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Effect of pH on ionic liquid mediated synthesis of gold nanoparticle using elaiseguineensis (palm oil) kernel extract

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Abstract. This study was conducted for microwave assisted synthesis of stable gold nanoparticles (AuNPs) by reduction of chloroauric acid with Elaeis Guineensis (palm oil) kernel (POK) extract which was prepared in aqueous solution of ionic liquid, [EMIM][OAc], 1-Ethyl-3-methylimidazolium acetate. Effect of initial pH of reaction mixture (3.5 - 8.5) was observed on SPR absorbance, maximum wavelength (λ_{max}) and size distribution of AuNPs. Change of pH of reaction mixture from acidic to basic region resulted in appearance of strong SPR absorption peaks and blue shifting of λ_{max} from 533 nm to 522 nm. TEM analysis revealed the formation of predominantly spherical AuNPs with mean diameter of 8.51 nm. Presence of reducing moieties such as flavonoids, phenolic and carboxylic groups in POK extract was confirmed by FTIR analysis. Colloidal solution of AuNPs was remained stable at room temperature and insignificant difference in zeta value was recorded within experimental tenure of 4 months.

1. Introduction

The synthesis of gold nanoparticles (AuNPs) has got immense attention due to their ingenious applications in various industrial sectors such as environment science & engineering, catalysis, optical fibers, food & pharma, electronics and medical science [1]. Conventionally, synthesis of AuNPs can be performed by many physical, chemical and green synthesis methods [2]. However, high cost and toxic chemicals are major challenges for applying physical and chemical methods therefore bio synthesis got edge due to its simple, eco-friendly and low cost process [3]. Phytochemicals present in biomass are efficient to reduce chloroauric acid to form AuNPs. In fact, synthesis of nanomaterials using bio-synthesis approach has provided a common junction between nanotechnology and bio technology which led to the fabrication of unique materials with tunable size and shapes.

The role of pH is significant in changing the size and shape of nanoparticles. Numbers of studies has shown the stability of AuNPs at basic pH while many achieved stable suspension in acidic region. Olive leaf extract was used to synthesize stable AuNPs at basic pH, however, particles were precipitated within 12 h in acidic region [4]. Contrariwise, AuNPs synthesized using banana peel extract were stable at pH value of 2-5 [5]. A broader range of pH i.e. 2-11 was taken to synthesize AuNPs using oil palm mill effluent and pH 3 was observed optimum to achieve definite shapes

particles [6]. Furthermore, the synthesis reaction, size, shape and stability of AuNPs could be controlled by adjusting the initial pH value of reaction mixture.

To get plant extract, traditionally, water is considered a cheap and eco-friendly solvent; however, synthesized AuNPs are sometime not much stable at room temperature and form aggregates diminishing the colloidal stability [7, 8]. Ionic liquids (ILs) are therefore considered as a substituent due to "green" nature and strong solvating interaction with polar and non-polar compounds [9]. ILs are composed of ions and have been reported as an efficient solvent to extract various phytochemicals over many other traditional solvents such as water, alcohol, acetone and ether [10]. These have also been used as stabilizers in conventional treatment method for synthesis of AuNPs [11].

Palm oil trees are abundantly available in Indonesia and Malaysia and could be a potential source for bio-synthesis of AuNPs due to occupying substantial amount of phytochemicals particularly flavonoids and phenolic compounds [12]. In this study, we have therefore aimed to synthesize AuNPs using palm oil kernel (POK) extract, in which dual role of ILs (i) for extraction of phytochemicals from POK and (ii) stabilizers for AuNPs were investigated in a single step. Moreover, influence of pH on the rate of reaction and morphological characteristics of AuNPs was also studied.

2. Materials and Methods

Gold (III) chloride hydrate ($HAuCl_4.3H_2O$) and IL[EMIM][OAc], 1-ethyl-3-methylimidazolium acetate were procured from Sigma-Aldrich. The palm oil kernels were collected from Felcra Berhad Nasaruddin Oil Palm Plantation located in Bota, Perak, Malaysia.

2.1 Preparation of POK extract

Fresh POKs were collected and washed with plenty of distilled water to remove dust contaminants. These POKs were dried in an oven at 70 °C for 12 h followed by grinding by using IKA® grinder with 0.25 mm sieve. To get POK extract, 10 g of finely grinded kernels were added to 100 mL of [EMIM][OAc] 2%(w/v) and heated at 90 °C for 20 min. The mixture was filtered via gravitational filtration using Whatman No. 1 filter paper. The filtrate was collected in 100 mL glass vial and stored at 4 °C for further use. This extract was used within three days for reaction with chloroauric acid to avoid any loss of reduction efficiency for synthesis of AuNPs [13].

2.2 Synthesis of AuNPs

Typical reaction mixture is prepared by drop wise addition of 2 mL of POK extract to an aqueous mixture of 2 mL of 2.28 mM chloroauric acid added to 10 mL distilled water. The resulting mixture was heated in a microwave oven (Sharp – R 268R/S-M) with an output power capacity of 800 W and frequency of 2450 MHz. Effect of pH was determined by using different prefixed initial pH values of reaction mixture (3.5 – 9.5). HCl or NaOH, 0.1 M were used to adjust pH value.

2.3 Characterization of AuNPs

Perkin Elmer Lambda 25 UV-Visible (*UV-Vis*) spectrophotometer was used to record SPR absorbance and maximum peak wavelength (λ_{max}) at 1 nm resolution and a scan speed of 480 nm/min. The FTIR spectrum was observed using Ziess Supra 55 CP FTIR spectrophotometer. FTIR analysis was performed for POK extract before and after its reaction with chloroauric acid to identify the bio-compounds that could involve in reduction of gold ions into aurum particles. Zeiss Libra 200 TEM was used to observe the morphological characteristics of synthesized AuNPs. Analysis was performed by putting one drop of colloidal gold solution on the copper grid and allowed to dry prior to TEM imaging and size measurement. To predict the charge stability of colloidal gold, zeta potential value was measured by using "Malvern, Zetasizer Nano-ZSP".

3. Results and Discussions

Initial colour of POK extract was translucent white however, an addition of the chloroauric acid and distilled water was resulted in a clear solution. After heating the mixture in MW oven for 2 min,

colour of the solution turned into light pink which became more intense with time. This change of colour from white to pinkish is primary indication for successful formation of AuNPs due to excitation of surface plasmon vibration in the AuNPs.

3.1 Effect of pH on biosynthesis of AuNPs

Reaction was performed at pH 3.5 - 9.5 to identify the effect of pH on formation of AuNPs. It was observed that absorbance of solution increased while changing the initial pH of the solution from acidic to basic region as shown in figure 1. With increase of pH, SPR band was also blue shifted toward low wavelength region (figure 1 inset). *UV-vis* results suggested that no reaction was occurred in acidic region at pH 3.5 which is in agreement with the previous studies [14, 15]. It was might be due to protonation of hydroxyl and carboxyl group presents in extracts [16].

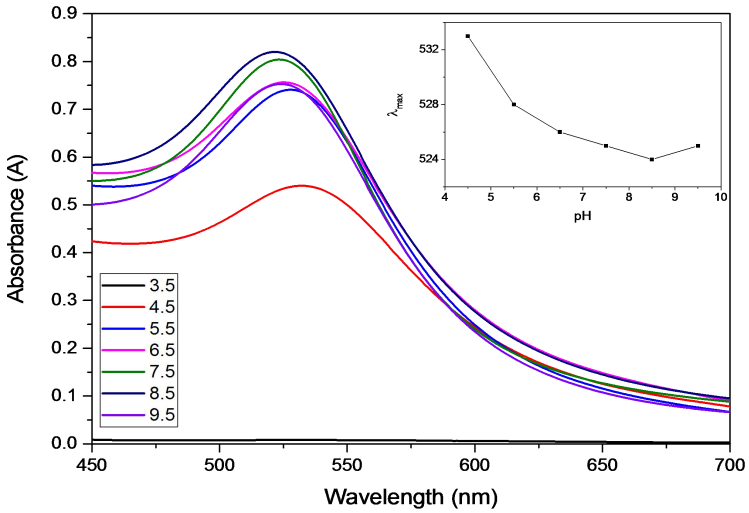

Figure 1: *UV-vis* spectra; effect of initial pH of reaction mixture (a) SPR peak positions (b) change of λ_{max}

Based on DLVO theory, first capping of AuNPs is done by anions therefore, anions are considered as a key source for enhanced colloidal stability [17]. However, strong acidic conditions protonated the acetate ions present in the reaction mixture and thus reducing their capping tendency and electrosteric forces to impart higher stability to particles which may resulted in slow reduction of gold ions or precipitation of AuNPs from solution. With increase of pH toward basic region, rapid change of colour was occurred with formation of sharp SPR peaks. Colloidal gold solution was remained stable at room temperature and there was nothing any aggregation or precipitation was noticed even after four months of their preparation indicating the strong stabilizing capability of IL.

TEM image analysis was performed for two representative sample of AuNPs synthesized at pH 4.5 and pH 7.5 as shown in figure 2a and 2b. The TEM images revealed that the AuNPs formed were predominantly spherical with narrow size distribution. At pH 4.5, the mean size of the AuNPs was 9.61 nm with size distribution ranged from 4.49 nm to 17.56 nm. However, when initial pH of reaction mixture was 7.5, mean sizes of the AuNPs obtained were relatively smaller. Particles were more uniform and well dispersed endorsing the validity of results driven from UV-vis. The size of the AuNPs ranged from 4.32 nm to 16.12 nm with the mean diameter of 8.51 nm as shown in figure 2b. Comparing the TEM images at both pH, it was obvious that AuNPs were more spherical, uniform and dispersed in basic region

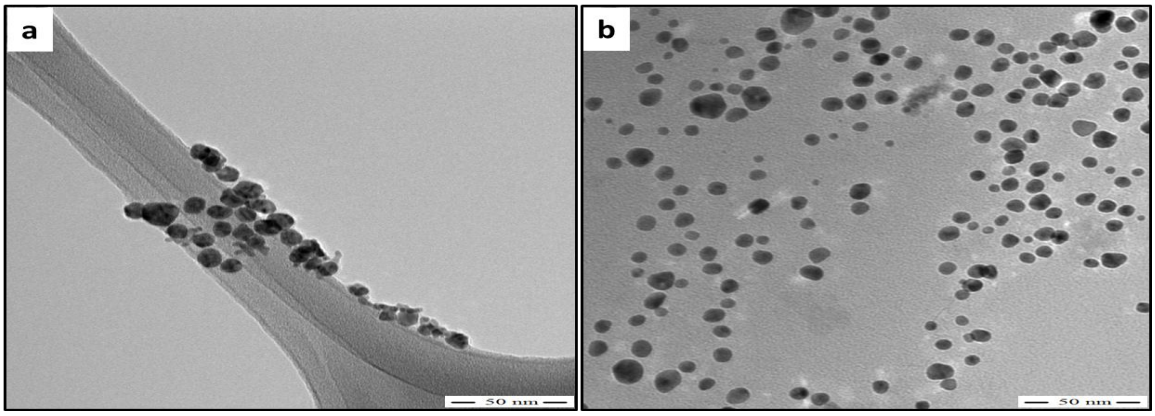

Figure 2: TEM image analysis of AuNPs at (a) pH 4.5, (b) 7.5

3.2 Zeta Potential

Colloidal stability of AuNPs depends upon the interaction between particles. A colloidal solution is stable when electrostatic repulsion forces are enough stronger than van der Waals attractive forces. Zeta potential value can be sued to identify the electrostatic repulsion. AuNPs are believed to be more stable if occupy zeta potential in between -30 mV to +30 mV [18]. The zeta value of synthesized AuNPs prepared at pH 7.5 was observed as -21.1 mV showing the good stability of colloidal solution. AuNPs solution was preserved at room temperature for four months and again tested for its zeta value which was found to be -19.5 mV as shown in figure 3. This value was still high and showed the enhanced colloidal stability of AuNPs.

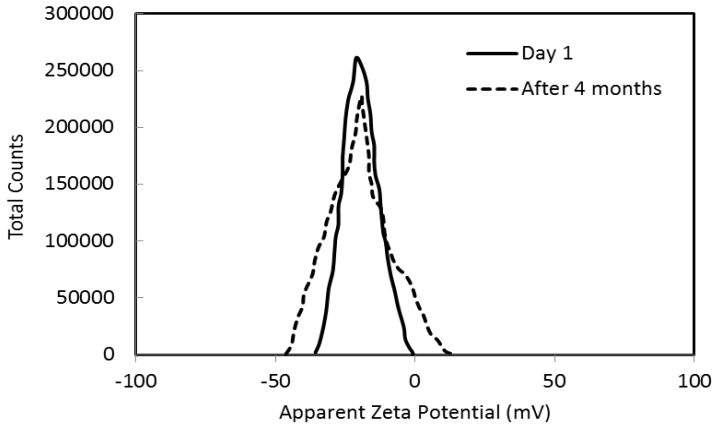

Figure 3: Zeta potential of AuNPs

3.3 FTIR Analysis

FTIR analysis was performed for POK extract and AuNPs mixture synthesized at pH 7.5 to identify the possible functional groups and other organic moieties involved in the synthesis of AuNPs. From the spectrum, various bands were observed at 691 cm^{-1}, 1114 cm^{-1}, 1642 cm^{-1} and 3430 cm^{-1} as shown in figure 4. These bands represented the presence of C-H aromatic, aliphatic amines, amide C=O and hydroxyl groups, respectively. A strong band at 3430 cm^{-1} indicated the presence of -OH groups which suggested the involvement of phenolic and flavonoids compounds as reducing agents for formation of AuNPs [19, 20]. Therefore, it could be presume that flavonoids and phenols which are abundant in palm oil biomass showed their characteristics peaks and seemed to be responsible for accelerated reduction of gold ions.

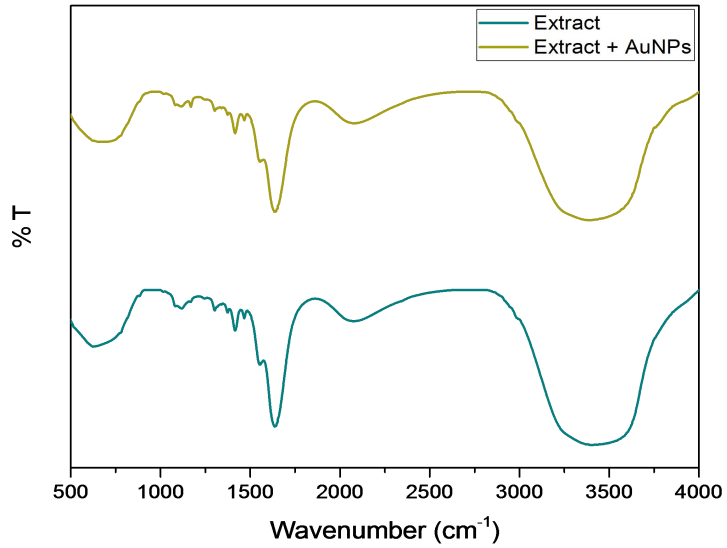

Figure 4: FTIR analysis for POK extract and AuNPs mixture

4. Conclusion

A single step method was established to synthesize AuNPs using POK extract prepared in [EMIM][OAc]. Substantial amount of flavonoids and phenolics compounds in POK were responsible to carry out the reduction reaction for bio-synthesis of AuNPs. Higher polarizability, strong MW absorbent and capping tendency of AuNPs made ILs as efficient solvents for rapid synthesis of stable AuNPs. The sizes and shape of synthesized AuNPs can also be tuned by manipulating pH of the reaction mixture. Colloidal gold solution was remained stable at room temperature without any aggregation. Higher stability of AuNPs was also exhibited by high zeta value of AuNPs even after four months.

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