SYNTHESIS OF GALLIC ACID INTERCALATED Mg/Al-HYDROTALCITE BY DIRECT CO-PRECIPITATION METHOD AND ITS APPLICATION TO ADSORPTION OF Au(III)

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ABSTRACT

Intercalation of gallic acid (GA) on Mg/Al-HT has been performed by direct co-precipitation method of $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$ and GA at various molar ratios. The intercalation products of GA in Mg/Al-HT-GA were characterized by infrared spectrophotometer and XRD diffractometer. The effects of molar ratio variations on the synthesis of Mg/Al-HT-GA and adsorption capacity of Au(III) were also studied. The analysis using an infrared spectrometer and XRD diffractometer showed that GA had been intercalated in the interlayer of Mg/Al-HT with the value of d (basal spacing d_{003}) increased with increasing of the concentration of GA. The adsorption of Au(III) by Mg/Al-HT-GA synthesized was optimum at pH 10 and variation of Mg:Al:GA=2:1:0.5 with the adsorption capacity of 90.1%.

Keywords: Intercalation, Gallic Acid, Mg/Al-Hydrotalcite, Au(III), Adsorption.

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INTRODUCTION

Hydrotalcite (HT) is a type of clay material that is commonly used as adsorbents to adsorb organic and inorganic compounds in solution. The reason behind it is that the HT structure consists of double-layer hydroxides (Layered Double Hydroxides/LDHs) which have a layer of positively charged compounds so that it is capable to adsorb anionics.^{1,2} HT is commonly used for adsorption of anionic compounds in solution such as for the adsorption of sulfate,^{3,4} chromate³ like Cr(VI)¹² and Cr(IV),¹¹ nitrate,⁵ anionic dyes,^{6,13} gold in the form AuCl_4^- ,⁷⁻⁹ and Cu(II).¹⁰ The adsorption of AuCl_4^- or Au(III) in a solution using HT has been done by some researchers using HT for the recovery of gold in solution, however, the adsorbed AuCl_4^- has not been able to be reduced to Au(0).⁷

Modification of HT is necessary for the adsorption and reduction of Au(III) adsorbed on HT simultaneously. Those processes can be optimized by considering the multiple parameters such as the modification because of the surface and interlayer area structure of HT consists of two hydroxide layers.

The bio-adsorbents that have hydroxyl, carbonyl functional groups, etc. can be used as bio-adsorbent for metal ions such as Cr (VI).¹⁴ The modification is typically made by using an organic compound which has a sizeable potential reduction, such as a derivative of phenol compounds that can reduce metal ion.¹⁵⁻²¹

Fitriani⁸ used the derivatives of phenol i.e. gallic acid (GA) to prepare HT-GA which was applied to the adsorption and reduction of Au(III) to Au(0). The results showed better adsorption and reduction activities in the modified adsorbent. Another important parameter in optimizing adsorption and reduction of Au(III) is the optimization of the area of HT through the intercalation between layers using a modifier.

The intercalation between the layers by using a modifier can typically occur via (a) thermal reaction, (b) rehydration of Mg/Al-HT-calcined with a solution containing anions, (c) anion exchange and (d) co-precipitation (direct synthesis) with the addition of a solution of M^{2+} and M^{3+} to the solution anion.²² The intercalation through anion exchange methods was carried out by reacting an anion solution with HT material,⁸ it is observed from the study that the method failed in intercalating the modifier into the interlayer of HT, however, it is only immobilized on the surface.

The direct co-precipitation method (direct synthesis) is a direct deposition process of all metal-forming precursors of HT and modifiers simultaneously under the alkaline conditions. The research on intercalation with direct co-precipitation has shown that method can produce a greater basal spacing than the ion exchange method,²³ so direct co-precipitation method is very effective for the intercalation of the compound in the interlayers of Mg/Al-HT.

EXPERIMENTAL

Material and Methods

This research used materials from E.Merck with pro analysis (p.a) quality i.e. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, HCl, NaOH, HNO_3 and $\text{C}_7\text{H}_6\text{O}_5 \cdot \text{H}_2\text{O}$ (3,4,5-trihydroxy benzoic acid/gallic acid/GA) from Sigma-Aldrich. For the preparation of the Au(III) solution was used Au metal from ANTAM Indonesia.

General Procedure

The synthesis of Mg/Al-HT-GA was carried out using GA of various concentrations of 0.05, 0.1, 0.2, 0.3, 0.5 M and fixed molar composition of Mg: Al (2:1) in alkaline condition (pH=10). The mixture was treated using a hydrothermal method at 120 °C for 5 hours and then was cooled at room temperature. The precipitate was separated from the solution by centrifugation. The precipitate was washed with decarbonized water, filtered and dried at 70 °C for 48 hours. The adsorption of 10 mL Au(III) of 500 $\text{mg} \cdot \text{L}^{-1}$ was performed by using 10 mg Mg/Al-HT-GA at pH=3 for 4.5 hours. After mixing Au(III) and Mg/Al-HT-GA, the solution was filtered using a Whatman paper and was dried at 70 °C for 6 hours.

Detection Method

The characterization of all materials from Mg/Al-HT-GA was performed by using a spectrophotometer Fourier Transform Infra-Red (FTIR) (Shimadzu Prestige-21) to determine the functional group and X-Ray Diffraction (Shimadzu X6000) determine the crystallinity and the distance of the interlayer of Mg/Al-HT-GA. The residue of Au(III) was measured by using Atomic Absorption Spectroscopy (AAS) (Elmer 3110).

RESULTS AND DISCUSSION

The XRD pattern shown in Fig.-1 and Table-1 on the identification of 2-theta (2θ) peak showed considerable differences clearly in the gallic acid intercalated Mg/Al HT depending on the variation of the molar concentration of Mg:Al:GA. The greater concentration of GA caused d_{003} peak shift toward the smaller 2-theta. This indicates that the anion of GA has entered into the interlayers of Mg/Al-HT (interlayer of Mg/Al-HT). The greatest shifting of d_{003} basal spacing occurred on gallic acid intercalated Mg/Al-HT with a molar ratio of Mg:Al:GA was 2:1:0.5 and the value of d_{003} was 9.46 Å.

Fig.-1: XRD Pattern of Mg/Al-HT-GA at Various GA Concentration; (a) 0.05, (b) 0.1, (c) 0.2, (d) 0.3 and (e) 0.5

The result in Fig.-1 and Table-1 showed that the more AG were used for the synthesis of the gallic acid intercalated Mg/Al-HT, and then anion of GA could shift the presence of NO_3^- anions in the interlayer of

Mg/Al-HT, which causes the increase in the basal spacing value of d_{003} . The changes in the basal spacing value of d_{003} reached 1.51 Å on the gallic acid intercalated Mg/Al-HT when the molar ratio of Mg: Al: GA was 2:1:0.5.

Table-1: Identification of 2-theta d_{003} of XRD Pattern of Mg/Al HT-GA in a Various Molar Ratio of Mg:Al: GA

Sample	Mole Ratio (Mg:Al:GA)	2 θ d_{003} (deg)	d_{003} (Å)
a	(2:1:0.05)	11.12	7.95
b	(2:1:0.1)	11.29	7.82
c	(2:1:0.2)	11.29	7.83
d	(2:1:0.3)	10.66	8.29
e	(2:1:0.5)	09.34	9.46

The results of the characterization using FTIR spectrophotometer on gallic acid (GA) intercalated Mg/Al-HT, which was synthesized at the molar ratio of Mg:Al:GA, showed some differences (Fig.-2 and Table-2). The declining peaks of the absorption at 1381 cm^{-1} with the increasing concentration of gallic acid used in the synthesis of gallic acid (GA) intercalated Mg/Al-HT (Fig.-1a to e). The absorption peak at 1381 cm^{-1} is assigned to vibration of the N–O stretching of the anion NO_3^- . This indicates that the number of NO_3^- which was replaced by GA on the HT interlayer raised. The absorption peaks at 1635 and 3464 cm^{-1} were due to respectively the vibration of bending and stretching of O–H from the hydroxyl group of HT. This is due to the increased concentration of GA that could shift the presence of the hydroxyl groups on the surface layer of Mg/Al-HT and H_2O molecules in the interlayers of Mg/Al-HT. The new absorption peaks were observed at 1273 cm^{-1} which was C–O stretching vibration of the carboxylate and the sharp peak at 2931 cm^{-1} was a C–H stretching vibration (sp^2) on the aromatic ring of gallic acid (GA). This phenomenon indicated that the material Mg/Al-HT has intercalated GA under the condition of the higher concentration of GA.

Fig.-2: FTIR Spectra of Mg/Al-HT-GA at Various Concentration of GA; (a) 0.05, (b) 0.1, (c) 0.2, (d) 0.3 and (e) 0.5

Table-2: Identification of FTIR Spectra From Gallic Acid Intercalated Mg/Al-HT at Some Molar Ratios of Mg: Al: GA

Characteristic Band	Wave Number (cm^{-1}) on the Molar Ratio of Mg:Al: GA				
	2:1:0.05	2:1:0.1	2:1:0.2	2:1:0.3	2:1:0.5
O–H stretching	3464	3464	3448	3448	3417
O–H bending	1635	1635	1635	1635	1635
C–H stretching (sp^2)	-	2931	2931	2931	2924
N–O stretching (NO_3^-)	1381	1373	1373	1373	1383
C–O stretching	-	-	-	-	1273
Mg–O–Al vibration	<500	<500	<500	<500	<500

The changes were reinforced by the shift of the vibration absorption peak of O–H stretching toward the smaller wave number. This phenomenon is the same as the character of bentonite after the process of pillarization (intercalation).²⁴ The shift was influenced by strong bonds between atoms due to the difference in electronegativity of each atom. The vibration of O–H stretching diminished after the addition of gallic acid (GA), where previously the group O–H at HT binds with a nitrogen atom (N) of the nitrate anions (NO_3^-). The electronegativity of $\text{O} > \text{N}$ causes the O–H bonds in HT with the O atoms in gallic anions to weaken after HT binds to gallic anion. So that the energy to vibrate the O–H bond from HT is also smaller. Energy will be equivalent to the wavenumber, if the vibrational energy is low then, the wavenumber will also be smaller. Therefore, the wave number on the OH vibration on HT that has remembered the gallic anion will shift towards smaller wavenumbers. It was shown by Fig.-3e, i.e. Mg/Al-HT-GA with a variation of the molar concentration of 2:1:0.5 (Mg:Al:GA).

Fig.-3: The Adsorption Percentage of 10 mL Au(III) 500 mg.L⁻¹ by 10 mL Mg/Al HT-GA Synthesized at Mole Ratios (Mg:Al:GA) a (2:1:0.05), b (2:1:0.1), c (2:1:0.2), d (2:1:3) and e (2:1:0.5) at pH 3 for 270 Minutes.

Figure-3 shows that the adsorption of Au(III) by the adsorbent of Mg/Al-HT-GA increased along with the increasing concentration of gallic acid used in the synthesis of gallic acid intercalated Mg/Al-HT. This was because, at pH 3, H^+ of the gallic acid molecule will act as a hydrogen bridge between the groups with Au(III). Based on these statements it can be concluded that the greater the concentration of gallic acid (GA), the more adsorption of Au (III) will be increased, accompanied by the reduction of Au(III) to Au(0). The adsorption of Au(III) under optimum conditions has an adsorption capacity of 90.1%. The optimum condition occurs at Mg/Al-HT-GA with a molar ratio of Mg:Al: GA (2: 1: 0.5) under acidic conditions (pH = 3) during 270 minutes.

CONCLUSION

The higher concentration of GA used in the modification of Mg/Al-HT caused the occurrence of GA intercalation on the interlayer Mg/Al-HT. GA intercalation in the interlayer HT is known to increase in the basal spacing d_{003} in HT (9.46 Å) with a variation of Mg:Al: GA (2:1:0.05). The higher concentration of GA could cause the replacements of NO_3^- in HT interlayer which was reduced the intensity of absorption peak at 1373-1383 cm^{-1} shown in FTIR spectra, the sharpness of the peak becomes be lower. The greater concentration of GA used in the HT modification causes the increase in Au adsorption capacity up to 90.1%.

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