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Utilization of hydrotalcite modified with 3,4,5-trihydroxybenzoic acid for the treatment of silver-containing wastewater

I Yanti^{1*}, W F Winata², M Anugrahwati¹

¹Chemistry Department, Universitas Islam Indonesia, Yogyakarta, Indonesia

²Environmental Engineering, Universitas Proklamasi 45, Yogyakarta, Indonesia

*E-mail: ika.yanti@uui.ac.id

Abstract. Utilization of hydrotalcite modified with 3,4,5-trihydroxybenzoic acid as a medium for the treatment of silver-containing wastewater has been done by using adsorption method. The modified hydrotalcite was prepared by direct precipitation using Mg and Al metals precursor and an organic compound of 3,4,5-trihydroxybenzoic acid. The modified material was then used for the treatment of silver-containing wastewater through adsorption method together with the determination of adsorption capacity, kinetics study as well as the material characterization after the treatment process. It could be observed from the results that the adsorption of silver onto the modified hydrotalcite was in accordance with Langmuir adsorption model with the adsorption capacity (q_{\max}) of 400 mg.g⁻¹. Moreover, the adsorption kinetics of the treatment showed that the process followed the kinetics model of pseudo-second-order of Ho with the velocity constant (k) of 1.15x10⁻⁴g.mg⁻¹.minute⁻¹. The adsorption process exhibited an exergonic property with the adsorption energy of 28.10x10³ J.mol⁻¹. All of the adsorption processes were conducted in the condition of pH_{adsorption} = 3. Meanwhile, results from the characterization using FTIR showed the functional groups of C=C, -OH and NO₃⁻ on the modified hydrotalcite underwent some alteration after the adsorption process of Ag(I). Therefore it can be observed that the functional groups of COOH and OH had an important role in the adsorption of silver from wastewater.

1. Introduction

Silver-containing wastes are presented in the environment either in the form of solid or liquid waste. The waste in the form of liquid is generated for example from the photography industry because the process of photo printing using a washing solution and fixer which each of them contains silver solution [1]. Silver-containing waste in a solid form is produced from electronic material that contain various metals such as Au 0.1%; Ag 0.2%; Pd 0.005%; Cu 20%; Ni 2%; Sn 4% and Pb 2% [2].

The treatment process of industrial waste particularly the silver-containing one can be done by using materials as adsorbent through adsorption process. Adsorption method has been used for metal recovery from water [3]. The election of adsorbent in this process is tremendously important. The chosen adsorbent must provide a high adsorption capacity, low cost, and an effective capability in adsorption process [4].

Clay material is a layered hydroxide material which is commonly applied in many fields. One of the clay which numerously applied as an adsorbent is hydrotalcite (HT) [5]. Utilization of HT is also applied in the adsorption process of Cu(II), Zn(II) dan Cd(II) [6,7], Pb(II) [8], Cr, As, Se and Hg in the form of species; CrO₄²⁻, Cr₂O₇²⁻, H₂AsO₃⁻, AsO₄³⁻, SeO₃²⁻, SeO₄²⁻, HgCl₄²⁻[9], respectively. HT which is modified with organic compound such as decanoic acid, can increase the adsorption capacity for adsorption process of dyes in a solution [10]. Therefore, in this research, HT modified with 3,4,5-



trihydroxybenzoic acid was prepared to be used in the process of adsorption of silver in a solution, together with the observation of the kinetics studies, adsorption and material characterization for the initial and the final adsorption process.

2. Experimental

2.1. Materials

Materials which were used in this research acquired in 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 , $\text{Ag}(\text{NO}_3)$ and 3,4,5-trihydroxybenzoic acid ($\text{C}_7\text{H}_6\text{O}_5 \cdot \text{H}_2\text{O}$), H_2O , N_2 gas and Whatman filter paper no. 42.

2.2. Instruments

Some laboratory equipments were used in the research, i.e. magnetic stirrer, analytical balance, pH-meter, oven, mortar and pestle. Moreover, analytical instruments which were used i.e. *Fourier Transform Infrared* (FTIR), *Atomic Absorption Spectroscopy* (AAS), *shaker*, glassware and plastic apparatuses.

2.3. Synthesis of Hydrotalcite Modified with 3,4,5-trihydroxybenzoic acid

Some amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dan ($\text{C}_7\text{H}_6\text{O}_5 \cdot \text{H}_2\text{O}$) in a mole ratio of 2:1:0.5 were mixed and dissolved in a 100 mL volumetric flask with CO_2 -free aquadest. The mixture was then added with 0,5 M NaOH solution dropwise until the solution pH was 9 and continued with stirring for ± 30 min under the N_2 flow. The mixture was then heated at 120°C for 5 h, and cooled until the precipitation process was complete. The precipitate was separated by centrifugation then washed using CO_2 -free aquadest until the pH was neutral. The colloidal precipitate still contained with water was then filtered by using Whatman filter paper no. 42 and dried at 70°C for 48 h in an oven. The dried solid was then grinded using porcelain mortar and pestle. Finally the solid was characterized using FTIR in order to observe the vibration of some functional groups contained in the adsorbent.

2.4. Kinetics study of Ag(I) adsorption using the synthesized adsorbent.

As much as 10 mg hydrotalcite modified with 3,4,5-trihydroxybenzoate was interacted with 10 mL solution of Ag(I) $500\text{ mg}\cdot\text{L}^{-1}$ in the pH of 3, the mixture was then shaken in the various time i.e. 0, 10, 20, 30, 60, 90, 120, 150, 200, 250, 300 and 350 min., afterwards, it was filtered by using Whatman filter paper no. 42. At last, the concentration of Ag(I) was measured using AAS.

2.5. Study of adsorption isotherm of Ag(I) onto hydrotalcite modified with 3,4,5-trihydroxybenzoic acid

As much as 10 mg of the modified hydrotalcite was interacted with 10 mL of Ag(I) solution in the concentration variation of 0, 100, 200, 400, 600, 800 and $1000\text{ mg}\cdot\text{L}^{-1}$ under the condition of pH of 3. Then the mixture was stirred for 120 min. and filtered with Whatman filter paper no. 42. Concentration of Ag (I) was analyzed using AAS.

3. Result and Discussion

Study of Ag(I) adsorption was conducted via two methods i.e. (1) determination of adsorption kinetics of Ag(I) by adsorbent of hydrotalcite modified with 3,4,5-trihydroxybenzoic acid in the variation of time and constant concentration of Ag(I), constant pH system, and constant mass of the adsorbent i.e. $500\text{ mg}\cdot\text{L}^{-1}$, pH=3 and 10 mg, respectively, and (2) determination of the model of adsorption isotherm of

Ag(I) by the modified hydrotalcite to determine the adsorption capacity of Ag(I) by the adsorbent in a various concentration of Ag(I) in the constant mass of the adsorbent and the constant pH i.e. 10 mg and pH=3, respectively. Under the condition of pH=3 (adsorption process), Ag ion was present in the form of Ag(I) [11].

Adsorption kinetics of Ag(I) onto the modified hydrotalcite which was synthesized in the mole ratio of $Mg^{2+}:Al^{3+}:AG$ (2:1:0,5) and one which was synthesized in the pH of 9 was observed by interacting as much as 10 mg of the modified hydrotalcite with 10 mL of Ag(I) $500\text{ mg}\cdot\text{L}^{-1}$ solution in a time variation of 0, 15, 30, 60, 90, 120, 150, 200, 250 and 300 min. so that the adsorption equilibrium could be obtained. Active sites on the modified adsorbent would be more actively interact with Ag(I) along with the contact time until the adsorption equilibrium was achieved between the adsorbent and the adsorbate.

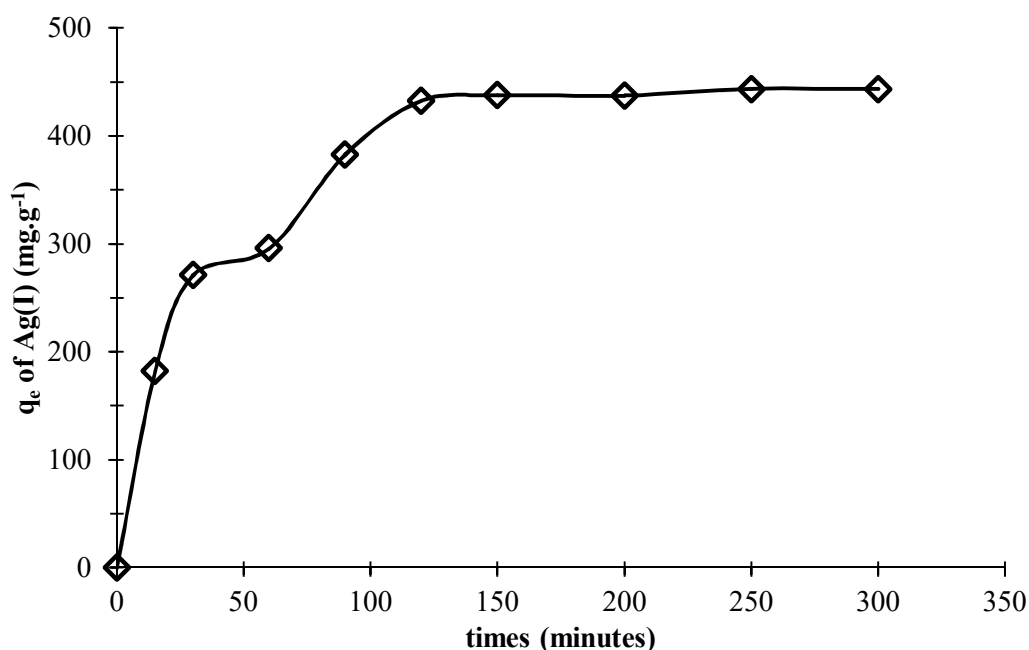


Figure 1. Effect of time on the adsorption of Ag(I) by hydrotalcite modified with 3,4,5-trihydroxybenzoic acid

Based on the results which is shown in Figure 1 adsorption equilibrium of Ag(I) (q_e) by the modified hydrotalcite occurred at the minute of 120 (2 h). After the equilibrium was reached, the adsorption of Ag(I) increased along with the time, however, after 120 min the increase was less significant. Therefore it can be concluded whether the adsorption equilibrium was occurred at the minute of 120. Model of adsorption kinetics of Ag(I) by the adsorbent was observed using kinetics models of Langmuir-Hinshelwood, Lagergreen, Santosa and Ho. Thus, from the kinetics models were obtained some data as it is exhibited in the Table 1.

The model of adsorption kinetics from Langmuir-Hinshelwood is shown an equation in Equation 1.

$$\frac{\ln \frac{C_0}{C_A}}{C_0 - C_A} + K = \frac{k \cdot t}{C_0 - C_A} \quad (1)$$

In which C_0 is an initial concentration, C_A is solution concentration at t , t is adsorption time, k is adsorption rate constant and K is equilibrium constant.

The kinetics model of Langmuir-Hinshelwood was obtained by using linier curve between $\frac{\ln \frac{C_0}{C_A}}{C_0 - C_A}$ vs $\frac{t}{C_0 - C_A}$ so that the slope of the resulting linier equation was assumed as k and the intercept as K . In the

kinetics model, the obtaining K value was negative and it was irrational for the adsorption, therefore the other equation of kinetics model was used. In which, this new model assumed that the adsorption rate of the process involved an adsorption in the order one [12]. This model is called as Santosa kinetics model of adsorption, which is written as Equation 2.

$$\frac{\ln \frac{C_0}{C_A}}{C_A} = \frac{k \cdot t}{C_A} + K \quad (2)$$

The Santosa model was obtained by plotting a linier curve between $\frac{\ln \frac{C_0}{C_A}}{C_A}$ vs $\frac{t}{C_A}$ so that the obtaining slope was assumed as k and the intercept as K . Equation of Santosa kinetics model is more realistic because it gives k and K as a positive value. Another kinetics model which is known as Lagergreen (pseudo-first-order) kinetics model, has an equation of kinetics model shown in Equation 3.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k}{2.303} \right) t \quad (3)$$

Where, q_e is an adsorption capacity in equilibrium and q_t is an adsorption capacity at a certain t . Lagergreen kinetics model was obtained by plotting a linier curve between $\log q_e - q_t$ vs t so that the obtaining slope was assumed as $(k/2.303)$ and the intercept was $\log q_e$ value. The adsorption kinetics was based on the adsorption capacity in solid phases which was mentioned as pseudo-second-order [13]. In the kinetics model of adsorption based on Ho, it was stated as Equation 4.

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (4)$$

Initial adsorption rate was stated in a symbol of h (min^{-1}) and the adsorption rate constant in a symbol of k ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). Kinetics model of pseudo-second-order which was expressed by Ho was obtained by plotting a linier curve between $\frac{t}{q_t}$ vs t so that the obtaining slope was assumed as $\frac{1}{q_e}$ and the intercept as $\frac{1}{h}$, in the equation of $h = kq_e^2$ [13].

Table 1. Calculation results of adsorption kinetics of Ag(I) by hydrotalcite which was modified with 3,4,5-trihydroxybenzoic acid by using several kinetics model

Kinetics model	Kinetics parameters
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	R^2	k	K	h
Langmuir-Hinshelwood	0.0167	$6 \times 10^{-7} \text{ min}^{-1}$	$0.2519 \text{ L.mol}^{-1}$	-
Santosa	0.8873	0.01 min^{-1}	$904.92 \text{ L.mol}^{-1}$	-
Lagergreen	0.9412	0.0094 min^{-1}	-	-
Ho	0.9916	$1.151 \times 10^{-4} \text{ g.mg}^{-1} \cdot \text{min}^{-1}$	-	$26.109 \text{ mg.g}^{-1} \cdot \text{min}^{-1}$

Based on Table 1 concerning the parameters calculation of adsorption kinetics of Ag(I) onto the hydrotalcite, from the four models, it was seen that Ho kinetics model gave the best R^2 value in which $R^2 \approx 1$, compared to the other models. Thus, the adsorption process of Ag(I) by the modified adsorbent was more likely to follow the kinetics model of pseudo-second-order from Ho, with the adsorption rate constant of $1.151 \times 10^{-4} \text{ g.mg}^{-1} \cdot \text{min}^{-1}$. It meant that $1.151 \times 10^{-4} \text{ g}$ of the adsorbent could adsorb 1.0 mg of the adsorbate in 1 min. It could be indirectly assumed that there are two factors which affected adsorption rate of Ag(I) onto the modified hydrotalcite. Moreover, the adsorption constant of Ag(I) could reach $3.798 \times 10^{-4} \text{ g.mg}^{-1} \cdot \text{min}^{-1}$ by using the Ho, kinetics model.

Model of adsorption isotherm which could figure the adsorption pattern of adsorbate onto the adsorbent surface usually was observed by using isotherm model of Langmuir dan Freundlich. The model of adsorption isotherm of Langmuir in the Equation (5) was based on the assumption that adsorption energy depends on the closure of the active sites of the adsorbent in which the sites have a homogenous property so that if the sites have been contained by the adsorbate, it will cause the formation of an only monolayer of the adsorbate on the adsorbent's surface [14-17].

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{maks}} K_L} + \frac{C_e}{q_{\text{maks}}} \quad (5)$$

C_e is the adsorbate concentration at the equilibrium in a solution (mg.L^{-1}), q_e is the amount of adsorbate which was adsorbed at the equilibrium by each g of adsorbent (mg.g^{-1}), K_L is Langmuir constant (L.mg^{-1}) dan q_{maks} is the maximum capacity of the adsorbent (mg.g^{-1}). Determination of the maximum adsorption capacity (q_{maks}) was conducted by the model of Langmuir isotherm, i.e. by plotting a linear curve between C_e/q_e vs C_e .

$$\log q_e = \log K_F - \frac{1}{n} \log C_e \quad (6)$$

Model of adsorption isotherm of Langmuir in the Equation 6 was based on the assumption that the adsorption energy depends on the interaction of adsorbate with the adsorbent's surface which has a heterogeneous property [14-17]. The surface heterogeneity could cause different interaction among one active site and the others with the adsorbate molecule so that the adsorbate's surface which was bonded on the adsorbent's surface could form more than one layer (*multilayers*).

Table 2. Parameters of adsorption isotherm of Freundlich and Langmuir in the adsorption process of Ag(I) by hydrotalcite modified with 3,4,5-trihydroxybenzoic acid

Isotherm Model	Parameters			
	R^2	K	n	q_{max}

Freundlich	0.5294	366.7 mg.g ⁻¹ (K _F)	50.761	-
Langmuir	0.9992	8.4273x10 ⁴ L.mg ⁻¹ (K _L)	-	400 mg.g ⁻¹

In the Tabel 2, it is known that the adsorption process of Ag(I) by the modified hydrotalcite followed the model of Langmuir isotherm with the R² value was 0.9992, and the adsorption capacity was 400 mg.g⁻¹. Based on the model, it was assumed that the adsorbent's surface was homogenous which caused the formation of the adsorbate monolayer from the Ag(I) adsorption onto the adsorbent's active sites. It occurred as the active sites had the same adsorption energy to the adsorbate so that it was more likely to form the adsorbate monolayer. It went to the same way for the adsorption isotherm of Ag(I) onto the modified hydrotalcite which was known to follow the isotherm model of Langmuir (Figure 2).

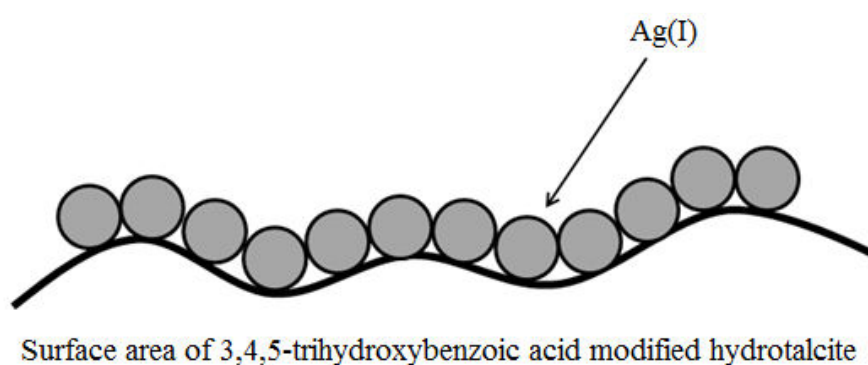


Figure 2. Illustration of the adsorption model of Langmuir in the adsorption peocess of Ag(I) onto the hydrotalcite modified with 3,4,5-trihydroxybenzoic acid

The adsorption energy was calculated by the equation of Gibbs free energy as mentioned in the Equation 1. According to the equation, adsorption energy could be calculated from the Langmuir constant so that it could be obtained value of the adsorption energy of Ag(I) by the 3,4,5-trihydroxybenzoic acid modified hydrotalcite of $-28.100 \times 10^3 \text{ J.mol}^{-1}$ which was shown that the adsorption reaction had an *exergonic* property.

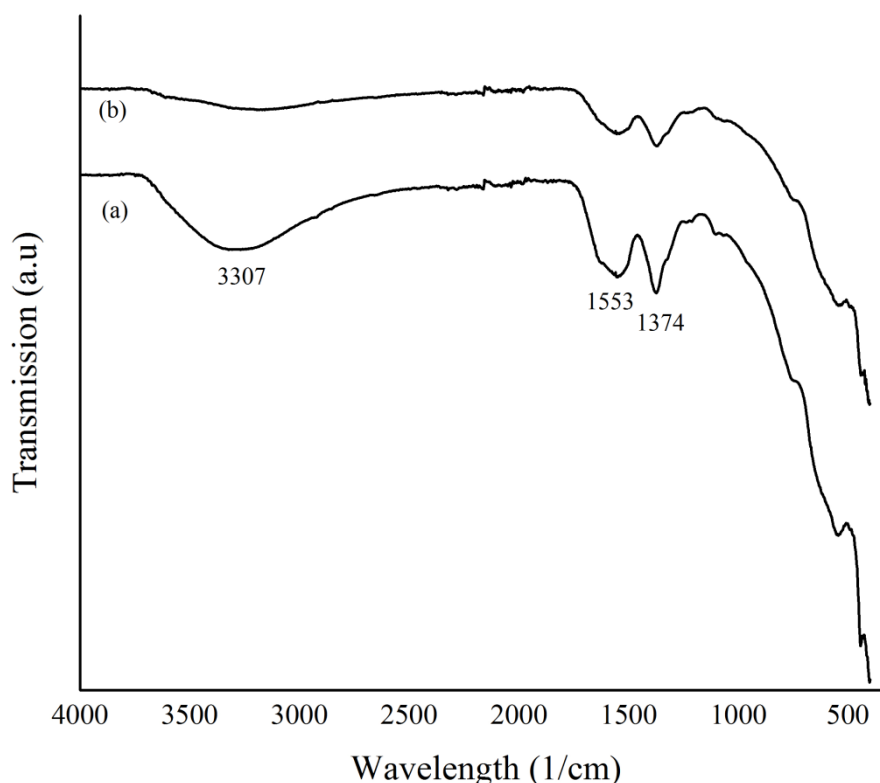


Figure 3. FT-IR spectra of 3,4,5-trihydroxybenzoic acid modified hydrotalcite (a) before and (b) after being used to remove Ag(I)

Based on the Figure 3., it could be seen that the functional groups in the 3,4,5-trihydroxybenzoic acid modified hydrotalcite had an important roles in the adsorption process of Ag(I) in the solution. It was observed from the alteration in the wavenumber of 3307 cm^{-1} which showed vibration of -OH either from the groups of 3,4,5-trihydroxybenzoic acid or from the hydroxyl group in the hydrotalcite itself. The alteration in the wavenumber of 1553 cm^{-1} showed the vibration of aromatic $\text{C}=\text{C}$ owned by 3,4,5-trihydroxybenzoic acid. Finally, the wavenumber of 1374 cm^{-1} illustrated the vibration of N-O from the NO_3^- group which filled the interlayer area of hydrotalcite.

4. Conclusion

Adsorption model of the Ag(I) containing wastewater by using 3,4,5-trihydroxybenzoic acid modified hydrotalcite followed the adsorption model of Langmuir with the adsorption capacity (q_{max}) of 400 mg.g^{-1} . The results of the kinetics study from the adsorption process showed that it followed the Ho kinetics model of pseudo-second-order with the rate constant (k) of $1.15 \times 10^{-4}\text{ g.mg}^{-1}.\text{min}^{-1}$. The adsorption process was exergonic with the adsorption energy value of $28.10 \times 10^3\text{ J.mol}^{-1}$. All of the adsorption conditions was set at $\text{pH}_{\text{adsorption}}=3$. The results from the characterization using FTIR figured that the functional groups of $\text{C}=\text{C}$, -OH dan NO_3^- in the modified hydrotalcite underwent some alterations after the Ag(I) adsorption process. Therefore, it could be assumed that the groups of COOH and OH had an important role in the adsorption of Ag(I) in a solution.

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