoholic group at 1380  $\text{cm}^{-1}$ , and the (C-H) at 2893  $\text{cm}^{-1}$ . The shift of the Fe-O stretching frequency from 591  $\text{cm}^{-1}$  in magnetite to 580  $\text{cm}^{-1}$  in the magnetic chitosan and of the N-H bending vibration from 1650  $\text{cm}^{-1}$  to 1612  $\text{cm}^{-1}$  strongly suggested the binding of Fe to



After the addition of hydrazine hydrate, a red shift was observed with the maximum absorption at 398 nm, indicating the formation of 4-nitrophenolate ions. After the addition of the Fe<sub>3</sub>O<sub>4</sub>-CS-AuNPs catalyst (Figure 5(c)), a gradual decrease in the absorbance for the 4-nitrophenolate ions peak at 398 nm was observed along with gradual increase of a new absorbance at 313 nm, indicating the formation of 4-aminophenol. Complete reduction of 4-nitrophenol occurred within 40 min.

The reduction of 4-nitrophenol to 4-aminophenol was also monitored in the absence of Fe<sub>3</sub>O<sub>4</sub>-CS-AuNPs catalyst. As can be seen in Figure 5(b), the peak at 398 nm showed almost no change in intensity after 40 min of reaction time, hence suggesting that no significant reduction has occurred without the presence of biostabilised Fe<sub>3</sub>O<sub>4</sub>-CS-AuNPs catalyst.

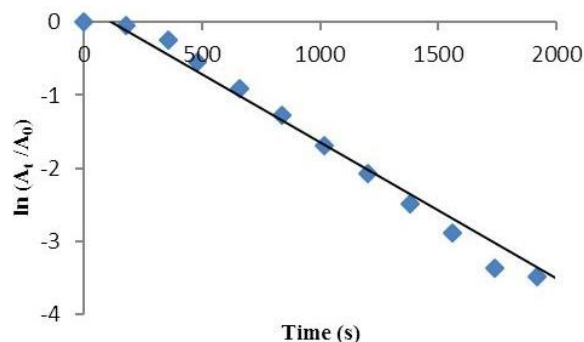


**Figure 5** (a) UV-visible spectra of 4-nitrophenol and after the addition of N<sub>2</sub>H<sub>4</sub> (b) UV-visible spectrum of (4-nitrophenol + N<sub>2</sub>H<sub>4</sub>) in 40 minutes time of reaction (c) UV-visible spectra of (4-nitrophenol + N<sub>2</sub>H<sub>4</sub> + biostabilised AuNPs) in 40 minutes time of reaction.

The catalytic reaction was studied in excess of N<sub>2</sub>H<sub>4</sub> concentration as compared to 4-nitrophenol. Thus, the concentration of N<sub>2</sub>H<sub>4</sub> was considered as constant and the reaction rate constant ( $k_a$ ) of the reduction was only depended on the 4-nitrophenol concentration. Hence, the reaction was assumed to follow the pseudo first-order kinetics and calculated by using the following kinetic equation:

$$-k_a t = \ln(C_t/C_0) = \ln(A_t/A_0) \quad (1)$$

where  $C_t$  and  $A_t$  are the concentration and absorption of 4-nitrophenol at time ( $t$ ) while  $C_0$  and  $A_0$  are the concentration and absorption of 4-nitrophenol at the initial time of the reaction [15]. The rate constant ( $k_a$ ) was calculated from the slope of the plot of  $\ln(A_t/A_0)$  versus the reaction time ( $t$ ) as displayed in Figure 6. The rate constant obtained from the reaction using 10 mg AuNPs and 5.4% Au loading of Fe<sub>3</sub>O<sub>4</sub>-CS-AuNPs was 0.0046 s<sup>-1</sup>.



**Figure 6** Plot of  $\ln(A_t/A_0)$  versus time ( $t$ ) for the reduction of 4-nitrophenol by using 10 mg AuNPs and 5.4% Au loading of Fe<sub>3</sub>O<sub>4</sub>-CS-AuNPs.

## CONCLUSION

In summary, biostabilised AuNPs have been successfully supported onto the Fe<sub>3</sub>O<sub>4</sub>-CS support. The use of Fe<sub>3</sub>O<sub>4</sub>-CS as catalyst support provides a good dispersity of the AuNPs catalyst with less agglomeration. The biosynthesised AuNPs are mostly spherical with an average size of 7.3 nm. The magnetic chitosan supported biostabilised AuNPs showed good catalytic activity in the reduction of 4-nitrophenol to 4-aminophenol in the presence of N<sub>2</sub>H<sub>4</sub> where the reduction was complete in 40 minutes with the rate of reaction of 0.0046 s<sup>-1</sup>. The synthesised magnetic AuNPs catalyst can also be tested in the other organic transformations such catalytic oxidation of benzylic and allylic alcohols, reduction of nitroaromatics and epoxidations.

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