A COMPARATIVE ASSESSMENT OF Au NANOPARTICLES SYNTHESIZED VIA GREENER PATHWAYS USING NATURAL HYDROCOLLOIDS

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Abstract

This paper presents the synthesis and stabilization of Gold nanoparticles (Au NPs) using five different hydrocolloids [Tragacanth (Tg), Karaya (Kg), Guar (Gg), Carrageenan (Cg), and Xanthan (Xg)] via greener pathways. The particle size, morphology, stabilization characteristics and catalytic efficiencies of the synthesized Au NPs were analyzed using spectroscopic and microscopic techniques. The Gg stabilized Au NPs was extremely stable (particle size 8.0 ± 1 nm) at 4 °C for a period up to three months as compared to other Au NPs synthesized and stabilized via other polysaccharides. However, zeta potential and UV-vis analysis of Au NPs produced by Tg, Kg, Gg, Cg and Xg did not show much variation in magnitudes during the tested periods (0 to 90 days). The catalytic performance of hydrocolloid stabilized Au NPs were also evaluated and compared their kinetics reaction rates, and stability for the degradation of 4-Nitrophenol (p-NP) to 4-Amino phenol (p-AP). The reduction of p-NP follows the pseudo-first order. The highest kinetic rate value is found to be 10.6 x 10^{-3} s^{-1} for Au Guar composites (5.1 x 10^{-6} mM).

Keywords: Hydrocolloids, Au NP, green synthesis, catalysis

1. INTRODUCTION

Synthesized metal nanoparticles have received considerable interest due to their unique chemical, physical, optical, electrical, and catalytic properties which totally differ from the bulk materials. Among the various nanomaterials, gold nanoparticles (Au NPs) are the most widespread materials in many applications especially in the fields of physics, chemistry, optics, catalysis, biology, electronics, and material science [1-5]. This is due to their stability, less toxicity, and biocompatibility [6]. There are several chemical agents used for the reduction of electropositive (Au^{+3}) to neutral atoms. The first reducing agent to prepare Au NPs was phosphorus that was used by Michael Faradey, after that sodium borohydride [7], citrate [8,9], hydrogen peroxide [10,11], and other organic compounds such as ethylene glycol [12]. However, these chemicals are highly reactive, and may be associated with environmental toxicity or biological risks.

In order to overcome these concerns, researchers agree to embrace the principle of green chemistry to achieve the safest possible future for advancing nanotechnology in sustainable world [13]. Green nanotechnology aims to eliminate or reduce the harmful polluting substances in the synthesis of nanomaterials or to utilize the produced nanomaterials in eliminating or reducing these pollutants. Recently there are several studies of green synthesis for Au NPs by using harmless alternative biocompatible molecules. There are many studies reported the efficient use of hydrocolloids (starch, chitosan, xanthan, cellulose, carrageenan, and tree gums) as reducing and stablizing agents [14,15].

4 Nitro-phenol (p-NP) is one of the hazardous and toxic pollutants [15] that are widely used in industry. It is known to be highly soluble and stable in water, hence traditional methods for water purification are not effective. There are many techniques that were developed for the removal of p-NP and include: microbial degradation, microwave-assisted catalytic oxidation, electron fenton method, electrochemical treatment, and electrocoagulation [14,16,17]. However, these techniques are energy-consuming and involve the use of organic solvents [18]. Therefore, it is important to employ aqueous phase degradation of p-NP under mild conditions by using catalytic reduction methods. Au NPs are known for their excellent catalytic behaviour, and

the catalytic behaviour of nanocrystals was generally recognised as dependant on their exposed facets and their structure [18-21].

In this study, we provide a green synthesis method for Au NPs and an assessment for the NPs produced by five different hydrocolloids. This assessment is based on the size, surface resonance plasmon band, and stability of these nanoparticles in aqueous solutions for nearly 3 months. These hydrocolloids are cost effective, non-toxic, and abundant in nature, which supports their sustainability. The hydrocolloids used in this study come from different resources such as: karaya (Kg) and tragacanth (Tg) from plant exudates, guar (Gg) from seed gums, xanthan (Xg) from microbial exudates, and carrageenan (Cg) from seaweed polysaccharides. In this study we also fulfilled the concept of green nanotechnology by providing a green synthesis of Au NPs and using these nanoparticles in the degradation of 4-Nitrophenol (p-NP) to 4-Amino phenol (p-AP). We have characterized these gold nanoparticles by centrifugal particle sedimentation (CPS), transmission electron microscopy (TEM), ultraviolent-visible (UV-Vis) spectroscopy, and Zetasizer.

2. MATERIALS AND METHODS

2.1. Materials

Guar, Xanthan, Karaya, Tragacanth, and Carrageenan and have been used without purification. Chloroauric acid ($HAuCl_4$), sodium hydroxide (NaOH) for adjusting pH, 4-nitrophenol, and Sodium borohydride were purchased from Sigma-Aldrich.

2.2. Synthesis of gold nanoparticles

5 ml of 0.1 % chloroauric acid ($H[AuCl_4]$) were added to 2 ml of 0.1 % hydrocolloids solutions and 3 ml of distilled water. The pH of the reactions were maintained at 8 by 0.1 % NaOH and the mixture was stirred at 70 °C for 15 minutes or until a colour change (the colour changed to wine red in the case of Gaur, and to purple with other hydrocolloids).

2.3. Characterization of Au NPs

UV-Vis spectroscopy (cintra 202 UV-VIS spectrophotometer, GBC, Australia), centrifugal particle sedimentation (DC24000UHR, CPS Instruments Inc., USA), zetasizer, ATR-FTIR spectrometry, transmission electron microscope (TEM), and selected area electron diffraction (SAED).

2.4. Catalytic properties of gold nanoparticles in reducing 4-nitro-phenols

For a catalytic reduction of 4-nitrophenol (p-NP), 23.4 µl of p-NP (3 mM), and 340 µl of sodium borohydride (63 mM) were added to a quartz cuvette containing 615 µl of deionized water. Thereafter, 21.6 µl of Au NPs (8×10^{-4}mM) were added to start the reaction. The intensity of the absorption peak at 400 nm was used to monitor the reduction of the 4-nitrophenol (p-NP) to 4-aminophenol (p-AP) in the UV-vis spectrograms.

3. RESULTS AND DISCUSSION

All the five aforementioned biopolymers have been used for the synthesis of Au NPs by chemical reduction. The formation of nanoparticles was visually observed by changing the colour of the solution from the colourless, at the beginning, to the wine red with guar bio-template or the purple with other hydrocolloids.

3.1. Stability of NPs

In order to study the NPs stability for a long term, UV-vis spectral were analyzed and the zeta potential of the solutions were recorded over time. The long term stability of the produced nanoparticles are also confirmed through the steady data of surface plasmon resonance (SPR) and zeta potential over time. **Figure 1** shows UV -Vis spectra for Au NPs colloids as a function of the ageing time.

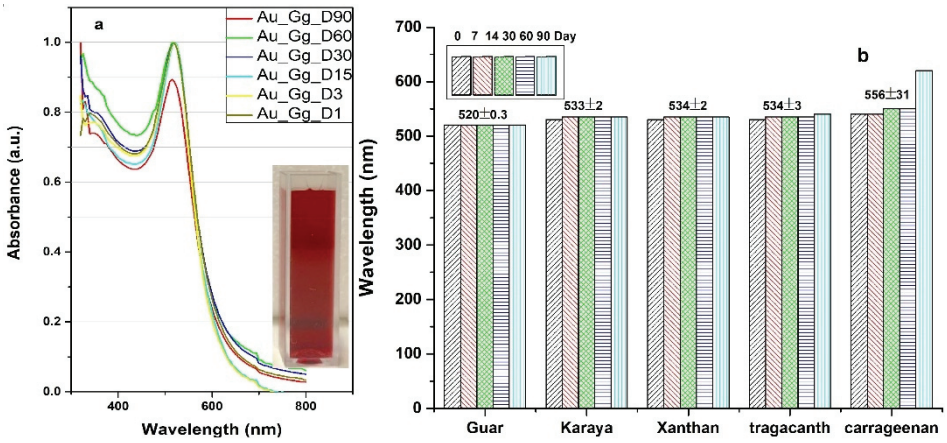

Figure 1 UV spectra of Au NP synthesized by Gg (a), all hydrocolloids (b)

Figure 1a shows Au NPs synthesized by guar where SPR band occurs at 520 ± 0.3 nm, without any shift in the peak for 90 days, which indicates the stability of gold nanoparticles synthesized by guar. The other hydrocolloids experience relatively small red shift over time as shown in **Figure 1b**. For more study about stability, the surface charge was measured at different time intervals. The values for zeta potential are shown in **Figure 2**.

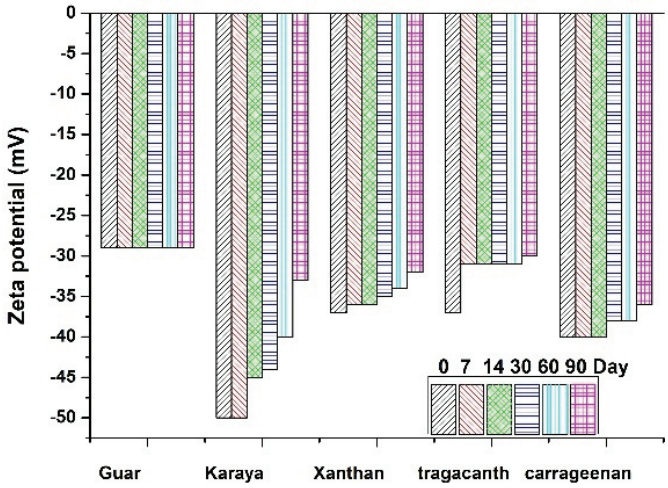

Figure 2 Zeta potential values for Au NPs composites at different time interval (0 to 90 days)

The surface charge for higher stable nanoparticles should be outside the range of -25 mV to 25 mV [22], [23], and the five used hydrocolloids were measured outside this range. Moreover, their values are quite stable even after 90 days, which indicates a good dispersion of the nanoparticles. For Au NPs guar composites, zeta potential values remained steady at -29 mV over the entire time of study (90 days). For other NPs composites, zeta potential were larger than -30 mV, which is high enough to cause repulsive forces between the nanoparticles, as long as the distances between these nanoparticles are not enough to overcome the Van der Waals attraction.

The nanoparticle have been analysed by CPS, as shown in **Figure 3**. The smallest particles size is 8 ± 1 nm for gold nanoparticles synthesized by guar. This was visually clear from its intense red colour shown in **Figure 1a** [24], and this value remains constant in agreement with both records from UV-Vis and zeta potential. For xanthan Au NPs, the measured diameter is 9 ± 1 nm. The largest size was for nanoparticles synthesized by carrageenan with a diameter of 17 ± 3 nm that tends to increase to 25 ± 4 nm at the end of the study (i.e. after 90 days).

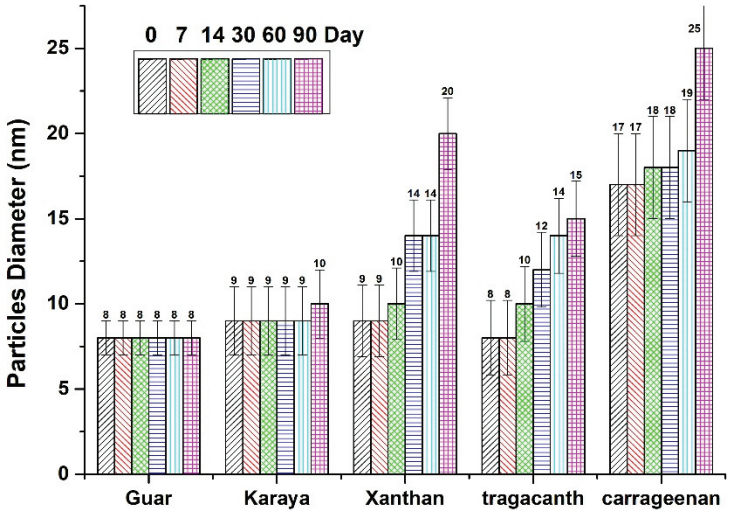

Figure 3 Particles size distribution by CPS at different time intervals.

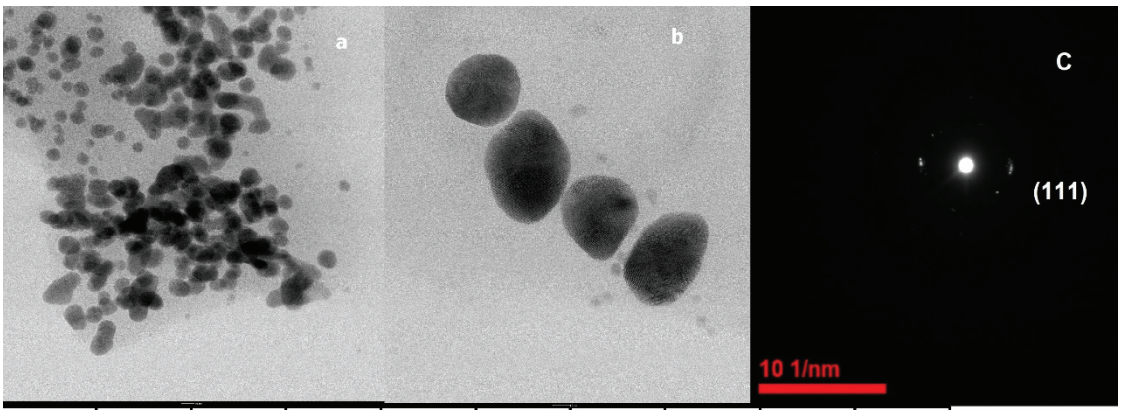

Figure 4 HRTEM images for Au NPs from Tg (a), Au NPs from Cg (b), and SAED for Au NPs from Cg (c)

Figure 4 shows images from high resolution TEM. These images show the well dispersity of nanoparticles in the solution. The average diameter is 11 ± 2 nm in the case of Au Tg and Au Cg. The representative selected area electron (SAED) in **Figure 4c** for Au Cg nanocomposites show a predominant (111) planes of face-centered cubic FCC structure.

3.2. Catalytic application of Au NPs for 4-nitrophenol reduction

The reduction of 4-NP was studied as a model reaction for the catalytic activity of the gold nanoparticles. 23.4 µL of 3 mM 4-NP, 340 µL of $NaBH_4$ of 63 mM were added to 615 µL distilled water at 10 pH. Before adding the Au NPs, the yellow colour of the solution remains the same even after one day. After adding 6.4 µL of $8x10^{-4}$ mM Au NPs (5.1 x 10-6 mM in the final reaction), the colour gradually disappeared which indicates the reduction of 4-NPs to 4-APs. The reaction was monitored by measuring the intensity of the absorption peak of 4-NPs at 400 nm and it was found to decrease over time. As the initial concentration of $NaBH_4$ was largely greater than the initial concentration of 4-NPs, we assumed the reaction follow the pseudo-first order.

The linear correlation shown in **Figure 5** suggests that, the reactions catalysed by Au NPs follow the first order kinetics. The kinetic rate constants (K) were determined by the slopes of the linear relationships. The highest value of 10.6 x 10^{-3} s^{-1} was found for Au guar composites, which was expected from its smallest size of 8 nm. The kinetic rate constants (K) for other nanocomposites are 10.6 x 10^{-3}, 9 x 10^{-3}, 7.9 x 10^{-3}, 7.9 x 10^{-3} s^{-1}, and 6 x 10^{-3} s^{-1} for Au Gg, Au Cg, Au Kg, Au Tg, and Au Xg, respectively.

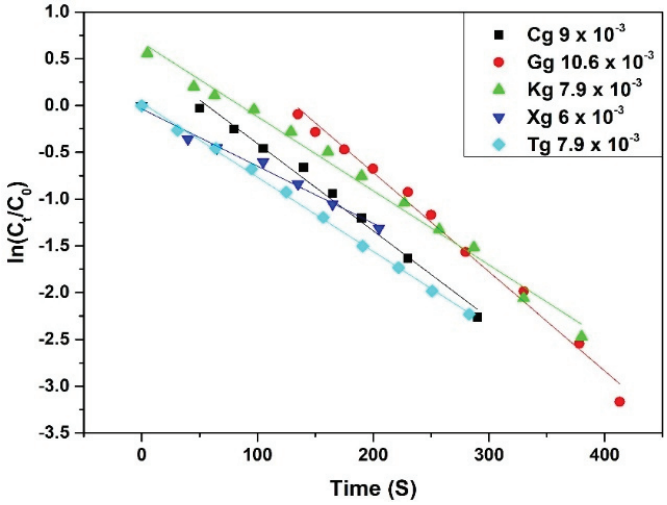

Figure 5 shows a plot of ln (Ct/C_0) versus time for Au Nps synthesized by different hydrocolloids

4. CONCLUSION

A green synthesis of the gold nanoparticles has been reported herein with an assessment of their composites that were synthesized by green, biocompatible, sustainable, cost effective, and eco-friendly routes. The study shows that, guar Au NPs composite has the smallest particle size (8 nm) with utmost stability for 3 months and a high kinetic rate (10.6 x 10^{-3} s^{-1}) for the degradation of p-NP to p-AP. The zeta potential and the UV-vis analysis of Au NPs produced by Tg, Kg, Gg, Cg and Xg did not show much variation in magnitudes during the tested periods (0 to 90 days). Zeta potential values for all Au NPs composites are largely greater than 30 mV, which is a clear indication for their stability without any sign of aggregation during the study time which was three months.

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