Synthesis of Citrate-Capped Gold Nanoparticles from Reduced [AuCl4]− on Ascorbic Acid-Immobilized Mg/Al Hydrotalcite

Agustina Sus Andreani, Suyanta, Eko Sri Kunarti, and Sri Juari Santosa*

*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada,
Sekip Utara, Yogyakarta 55281, Indonesia*

ABSTRACT

Reductive adsorption of [AuCl4]− by using ascorbic acid immobilized on Mg/Al hydrotalcite (Mg/Al HT) and synthesis of gold nanoparticles (AuNPs) from the reduced gold using sodium citrate have been conducted. Mg/Al HT was synthesized by co-precipitation method at pH 10 with molar ratio of Mg(II) and Al(III) 2:1. Ascorbic acid (AA) was then immobilized on Mg/Al HT to form hybrid of AA and Mg/Al HT (Mg/Al HT-AA). Mg/Al HT-AA was used to reductively adsorb [AuCl4]− and the formed Au(0) was extracted by using sodium citrate to form citrate-capped AuNPs. The formation of AuNPs from 100 mg/L [AuCl4]− solution removed by 60 mg Mg/Al HT-AA was optimum at pH 5.0, by using 70 mM sodium citrate and 2 h sonication time. This optimum condition was successfully applied to synthesize AuNPs from [AuCl4]− as the leaching product of gold from PCB using aquaregia.

Keywords: *gold nanoparticles; sodium citrate; Mg/Al hydrotalcite*

ABSTRAK

Telah dilakukan adsorpsi reduktif [AuCl4]− menggunakan asam askorbat terimobilisasi pada Mg/Al hidrotalsit (Mg/Al HT) dan pembuatan nanopartikel emas (AuNPs) dari emas hasil reduksinya menggunakan natrium sitrat. Mg/Al HT disintesis dengan metode co-presipitasi pada pH 10 dengan rasio molar Mg(II) dan Al(III) 2:1. Asam askorbat (AA) kemudian diimobilisasikan pada Mg/Al HT untuk membentuk hibrida AA dan Mg/Al HT (Mg/Al HT-AA). Mg/Al HT-AA digunakan untuk adsorpsi reduktif [AuCl4]− dan Au(0) yang terbentuk diekstraksi dengan menggunakan natrium sitrat untuk membentuk AuNPs tercaping sitrat. Pembentukan AuNPs dari 100 mg/L larutan standar [AuCl4]− yang diserap oleh 60 mg Mg/Al HT-AA dengan agen pengkaping natrium sitrat optimum pada pH 5, konsentrasi natrium sitrat 70 mM dan waktu sonikasi 2 jam. Kondisi optimum ini berhasil diterapkan untuk mensintesis AuNPs dari [AuCl4]− sebagai hasil leaching emas dari PCB menggunakan aqua regia.

Kata Kunci: *nanopartikel emas; natrium sitrat; Mg/Al hidrotalsit*

INTRODUCTION

Gold is one of noble metals that has numerous unique properties like soft, conductive, and malleable with another metal. The primary source of gold is from gold mining, but uptake of gold from this source will lead to decrease of gold availability in nature. Another source known as secondary source of gold is from waste of electronic equipment which usually known as Waste of Electronic and Electronic Equipment (WEEE). The number of this waste is increasing by year [1]. Waste of electronic equipment contains gold as much 0.1% of total metal in the waste [2]. Though the amount of gold contained in WEEE is relatively low, but this amount is higher than total amount of gold contained in gold ore. Recycling metals from WEEE saved the preservation or continuity of metal resources that were not renewable, even gave the benefits for environmental, industrial, and financial for gained valuable goods from the waste [3].

Thus, gold extracted from secondary source is considerably more economic and eco-friendly.

There are several methods to extract gold from secondary resources. One of the common method that has been widely used is cyanide due to it's the most efficient, low cost and simplest method to extract gold from electronic waste [4]. However, cyanide also known to be toxic to the both environment and organism health, therefore the use of cyanide is highly avoidable. Hence, its need an alternative method to extract gold without harming environment and organism health.

Among many methods, adsorption is noticed as not only effective, low cost and easy handling, but also environmentally friendly for gold recovery. In order to perform an eco-friendly material, adsorbent used for adsorption process could be obtained from natural resource. This includes, carbon active, humic substances, natural iron, hydrotalcite, etc. [5-9]. In this

research, hydrotalcite was used due to it has high activity for the anion removal in the aquatic medium, include gold ion. The gold ion, however, cannot be reduced due to hydrotalcite has no functional group that able to reduce Au(III) to Au(0) [10]. Therefore, ascorbic acid–an organic acid with highest activity to reduce Au(III) has been used. This activity is provided by the presence of donating electron functional group, –OH, within the ascorbic acid's molecule [11-12].

Noble metal's nanoparticles, particularly gold nanoparticles and its application, have been attracted a considerably high attention of nano–society [3]. Recently, gold nanoparticles have been frequently used in various applications such as catalysis, optics, electronics, biotechnology, bioengineering, textile engineering, water treatment, silver based consumer products, biosensor and biological imaging [13]. Therefore, it is will be very interesting to broaden the knowledge about how to extract gold nanoparticles from secondary resources using Mg/Al HT-AA.

In this study, briefly, the Mg/Al HT AA was used for gold nanoparticles extraction by means of citric acid. Although ascorbic acid has high ability to reduce gold, however, the reduced gold is in bulk state and hardly separated from its surface. The Au(0) could be released from adsorbent using NaOH, but only about 60% is released with the various range of size [14-15]. Hence, in this study the citric anion was used in order to leach the reduced gold from the adsorbent and to maintain the nano state of Au(0). Citric anion has dicarboxylic group which could act as a barrier agent that limiting and obstruct the rate of particle growth.

In this research, Mg/Al HT-AA was synthesized and used to reductively adsorb $[AuCl_4]^-$ from $[AuCl_4]^-$ standard solution and aquaregia–leached $[AuCl_4]^-$ from printed circuit board (PCB) of computer. The formed Au(0) on the surface of Mg/Al HT-AA was then desorbed by sodium citrate to form citrate–capped AuNPs. The optimum condition for the formation of AuNPs was examined and the particle size as well as the stability of the formed AuNPs from both $[AuCl_4]^-$ standard solution and aquaregia–leached $[AuCl_4]^-$ from PCB were determined and compared.

EXPERIMENTAL SECTION

Materials

$Mg(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, sodium citrate, sodium dodecyl sulfate, and ascorbic acid solution were purchased from E. Merck and used as received. N_2 gas was purchased from CV. Mandiri Perkasa, and filter paper Whatman 42 was purchased from GE Heathcare UK Limited. The pretreatment of PCB was done to remove copper content using double oxidizing agent

H_2O_2 30% and H_2SO_4 6 M with a molar ratio $H_2O_2:H_2SO_4$ 3:1 and soaked for three days by five time repetitions [16]. Aquaregia solution was prepared by mixing HCl 30% and HNO_3 98% with a molar ratio $HCl:HNO_3$ 3:1. $HAuCl_4$ standard solution 100 mg/L was prepared by dissolving 0.1 g pure gold in 1000 mL of aquaregia solution, while $HAuCl_4$ leached from PCB was prepared by leaching 1 g of crushed PCB in 1 cm average size using10 mL aquaregia solution.

Instrumentation

Infrared spectra of samples was recorded on Shimadzu Prastige-21 infrared Spectrophotometer using solid KBr pellets to investigate their related functional groups qualitatively. The crystal structure was characterized by X-ray diffraction pattern at a scanning rate of 4 degree/minute in 2 theta range from 0° to 80°, using a Shimadzu XRD-6000 diffractometer equipped with monochromatic high intensity CuK_α radiation (λ = 0.15418) produced at 40 kV and 30 mA. Ultraviolet-visible spectra was recorded on Shimadzu s-600 UV-Vis spectrophotometer in the range of 300 to 600 nm.

Procedure

Immobilization of ascorbic acid onto Mg/Al HT

Mg/Al HT was synthesized by co-precipitation method at pH 10 with a molar ratio of Mg(II):Al(III) 2:1 [15]. The synthesized Mg/Al HT 0.1 mg was then added into 200 mg/L of AA solution at pH 5 and shaken for 90 min. The precipitation, i.e. Mg/Al HT-AA was filtered, dried at 60 °C to constant weight and characterized with infrared spectrophotometer and X-ray diffractometer.

Reductive adsorption of $[AuCl_4]^-$ on Mg/Al HT-AA

Reductive adsorption of $[AuCl_4]^-$ was studied by adding 0.1 g of Mg/Al HT-AA to every 100 mg/L of $[AuCl_4]^-$ standard solution and 100 mg/L of $[AuCl_4]^-$ solution leached from PCB that was adjusted of pH 3 and then shaken for 5 h. The precipitations were filtered, dried at 60°, and then characterized with infrared spectrophotometer and X-ray diffractometer. This reductive adsorption process yielded two kinds of precipitation which were then named as HT-AA-Au$_{std}$ (for precipitation obtained from $[AuCl_4]^-$ standard solution) and HT-AA-Au$_{PCB}$ (for precipitation obtained from $[AuCl_4]^-$ solution leached from PCB).

Synthesis of gold nanoparticle from HT-AA-Au$_{std}$
Effect of pH. Effect of pH on the AuNPs formation was performed by adding 60 mg of HT-AA-Au$_{std}$ to every 10 mL of sodium citrate solution 90 mM at pH of 3.00,

5.00, 7.00, 9.00, and 11.00. After sonication for 3 h, the final pH was measured and every mixture was then filtered and the filtrate was analyzed with UV-Vis Spectrophotometer.

Effect of citrate concentration. Effect of citrate concentration was performed by adding 60 mg of HT-AA-Au$_{std}$ to every 10 mL of sodium citrate solution at concentration of 20, 30, 40, 50, 60, 70, 80, 90, and 100 mM at optimum pH. After sonication for 3 h, the final pH was measured and each solution was then filtered and the filtrate was analyzed with UV-Vis Spectrophotometer.

Effect of sonication time. Effect of sonication time was examined by adding 60 mg of HT-AA-Au$_{std}$ to 10 mL of sodium citrate solution at optimum pH and concentration and the mixed solution was then sonicated at sonication time 1, 2, 3, 4, 5 h. After being sonicated, the pH of each solution was measured and followed by filtration and analysis with UV-Vis spectrophotometer.

Synthesis of gold nanoparticles from HT-AA-Au$_{PCB}$

The synthesis of AuNPs from HT-AA-Au$_{PCB}$ was carried out by using 60 mg of HT-AA-Au$_{PCB}$ and 10 mL of sodium citrate solution under the optimum condition obtained for the synthesis of AuNPs from HT-AA-Au$_{STD}$.

### *Characterization of HT-AA-Au after desorption*

Residues obtained after the desorption of AuNPs from HT-AA-Au$_{STD}$ and HT-AA-Au$_{PCB}$ were first dried to constant weight and then characterized by infrared spectrophotometer and X-ray diffractometer.

RESULT AND DISCUSSION

Adsorption of [AuCl$_4$]⁻ by Mg/Al HT-AA

The adsorption of AA on Mg/Al HT was optimum at pH 5 [15]. This adsorption of AA on Mg/Al HT might be governed by an electrostatic interaction since at pH below 8.78, HT is positively charged species while AA is negatively charged species at pH above 4.04. In this study, the immobilization of AA on Mg/Al HT to form Mg/Al HT-AA was carried out at pH 5 and the Mg/Al HT-AA was then used to remove [AuCl$_4$]⁻ from aqueous solution to form Mg/Al HT-AA-Au.

The characterization results of Mg/Al HT, Mg/Al HT-AA, and Mg/Al HT-AA-Au were summarized in Fig. 1. Compared to Mg/Al HT, immobilization of AA on Mg/Al HT (Mg/Al HT-AA) yielded new absorption bands at 2931 and 1049 cm⁻¹ which corresponded to the stretching vibration of C–H (sp₃) and C–O, respectively. Since the Mg/Al HT contains no methyl and C–O containing functional groups, so the appearance of those new absorption bands must be caused by the immobilized AA on Mg/Al HT. After being used to remove
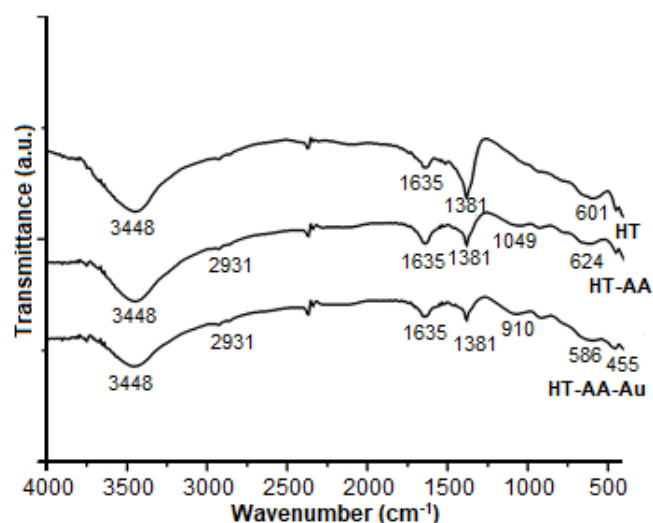
Fig 1. FTIR spectra of Mg/Al HT, Mg/Al HT-AA, and Mg/Al HT-AA-Au$_{STD}$
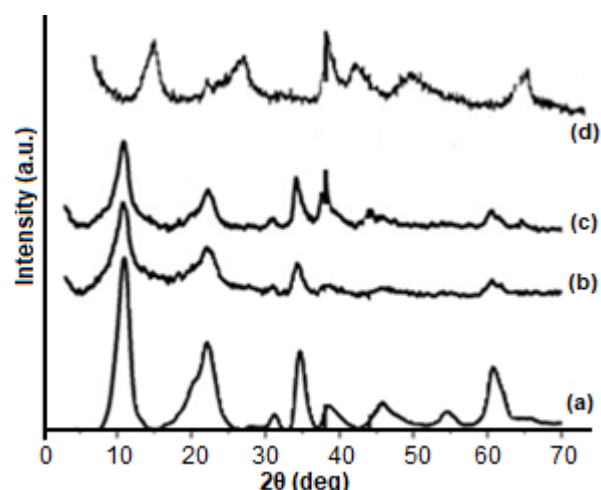
Fig 2. XRD pattern of Mg/Al HT (a), Mg/Al HT-AA(b), and Mg/Al HT-AA-Au$_{STD}$(c), Mg/Al HT-AA-Au$_{PCB}$(d)

[AuCl$_4$]⁻, the main peaks of Mg/Al HT-AA on 3448 cm⁻¹ (stretching vibration of –OH), 1635 cm⁻¹ (bending vibration of OH), 1381 cm⁻¹ (stretching vibration of NO), and 2931 cm⁻¹ (stretching vibration of C–H) were remain unchanged. The only small change was observed for the peak of stretching vibration of C–O at 1049 cm⁻¹ and that of metal–oxygen interaction at 624 cm⁻¹ that were shifted to 910 and 455 cm⁻¹, respectively. These shifts may indicate that both functional groups containing C–O and moiety containing metal–oxygen bonds are involved on the removal of [AuCl$_4$]⁻ on Mg/Al HT-AA.

The adsorbent of Mg/Al HT-AA that has been used for [AuCl$_4$]⁻ adsorption was characterized with XRD to determine the difference of characteristic peak and the shifts after immobilization of ascorbic acid (Fig. 2). The value of 2-theta for the Miller indices of Mg/Al

HT which are corresponding to d_{003}, d_{006}, d_{009} are 10.85° (8.14 Å); 2.13° (4.01 Å); 34.73° (2.58 Å), while the 2-theta of Mg/Al HT-AA for the same indices are 10.78° (8.23 Å); 22.28° (3.98 Å); 34.31° (2.61 Å) respectively. From the data above, it is obvious that the interlayer spacing (d) of Mg/Al HT before and after immobilization of AA is relatively the same. Since the value of d_{003} before and after immobilization of AA is relatively same, so the AA may only be adsorbed on the outer surface of Mg/Al HT without being accompanied by appreciable intercalation into the interlayer space.

From Fig. 2, the values of 2-theta for the Miller indices of Au which are corresponding to d_{111}, d_{200}, d_{220} on HT-AA-Au$_{STD}$ with Au was obtained from standard solution were 37.91° (2.37 Å); 44.111° (2.05 Å); 64.34° (1.45 Å). The 2-theta for Au from JCPDS 4-784 for the same indices are 38.19° (2.36 Å); 44.39° (2.04 Å); 64.58° (1.44 Å). The resemblance of these values proves that Mg/Al HT-AA has successfully reduced Au(III) into Au(0).

XRD data of HT-AA-Au$_{PCB}$ with Au was obtained from the dissolution of PCB (Fig. 3) showed the presence of not only Au(0) but also impurities NaCl at 2-theta 31.692° (2.813 Å); 45.449° (1.99 Å); 56.447° (1.626 Å). The 2–theta for NaCl from JCPDS no. 5-628 are 32.4° (2.821 Å); 46.4° (1.994 Å); 57.6° (1.629 Å), corresponding to d_{200}, d_{220}, d_{222}, respectively. By the addition of NaOH, a white precipitated was observed. It was assumed that NaCl formed due to the reaction between Cl$^-$ from aquaregia and Na$^+$ from NaOH. The presence of the NaCl leads to the aggregation of AuNPs$_{PCB}$ through H–bonding between –H of –COOH with Cl$^-$, resulting the darker purple color. Meanwhile, in opposite, the AnNPs$_{STD}$ has soft purple due to the absence of NaCl in the solution and no aggregation was occurred. To reach optimum adsorption onto Mg/Al HT, [AuCl$_4$]$^-_{PCB}$ was first adjusted to pH 3, through the addition of NaOH.

Synthesis of Gold Nanoparticle from HT-AA-Au

In the synthesis of AuNPs, sodium citrate was used as capping agent. Nanoparticles can aggregate and grow continuously if they are not covered by a capping agent [17]. Sodium citrate is a weak reductor that requires external energy to undergo reaction as a capping agent [18]. In this research, sonication was used in this study as an external energy.

In the formation of AuNPs using weak acid like citrate, the reduction of [AuCl$_4$]$^-$ into AuNPs was highly affected by pH [19]. In order to investigate the effect of pH, the formation of AuNPs from 60 mg of Mg/Al HT-Au was done by extraction using 90 mM of sodium citrate solution at pH 3.00, 5.00, 7.00, 9.00, and 11.00. According to the speciation diagram of sodium citrate, the
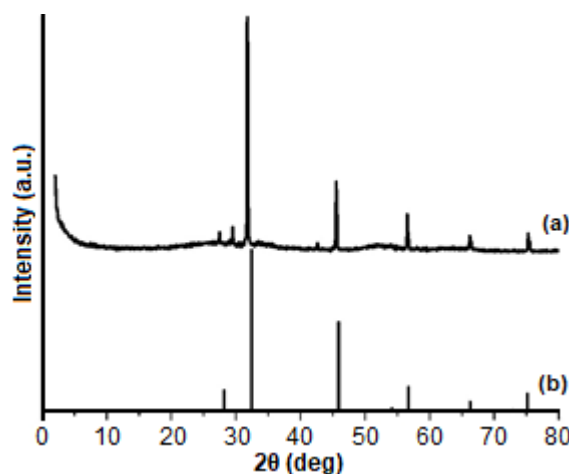

Fig 3. XRD pattern of NaCl from Mg/Al HT-AA-AuPCB impurities (a), NaCl from JCPDS no. 5-628 (b)

Table 1. pH of sodium citrate solution before and after being used to synthesize AuNPs

pH	
Before synthesis AuNPs	After synthesis AuNPs
3.00	3.01
5.01	5.00
7.00	6.78
9.03	8.19
11.05	9.48

citrate has three pKa values, pKa$_1$ = 3.14; pKa$_2$ = 4.67; pKa$_3$ = 6.40. So at a pH values between 3.14 and 4.67 citrates is dominantly as monodeprotonated species; at pH values between 4.67 and 6.40, dideprotonated citrate species is dominant and changes to trideprotonated species at pH above 6.40. The pH after leaching process of Au(0) decreased due to the redox reaction between citric acid and the remaining [AuCl$_4$]$^-$ on Mg/Al HT-AA. In this redox reaction, Au(III) in [AuCl$_4$]$^-$ was reduced to Au(0), while –OH groups of citric acid was deprotonated and followed by oxidation to ketone. The released H$^+$ from –OH groups of citric acid caused the decreasing of pH (Table 1) [20]. At initial pH value 7.00; 9.03; and 11.05 they decrease to 6.78, 8.19, and 9.48, respectively (Table 1). At pH above pH 7.00, 3 H$^+$ of citrate was all released for every molecule of citrate so that its pH decreases. At pH 3.00 and 5.00 only 1 and 2 H$^+$ are released for every molecule of citrate respectively, so it do not affect significantly to pH change.

In addition to pH, the formation of AuNPs was affected also by the concentration of sodium citrate and sonication time. The effects of pH, sodium citrate concentration, and sonication time for synthesis of AuNPs from HT-AA-Au$_{STD}$ were investigated and the optimum condition was used for synthesis of AuNPs from HT-AA-Au$_{PCB}$.
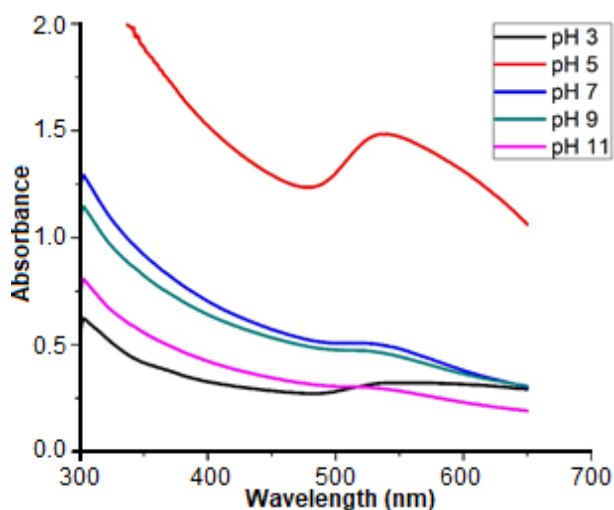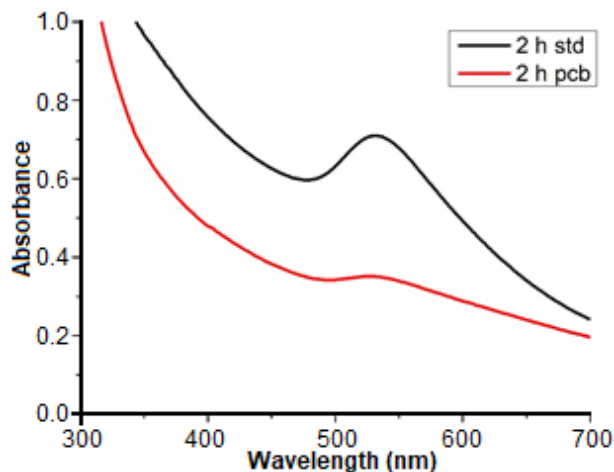
Fig 4. The UV-Vis spectra of AuNPs with capping agent at various pH
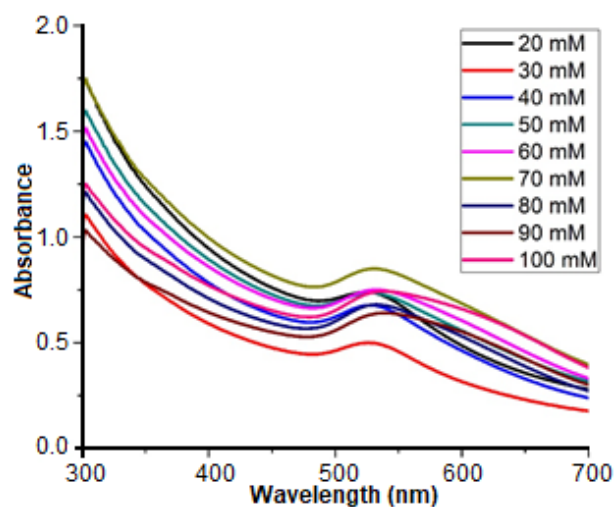
Fig 5. Effect of sodium citrate concentration on the UV-Vis spectra of the formed citrate-capped AuNPs
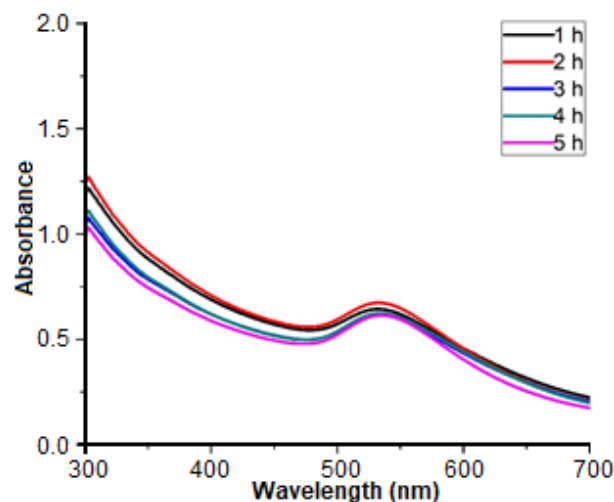
**Fig 6.** Effect of sonication time on the UV-Vis spectra of the formed citrate-capped AuNPs

Fig 7. UV-Vis spectra of AuNPS obtained from Mg/Al HT-AA-Au$_{STD}$(a) and Mg/Al HT-AA Au$_{PCB}$ (b) extracted using 70 mM sodium citrate

The optimum pH of AuNPs formation was pH 5.00 (Fig. 4) because according to the speciation diagram of sodium citrate, citrate species at pH 5.00 were dominated by monodiprotonated citrate species (CitH$_3^-$) [21]. The CitH$_3^-$ induces gold so that electrostatic interaction between citrate and gold could occur, in which gold is capped by citrate and the size of the formed gold could be restricted in the range of nanoscale [19]. At pH lower than 5.00, the formation of CitH$_3^-$ is more limited, the ability to stabilize AuNPs is limited and therefore AuNPs will aggregate to bigger size and eventually precipitate. At pH 7.00, 9.00, and 11.00, dominant citrate species change to CitH^{3-} and Cit^{4-}, and these species are predicted as poorer species in stabilizing AuNPs than CitH$_3^-$, so the aggregation of AuNPs may occur also at these pH values [20]. As a

results, at pH 9.00 and 11.00 citrates could not restrict the gold in nano size and therefore there is no surface plasmon resonance (SPR) for AuNPs at wavelength of 500–560 nm.

The effect of concentration was carried out by varying the concentration of 10 mL of sodium citrate ranging from 20 to 100 mM at optimum pH and fixed sonication time for 2 h. Based on UV-Vis analysis, it was found that the formed AuNPs increased with increasing the concentration of sodium citrate from 20 to 60 mM (Fig. 5). At concentration sodium citrate 70 mM, the formed AuNPs from 60 mg of Mg/Al HT-Au$_{STD}$ at pH 5 was maximum. SPR for the formed AuNPs was at λ_{max} 523 nm. At concentration of citrate above 70 mM, the number of negatively charged citrate species in the aqueous system were quite abundant and
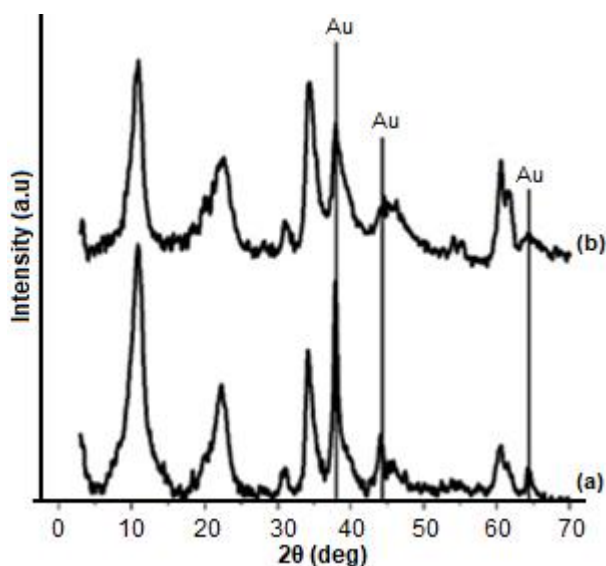
Fig 8. XRD pattern of HT-AA-Au$_{STD}$ before (a) and after desorption (b)

lead to the weak interaction with gold and destabilizing the formed AuNPs in the solution which leads to the aggregation of gold into higher size than nanosize [22].

The effect of sonication time was investigated by varying for 1, 2, 3, 4, 5 h at optimum pH and optimum concentration of sodium citrate. The optimum sonication time was 2 h (Fig. 6). However, overall resulted SPR peak showed insignificant difference. At all sonication time, the SPR peaks were relatively similar appearance and observed at 532–534 nm. It is a proof that sonication time did not affect significantly on the synthesis of AuNPs [23].

Gold nanoparticles that were synthesized from Mg/Al HT-AA-Au$_{PCB}$ were prepared at optimum condition obtained for AuNPs from Mg/Al HT-AA-Au$_{STD}$. Fig. 7 showed that the observed absorption was at the wavelength of 500–560 nm corresponded to the characteristic SPR of AuNPs. It is an indication that gold nanoparticles could also be formed from Mg/Al HT-AA-Au$_{PCB}$. The observed absorbance was relatively lower than absorbance of AuNPs obtained from Mg/Al HT-AA-Au$_{STD}$. It might be due to the formation of NaCl as side products that may negatively affect the formation of citrate capped AuNPs.

The diffraction pattern of Mg/Al HT-AA-Au$_{STD}$ before and after desorption using citrate was compared (Fig. 8). The characteristic peak of Mg/Al HT-AA$_{STD}$ did not show any significant change that proved the structure of Mg/Al HT-AA did not much change and appreciable amount Au still on the Mg/Al HT-AA after desorption. As shown in Fig. 8, the presence of Au(0) was still observed by characteristic diffraction pattern of Au(0) in HT-AA-Au$_{STD}$ after desorption. The content of Au(0) on Mg/Al HT-AA-Au$_{STD}$ after desorption was

smaller than that before desorption as shown by the lower intensities of the peaks for d$_{111}$, d$_{200}$, and d$_{220}$ (Fig. 8).

CONCLUSION

Citrate capped-AuNPs have been synthesized from both 60 mg of Mg/Al HT-AA-Au$_{STD}$ and Mg/Al HT-AA-Au$_{PCB}$. The optimum condition for the synthesis of AuNPs from 60 mg of Mg/Al HT-AA-Au$_{STD}$ by using 70 mM sodium citrate solution was at pH 5.00 and sonication time 2 h. This optimum condition was able to be used successfully to synthesize AuNPs from Mg/Al HT-AA-Au$_{PCB}$.

ACKNOWLEDGEMENT

REFERENCES

[1] Huang, K., Guo, J., and Xu, Z., 2009, Recycling of waste printed circuit boards : A review of current technologies and treatment status in China, *J. Hazard. Mater.*, 164 (2-3), 399–408.

[2] Gramatyka, P., Nowosielski, R., and Sakiewicz, P., 2015, Recycling of waste electrical and electronic Recycling of waste electrical and electronic equipment, *JAMME*, 20 (1-2), 535–538.

[3] Jain, P.K., Huang, X., El-sayed, I.H., and El-sayed, M.A., 2008, Noble metals on the nanoscale : Optical and photothermal properties and some applications in imaging, sensing, biology, and medicine, *Acc. Chem. Res.*, 41 (12), 1578–1586.

[4] Dai, X., Simons, A., and Breuer, P., 2012, A review of copper cyanide recovery technologies for the cyanidation of copper containing gold ores, *Miner. Eng.*, 25 (1), 1–13.

[5] El Maksod, I.H.A., Elzaharany, E.A., Kosa, S.A., and Hegazy, E.Z., 2016, Simulation program for zeolite A and X with an active carbon composite as an effective adsorbent for organic and inorganic pollutants, *Microporous Mesoporous Mater.*, 224, 89–94.

[6] Nakbanpote, W., Thiravetyan, P., and Kalambaheti, C., 2002, Comparison of gold adsorption by *Chlorella vulgaris*, rice husk and activated carbon, *Miner. Eng.*, 15 (7), 549–552.

[7] Santosa, S.J., Siswanta, D., Sudiono, S., and Utarianingrum, R., 2008, Chitin-humic acid hybrid as adsorbent for Cr(III) in effluent of tannery wastewater treatment, *Appl. Surf. Sci.*, 254 (23), 7846–7850.

[8] Aredes, S., Klein, B., and Pawlik, M., 2013, The removal of arsenic from water using natural iron oxide minerals, *J. Cleaner Prod.*, 29-30, 208–213.

[9] Santosa, S.J., Kunarti, E.S., and Karmanto, 2008, Synthesis and utilization of Mg/Al hydrotalcite for removing dissolved humic acid, *Appl. Surf. Sci.*, 254 (23), 7612–7617.

[10] Sulistyaningsih, T., Santosa, S.J., Siswanta, D., and Rusdiarso, B., 2016, Adsorption of $[AuCl_4]^-$ on ultrasonically and mechanical-stirring assisted Mg/Al-NO_3 hydrotalcite-magnetite, *Indones. J. Chem.*, 16 (3), 268–276.

[11] Qin, Y., Ji, X., Jing, J., Liu, H., Wu, H., and Yang, W., 2010, Size control over spherical silver nanoparticles by ascorbic acid reduction, *Colloids Surf., A*, 372 (1-3), 172–176.

[12] Jain, S., Jain, A., Kachhawah, P., and Devra, V., 2015, Synthesis and size control of copper nanoparticles and their catalytic application, *Trans. Nonferrous Met. Soc. China*, 25 (12), 3995–4000.

[13] Rao, C.N.R., and Cheetham, A.K., 2001, Science and technology of nanomaterials: Current status and future prospects, *J. Mater. Chem.*, 11 (12), 2887–2894.

[14] Iksan, N.A., 2011, Kajian Adsorpsi-desorpsi $[AuCl_4]^-$ pada Mg/Al Hidrotalsit, *Thesis*, Department of Chemistry, Universitas Gadjah Mada, Yogyakarta.

[15] Hidaiyanti, R., 2013, Immobilisasi Asam Askorbat pada Mg/Al Hidrotalsit dan Aplikasinya untuk Adsorpsi-Reduksi $[AuCl_4]^-$, *Thesis*, Department of Chemistry, Universitas Gadjah Mada, Yogyakarta.

[16] Behnamfard, A., Salarirad, M.M., and Veglio, F., 2013, Process development for recovery of copper and precious metals from waste printed circuit boards with emphasize on palladium and gold leaching and precipitation, *Waste Manag.*, 33 (11), 2354–2363.

[17] Yan, Y., Chen, K., Li, H., Hong, W., Hu, X., and Xu, Z., 2013, Capping effect of reducing agents and surfactants in synthesizing silver nanoplates, *Trans. Nonferrous Met. Soc. China*, 24 (11), 3732–3738.

[18] Slot, J.W., and Geuze, H.J., 1985, A new method of preparing gold probes for multiple-labeling cytochemistry, *Eur. J. Cell Biol.*, 38 (1), 87–93.

[19] Krishnamurthy, S., and Yun, Y.S., 2012, Recovery of microbially synthesized gold nanoparticles using sodium citrate and detergents, *Chem. Eng. J.*, 214, 253–261.

[20] Tabrizi, A., Ayhan, F., and Ayhan, H., 2009, Gold nanoparticle synthesis and characterization, *Hacettepe J. Biol. Chem.*, 37 (3), 217–226.

[21] Patungwasa, W., and Hodak, J.H., 2008, pH tunable morphology of the gold nanoparticles produced by citrate reduction, *Mater. Chem. Phys.*, 108 (1), 45–54.

[22] Kimling, J., Maier, M., Okenve, B., Kotaidis, V., Ballot, H., and Plech, A., 2006, Turkevich method for gold nanoparticle synthesis revisited, *J. Phys. Chem. B*, 110 (32), 15700–15707.

[23] Cubillana-Aguilera, L.M., Franco-Romano, M., Gil, M.L.A., Naranjo-Rodríguez, I., Hidalgo-Hidalgo de Cisneros, J.L., and Palacios-Santander, J.M., 2011, New, fast and green procedure for the synthesis of gold nanoparticles based on sonocatalysis, *Ultrason. Sonochem.*, 18 (3), 789–794.