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## The Effect Of Addition 2-Propanol Through Reduction Process $\text{AuCl}_4^-$ to $\text{Au}(0)$ by Mg/Al Hydrotalcite-Gallic Acid.

Dyah Fitriani\*, Evi Maryanti, and Deni Agustriawan.

Chemistry Department on University of Bengkulu, Indonesia.

### ABSTRACT

The effect of addition 2-propanol as OH radical scavenger through reduction process  $\text{AuCl}_4^-$  to  $\text{Au}(0)$  by Mg/Al Hydrotalcite that immobilized with Gallic acid has been done. Mg/Al hydrotalcite (Mg/Al HT) has been synthesized by coprecipitation method of  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Al}(\text{NO}_3)_3$  at pH 10 with Mg(II) and Al(III) molar ratio of 2 : 1. The synthesized Mg/Al HT as well as its immobilization product with gallic acid (Mg/Al HT-GA) before and after being used to remove  $\text{AuCl}_4^-$  were characterized by X-ray Diffraction and FT-IR Spectroscopy. Immobilization of gallic acid was reached at pH 5. The analytical result using FTIR and XRD showed that gallic acid has been immobilized on surface of Mg/Al HT. The addition of 2-propanol gave no significant effect on the reduction of  $\text{AuCl}_4^-$  to  $\text{Au}(0)$ , showing that OH radical did not have dominant role on the reduction of  $\text{AuCl}_4^-$  to  $\text{Au}(0)$ .

**Keyword:** Mg/Al hydrotalcite, gallic acid,  $\text{AuCl}_4^-$ , 2-propanol.

*\*Corresponding author*

## INTRODUCTION

Gold is one of heavy metal high value in terms of price and use, so that the metal is interesting to explore [1]. Gold has better conductivity than conventional conductors such as copper and aluminum, so its use is becoming widespread. Precious metals are widely used in computers and digital telecommunications equipment, and is now expanding its use to other electronic devices such as audiovisual equipment (TV and radio), air conditioning, and a variety of other equipment. The more rapid rate of technological progress resulted in the lifetime of electronic equipment was getting short, so that the waste generated increased from time to time.

Electronic waste most of which contain gold metal, recycling needs to be done. This process aims to recover the gold that can be economically profitable and also to maintain the environmental balance.

Various methods can be used to isolate gold from electronic waste, among which is the method of electrolysis, ion exchange, membrane separation and adsorption or resin. Adsorption method is one potential alternative methods because the process is relatively simple, can work at low concentrations, can be recycled, and the relatively low costs involved. Some commonly used adsorbent for gold are active carbon [2], lignofenol derivate [3], fenol derivate [4].

Hydrotalcite (HT) is one of the clay minerals is cheap and easily synthesized, have a large anion exchange capabilities and broad face are great. The general formula of this compound is adalah  $[M^{II}_x M^{III}_x (OH)_2]^{x+} [A^{m-}_{x/m} \cdot nH_2O]^{x-}$ , with the  $M^{II}$  and  $M^{III}$  form divalent and trivalent cations such as  $Mg^{2+}$  and  $Al^{3+}$ .  $A^{m-}$  is organic or inorganic anion and the value of  $x$  ranges from 0.20 to 0.33 [5].

Therefore, in order to HT have the ability to adsorb and reduced, need to do modifications to the adsorbent. Modification of HT was made by Anirudhan and Suchitra [6], they modify the surface of the Mg/Al HT with compound Tannates to adsorb metal cations Cu (II), Zn (II), and Cd (II).

In this study, before HT is used to adsorb and reduce  $AuCl_4^-$ , the adsorbent in advance interaction with gallic acid that serves as a reducing agent. With the presence of gallic acid compounds are immobilized on Mg/Al HT, it is expected that it will increase the adsorption and also can reduce  $AuCl_4^-$  to be metal ion Au (0).

## MATERIALS AND METHODS

### Materials and Equipment

$Mg(NO_3)_2 \cdot 6H_2O$ ,  $Al(NO_3)_3 \cdot 9H_2O$ , NaOH, gold ions (III) chloride  $[AuCl_4]^-$ ,  $HNO_3$ , HCl, 4 and 7 standard buffers. The materials are all production E. Merck,  $CO_2$  free distilled water, artificial aquabides basic chemical laboratory Science Faculty of UGM, nitrogen gas. The identification and characterization was supported by UV-Vis spectroscopy Shimadzu UV-1700 pharماسpec, Infrared Spectroscopy of Shimadzu FTIR-8201 PC, X-ray Diffractometer XRD Shimadzu-6000 and Atomic Absorption Spectroscopy (AAS) Analytic Jena contraAA 300.

### Methods

#### Synthesis of Mg/Al HT

A total of 100 ml solution containing 12,821 g (0,05 mol)  $Mg(NO_3)_2 \cdot 6H_2O$  and 9,378 g (0,025 mol)  $Al(NO_3)_3 \cdot 9H_2O$  titrated with 300 ml of 0.5 M NaOH until the pH reaches at 10. During the stirring gas flow  $N_2$  to remove  $CO_2$ . After the titration was complete, it was continued by stirring for about 30 minutes. Solution was heated at a temperature of 110 °C for five hours, then cooled to perfect the process of precipitation. The precipitate was separated from the solution by *centrifuge*. The precipitate obtained was washed with aquades free  $CO_2$  until pH neutral. Colloidal precipitate which still contains water was then filtered with Whatman paper 42 and dried in an oven at a temperature of 70 °C for 48 hours. After the dried solids obtained crushed in porcelain mortar and sieved with 270 mesh sieve *fisher*. Characterization of solid Mg/Al HT was carried out using Xray d iffraction and infrared spectroscopy.

To determine metal content in the Mg/Al HT used atomic absorption spectroscopy. Analysis of free H<sub>2</sub>O and H<sub>2</sub>O crystals in the Mg/Al hydrotalcite was done by weighing 0.2 g of Mg/Al hydrotalcite dried and then heated for 3 hours at a temperature of 110 °C, after which weigh heavily Mg/Al HT results of heating and heated again at a temperature of 180 °C dive 3 hours. The excess weight of samples before and after heating at a temperature of 180 °C was the H<sub>2</sub>O crystals.

#### **Immobilization Gallic Acid on Mg/Al HT**

a. Determination of wavelength of maximum solution of gallic acid

Solution of gallic acid with a concentration of 25 ppm measured absorbance at a wavelength of 200-700 nm.

b. Effect of medium acidity

A series of 10 mL of 100 mg/L gallic acid solution was prepared and their acidity was adjusted to pH 3; 5; 7; 9 and 11 by using either HCl or NaOH solution. Into every g gallic acid solution, 10 mg of Mg/Al HT was poured and then shaken for 1,5 h. After filtering through whatman paper 42, the concentration of gallic acids in the supernatants were analyzed by using UV-vis spectrometer at maximum wavelength.

#### **Removal of AuCl<sub>4</sub><sup>-</sup> by Mg/Al HT-GA**

##### **Effect of medium acidity**

A series of 10 mL of 100 mg/L AuCl<sub>4</sub><sup>-</sup> solution was prepared and their acidity was adjusted to pH 3; 5; 7; 9 and 11 by using either HCl or NaOH solution. Into every AuCl<sub>4</sub><sup>-</sup> solution, 10 mg of Mg/Al HT was poured and then shaken for 1,5 h. After filtering through whatman paper 42, the concentration of AuCl<sub>4</sub><sup>-</sup> in the supernatants were analyzed by using Atomic absorption spectroscopy (AAS)

##### **Effect of addition 2-propanol through reduction process AuCl<sub>4</sub><sup>-</sup> to Au(0) by Mg/Al HT-GA**

50 mg Mg/Al HT-GA was added to a series of 50 mL of 100 mg/L AuCl<sub>4</sub><sup>-</sup> solution at optimum pH. Into every AuCl<sub>4</sub><sup>-</sup> solution was added 2-propanol with various volume 0 mL (0% v/v); 1 mL (2% v/v); 2,5 mL (5% v/v); 5 mL (10% v/v); 10 mL (20% v/v), and 25 mL (50% v/v). Then shaken for 1,5 h, after shaking the solution were immediately filtered through whatman paper 42. The concentration of AuCl<sub>4</sub><sup>-</sup> in the supernatants were analyzed by using Atomic absorption spectroscopy (AAS). Solid was characterized by using X-ray diffractometer (XRD) and Fourier transform infrared (FT-IR) spectroscopy.

## **RESULT AND DISCUSSION**

#### **Immobilization gallic acid on Mg/Al HT**

##### **Effect of medium acidity**

pH optimum immobilization gallic acid on Mg/Al HT reached at pH 5, while at pH below and above 5, the adsorption decreased.

PH<sub>zpc</sub> value for Mg / Al HT between 8.78 [7] to 12.0 [8] the Mg / Al HT is expected to start positively charged at the pH of the medium in below 8.78. While gallic acid has pK<sub>a1</sub> = 4.4 and pK<sub>a2</sub> = 8.5 [9].

At pH ≈ 5, gallic acid has experienced dissociation and dominant negatively charged species. With the dominant species on the negatively charged gallic acid, making it easier species of negatively charged to interact with the surface Mg / Al HT. However, due to changes in pH values toward the greater value (pH > pH<sub>zpc</sub> and pH > pK<sub>a</sub>), the amount of gallic acid are absorbed in Mg / Al HT decreased, presumably because Mg / Al HT positively charged nature plus the wane. In conditions of high pH (alkaline conditions), the number of ions that OH<sup>-</sup> overflow is imminent competition between ion -OH<sup>-</sup> with gallic acid anion, which results in reduced adsorption.

## Removal of $\text{AuCl}_4^-$ by Mg/Al HT-GA

### Effect of medium acidity

The higher the pH the removal  $\text{AuCl}_4^-$  the wane. pH optimum is reached at pH 3, this can be due to the pH 3 solution is the dominant gold species  $\text{AuCl}_4^-$  [10] so that the process of removal  $\text{AuCl}_4^-$  take optimal.

### Characterization Mg/Al HT-GA after removal $\text{AuCl}_4^-$

Based on data analysis using FTIR, absorption band Mg / Al HT-AG before and after removal  $\text{AuCl}_4^-$  show results that are not much different or similar.

The presence of quinones that results in the oxidation of phenolic compounds as gallic acid were analyzed using infrared spectroscopy made possible overlap between groups  $\text{C} = \text{O}$  or  $\text{C} = \text{C}$  which are characteristic of the quinone carbonyl or carboxylic groups in the region  $1627 \text{ cm}^{-1}$ . It has indicated the formation of quinone compounds with keto-enol group caused reduction of  $\text{AuCl}_4^-$  by the the presence of gallic acid on the surface of the Mg/Al HT.

Meanwhile, the results of the analysis by X-ray diffraction can be seen in Figure 1.

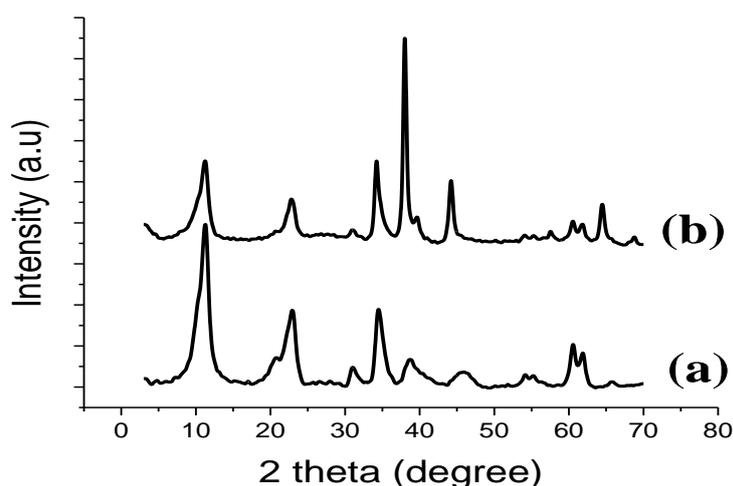


Figure 1. Diffractogram of Mg/Al HT-GA (a) before interaction with  $\text{AuCl}_4^-$ ; (b) after interaction with  $\text{AuCl}_4^-$

The emergence of the characteristic peaks of metallic gold on Mg/Al HT-GA after removal in the 2 theta  $38^\circ$ ,  $44^\circ$  and  $64^\circ$  to the X-ray diffractogram showed metallic Au (0). These three characteristics are the same as the peak of the diffractogram pattern of gold produced by Nakajima et al. [11] and Parajuli et al.[12]. The three characteristic peaks shows that the reflection plane [111], [200] and [220] (JCPDS 4-784). The presence of Au (0) on Mg/Al HT-GA after removal showed that Mg/Al HT-AG is not only able to remove the  $\text{AuCl}_4^-$  but  $\text{AuCl}_4^-$  also reduced to metallic Au (0). The ability of Mg/Al HT-GA in reducing  $\text{AuCl}_4^-$  metals into Au (0) can occur due to presence of gallic acid molecules on the surface of the Mg/Al HT, which has gallic acid 3 - OH group attached to an aromatic ring (Pyrogallol group). Electron-rich aromatic ring, making it easy to oxidize or acts as a reducing agent in the solution for  $\text{AuCl}_4^-$  [12].

### Effect of addition 2-propanol through reduction process $\text{AuCl}_4^-$ to Au(0) by Mg/Al HT-GA

The results of observations of the effect of adding 2-propanol are presented in Figure 2.

In Figure 2 it can be seen that the addition of 2-propanol volume did not significantly affect the removal process  $\text{AuCl}_4^-$ .

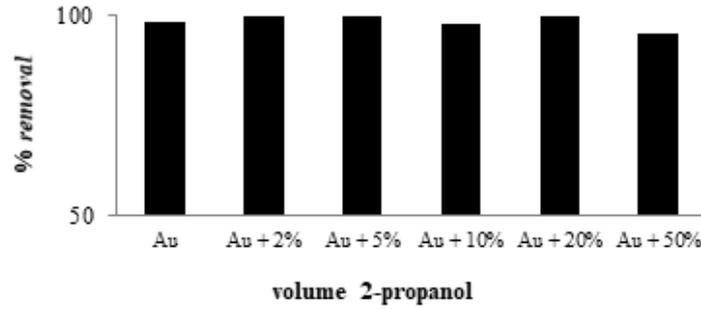


Figure 2. Percent of removal/  $AuCl_4^-$

In Figure 3 it can be seen that the presence of 2-propanol is not very significant influence on reduction of  $AuCl_4^-$  to be Au metal, so it can be said that OH radicals do not play a dominant role on the reduction of  $AuCl_4^-$  to be Au metal.

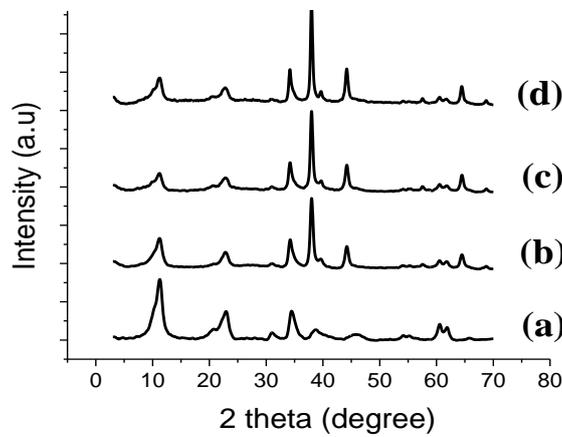


Figure 3. Diffractogram XRD (a) Mg/Al HT-GA prior to the interaction (b) Mg/Al HT-GA after interaction with  $AuCl_4^-$  (c) Mg/Al HT-GA after interaction with  $AuCl_4^-$  with the addition of 5% (v/v) 2-propanol (d) Mg/Al HT-GA after interaction with  $AuCl_4^-$  with the addition of 50% (v/v) 2-propanol.

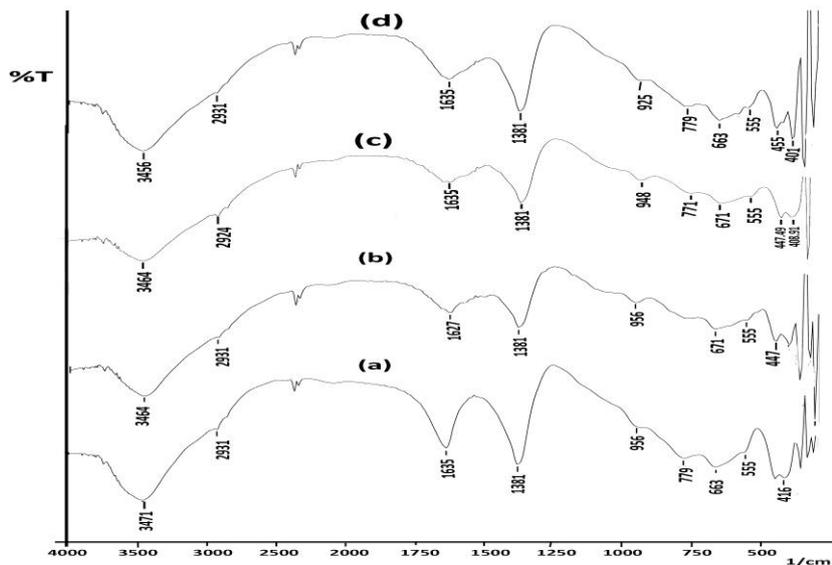


Figure 4. The spectra of infrared Mg/Al HT-GA (a) before the interaction (b) after interaction with  $AuCl_4^-$  (c) after interaction with  $AuCl_4^-$  by addition of 5% (v/v) 2-propanol (d) after interaction with  $AuCl_4^-$  with the addition of 50% (v/v) 2-propanol

Meanwhile, based on data analysis of FTIR with the addition of 2-propanol, there is no significant difference of the absorption peak before and after the addition of the 2-propanol

### CONCLUSION

Based on the XRD, Mg/Al HT has been successfully synthesized at pH 10 with the main peak at  $2\theta = 11.02^\circ$ ;  $22.92^\circ$ ;  $34.77^\circ$  and by FTIR spectra indicate the presence of Mg-O bond and the Al-O on the surface and nitrate anions in interlayer.

The absence of an increase in basal spacing  $d_{003}$  in Mg/Al HT-GA shown that gallic acid on the surface of Mg/Al HT instead on interlayer Mg/Al HT-GA is able to reduce  $\text{AuCl}_4^-$  into Au (0), XRD data indicated the emergence of peak at  $2\theta = 38^\circ$ ,  $44^\circ$  and  $64^\circ$ . The addition of 2-propanol no significant reduction in the  $\text{AuCl}_4^-$  to be Au metal.

### REFERENCES

- [1] Watling K. M., 2007., Spectroelectrochemical Studies of Surface Species in the Gold/Thiosulfate System., *Thesis.*, Grffith Science Environment Engineering and Technology., Griffth University, Australia.
- [2] Laatikainen, M. dan Paatero, E., 2005., Gold Recovery from Chloride Solutions with XAD-7 : Competitive Adsorption of Fe (III) and Te (IV)., *Hydrometallurgy.*, 79., 154 – 171.
- [3] Parajuli, D., Khunathai, K., Adhikari, C.R., Inoue, K., Ohto, K., Kawakita, H., Funaoka, M., and Hirota, K., 2009, Total Recovery of Gold, Palladium, and Platinum Using Lignophenol Derivative, *Miner. Eng.*, 22, 1173-1178
- [4] Hamamoto, K., Kawakita, H., Ohto, K., dan Inoue, K., 2009, Polymerization of Phenol Derivatives by Reduction of Gold Ions to Gold Metal, *React. Funct. Polym*, 69, 694-697.
- [5] Cavani, F., Trifiro, F., and Vaccari, A., 1991, Hydrotalcite-type Anionic Clays : Preparation, Properties and Applications, *Catal. Today*, 11, 173-301.
- [6] Anirudhan, T. S., and Suchithra, P. S., 2008, Synthesis and Characterization of Tannin-immobilized Hydrotalcite as a Potential Adsorbent of Heavy Metal Ions in Effluent Treatments, *Apply. Clay Sci.*, 42, 214-223.
- [7] Das, D. P., Das, J. P. And Parida, K., 2003, Physicochemical Characterization and Adsorption Behaviour of Calcined Zn/Al Hydrotalcites-like Compound (HTlc) Towards Removal of Fluoride from Aqueous Solution, *J. Colloid. Interf. Sci.*, 261, 213-220.
- [8] Martin, M.J.S., Villa, M.V. and Camazano, M.S., 1999, Glyphosate-Hydrotalcite Interaction as Influenced by pH, *Clay and Clays Minerals*, 47, 777-783.
- [9] Slawinska,, D., Polewski, K., Rolewski, P., and Slawinski, J., 2007, Synthesis and Properties of Model Humic Substances Derived from Gallic Acid, *Int. Agrophysics*, 21, 199-208.
- [10] Paclawski, K. dan Fitzner K., 2004, Kinetics of Gold (III) Chloride Complex Reduction Using Sulfur(IV), *Metallurgical and Materials Transactions B*, 35B, 1071-1085.
- [11] Nakajima, A., Ohe, K., Baba, Y., Kijima, T., 2003, Mechanism of Gold Adsorption by Persimmon Gel, *J. Anal. Sci.*, 19, 1075-1077.
- [12] Parajuli, D., Kawakita, H., Inoue, K., Ohto, K., and Kajiyama, K., 2007, Persimmon Peel Gel for the Selective Recovery Of Gold, *Hydrometallurgy*, 87, 133-139.