

Biogenic Gold and Silver Nanoparticles in the Degradation of Aromatic Nitrocompounds

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Abstract— We report for the first time the use of gold and silver nanoparticles synthesized at room temperature using fruit juice of *Punicagranatum* as nanocatalysts in the degradation of aromatic nitrocompounds. The protocol using the fruit extract of pomegranate is beneficial over other methods as it does not necessitate any specific environment and is easy to scale up the production of nanoparticles in a cost effective and less toxic manner. The formation, morphology and crystalline structure of the synthesized nanoparticles are determined using UV-visible spectroscopy, XRD and TEM. An attempt to reveal the partial role of phenolic hydroxyls and proteins in the reduction/stabilization of Au^{3+} and Ag^+ is done through FTIR analysis. The potential catalytic activity of synthesized nanoparticles in the degradation of nitrocompounds has been elucidated using the model degradation of 4-nitrophenol using sodium borohydride

Keywords—Gold nanoparticles, silver nanoparticles, nanocatalyst, rate constant

I. INTRODUCTION (HEADING 1)

Nitroaromatic compounds are used in the production of dyes, explosives and pesticides. Waste water treatment containing these pollutants is a serious concern as they are chemically very stable. Among these nitrocompounds, nitrophenols are the most carcinogenic and mutagenic posing serious issue to public health. Several traditional water treatment methods like chemical precipitation, ion exchange adsorption, filtration and membrane systems, remain slow and non-destructive. Nanocatalysis, metal nanoparticles (Nps) used as catalysts in chemical reactions, gain importance in this context. In this paper we have presented the potential catalytic activity of gold and silver Nps synthesized using pomegranate fruit juice. The use of biogenic material in the production of Nps is advantageous over other methods as it is cost effective and easy to scale up [1-3].

II. MATERIALS AND METHODS

A. Synthesis of gold and silver Nps

Chloroauric acid (HAuCl_4) and silver nitrate (AgNO_3) purchased from Sigma Aldrich are used as the source solutions. Ripe pomegranate seeds are crushed to obtain 1 ml of fresh concentrated juice. The juice is then made up to

50 mL using de-ionised (DI) water and filtered to get EG. 1 mL of the juice is made up to 25 mL using DI water and filtered to get the filtrate ES. The filtrate (EG) is used to reduce the bulk Au^{3+} at 2.9×10^{-4} M where as the filtrate (ES) of the juice is used for the reduction of bulk Ag^+ at 1.17×10^{-3} M.

To about 20 mL of HAuCl_4 solution 1mL of EG is mixed and vigorously stirred for 2 min to obtain (g_1). The effect of varied quantities of extract on the reduction of Au ions is investigated by repeating the experiment using 3, 5, 10, 15 and 20 mL EG to get colloids g_2, g_3, g_4, g_5, g_6 respectively. In order to synthesize silver colloids $s_1, s_2, s_3, s_4, s_5, s_6$ the filtrate ES is mixed with the AgNO_3 solution following the same experimental procedure.

B. Catalytic activity

The reduction of 4-NP using sodium borohydride is chosen as the model degradation reaction. 1mL of 5×10^{-3} M 4-NP is mixed with 1 mL of 0.25 M freshly prepared SB. The solution is continuously stirred for 10 minutes which is made up to 25 mL using de-ionized water. The prepared mixture is continuously stirred for another 5 minutes in presence of gold/silver Nps. It is observed that the bright yellow color of the solution rapidly decreases with time. The reduction rate of the reaction is determined by monitoring the decrease of absorbance at 400nm using UV-vis spectrometer.

C. Instrumentation

The optical properties of the synthesized particles are recorded using PerkinElmer Lambda-35 UV-Visible spectrophotometer. The morphology of the synthesized particles is analyzed using Tecnai G² 30 transmission electron microscopic images. The XRD patterns are obtained using XPERT-PRO diffractometer to elucidate the crystallographic structure of the as prepared particles. The catalytic potential of synthesized metal Nps in the chemical degradation of organic pollutants is investigated using PerkinElmer Lambda-35 UV-Visible spectrophotometer.

III. RESULTS AND DISCUSSION

The intense color in the visible range for colloidal solution of gold and silver Nps can be attributed to Surface Plasmon Resonance (SPR) [4, 5]. The appearance of violet color on addition of aqueous pg fruit extract to HAuCl_4 solution, within a few minutes indicates the reduction of Au^{3+} . Similar investigation on AgNO_3 solution using the

fruit extract ES showed a color change from watery to yellowish brown suggesting the formation of SNPs.

A. UV-vis spectroscopic studies

Fig 1 shows the UV- vis spectra of gold nanoparticle formation using different quantities of EG extract. The optical change in color from violet to reddish pink and then again to violet for increasing quantities of extract corresponds to the shift in SPR band of different sized Nps.

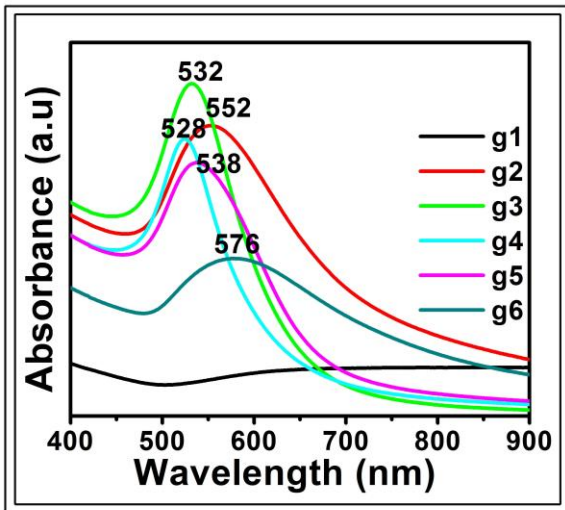


Fig 1. UV-vis spectra of gold nanoparticles

The relatively broad SPR band centred at 552nm observed for g₂ indicate large Nps formed due to lack of biomolecules required for capping and efficient stabilization at lower quantity of extract. The sharper SPR bands observed for g₃ (532nm) and g₄ (528nm) colloids indicate the formation of spherical Nps of rather smaller size. The broadening and red shift of absorbance band for colloids prepared using higher quantities of extract (g₅& g₆) can be attributed to the augmentation of nanoparticle aggregates.

Fig 2 shows the UV- visible absorbance spectra for silver nanoparticle formation using various quantities of ES extract. A consistent increase in the absorbance intensity with increase in the volume of extract is observed which corresponds to the enhanced formation of Nps. Broad peaks indicate the polydispersity of particles [6] which is further confirmed by TEM analysis.

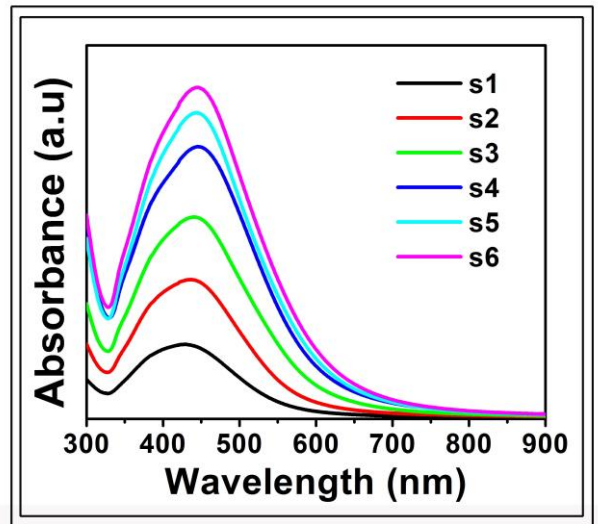


Fig 2. UV-vis spectra of silver nanoparticles

B. TEM analysis

The uniform and monodispersed morphology of g₄ colloid and polydispersed distribution of s₆ colloid as anticipated in UV-vis spectrum analysis is confirmed using TEM images of different magnifications (Figs.3& 4).The average particle diameter of GNPs is 18 nm and the particle size distribution is shown using histogram in the inset of Fig (3a)

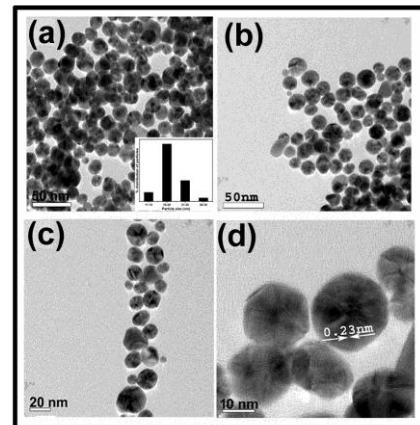


Fig. 3. TEM images of gold nanoparticles at different magnifications

The mean particle size calculated for almost spherical SNPs particles is 36 nm. The fringe spacing measured from the high resolution images for g₄ and s₆ colloids are shown in Fig (3d & 4d). This reveals that the growth preferentially occurs in the direction of (111) plane [7].

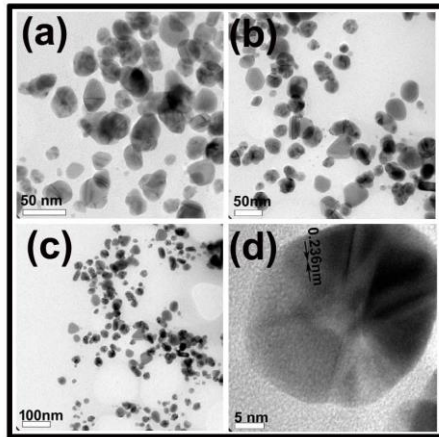


Fig. 3. TEM images of gold nanoparticles at different magnifications

C. XRD study

Fig 5(a) and (b) describe the crystalline nature of the as synthesized gold and silver Nps. The observed diffraction peaks (JCPDS no: 04-0784 & 04-0783) propose face centered cubic (fcc) structure of as-synthesized Au and Ag nanoparticle crystallites.

The preferential growth direction of prepared gold and silver nanoparticle is established by the most intense Bragg reflection from the (111) plane of fcc structure, in agreement with the HRTEM results.

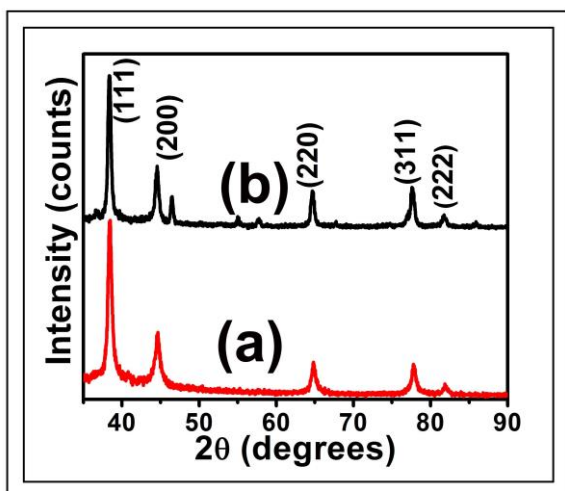


Fig. 5. XRD pattern of nanoparticles

D. FTIR analysis

The observed bands at 3412cm^{-1} , 2360cm^{-1} , 1630cm^{-1} and 1080cm^{-1} in the spectrum (Fig 6) correspond to the O-H stretching vibration of phenolic hydroxyls [8], stretching vibrations of NH_2^+ and NH_3^+ in protein/peptide bonds [5], carbonyl stretching in proteins [8] and C-OH vibrations of proteins [9] present in pg extract.

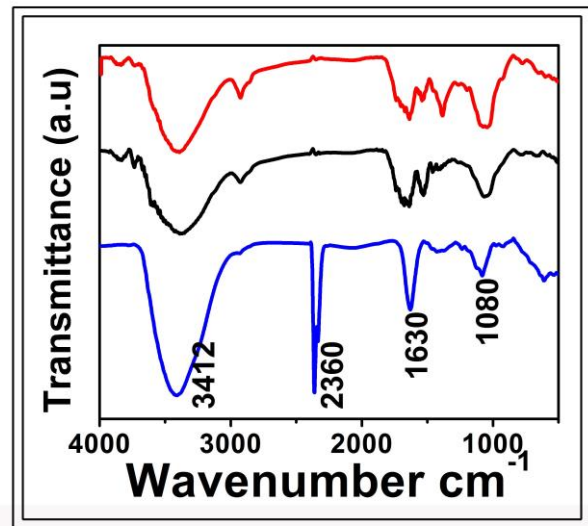


Fig. 6. FTIR spectra

The relative decrease in the intensity of phenolic hydroxyl stretching band in the spectrum of the extract functionalized gold and silver NPs (FNPs) can be attributed to the partial involvement of phenolic hydroxyls in the reduction/stabilization mechanism. Phenolic compounds mediate redox reactions by donating electrons and form quinones. Similar suggestions regarding the biosynthesis of metal Nps have been reported [5, 10]. The almost complete absence of the NH_2^+ and NH_3^+ stretching vibrations in the FTIR spectrum of FNPs can be related with the breakage of amino acid residues of proteins during the reaction (Fig 6 b & c). Previous comparable reports can be referred to elucidate the role of proteins in the reduction of metal NPs [11, 8].

E. Degradation of 4-nitrophenol

The synthesized gold and silver Nps are used as catalysts in the reduction of 4-NP in excess of SB. The color of the solution changed from light yellow to dark yellow due to the formation of 4-nitrophenolate ion on addition of SB and correspondingly the absorbance maximum of aqueous 4-NP at 317nm red shifts to 400nm. The nitro group ($-\text{NO}_2$) containing aromatic compounds are found to be inert to reduction using SB [12]. But, after the incorporation of gold and silver Nps to the solution the reduction can be visualized by the fading of greenish yellow color of the 4-nitrophenolate ions with time and can be spectrometrically monitored by the decrease of absorbance intensity at 400nm and increase of band at 290nm assigned to the formation of 4-aminophenol. The typical absorption spectrum showing reduction of 4-NP in presence of gold and silver NPs is shown in Fig. 7. It is verified experimentally the reactions do not proceed within this period in the absence of MNPs or in the presence of pg extract alone.

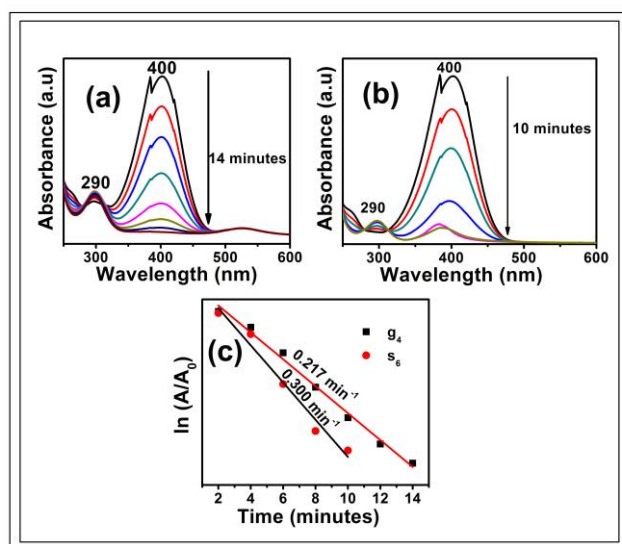


Fig.7. Catalytic degradation of 4-nitrophenol

The kinetic data of all the above degradation reactions is fitted in the pseudo first order rate equation [13] as the reaction can be considered independent of the concentration of sodium borohydride and the slope of the linear graph gives the rate constant for each of the reaction.

IV. CONCLUSIONS

The article presents the potential use of room temperature synthesized gold and silver NPs in the degradation of 4-nitrophenol. UV-vis spectroscopy and TEM analysis reveal the moderate size control obtained over the GNPs using varying quantities of extract and the polydispersed nature of synthesized SNPs. The rate constants of the reaction are established through pseudo first order linear data fit. Catalytically active gold and silver Nps with controllable size can be extended to the removal of other hazardous dyes.

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