

Hydrotalcite Mg/Al-NO₃ from Sea Water as Adsorbent of CU²⁺ and Cr⁶⁺ Metals

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Abstract- Seawater is a renewable natural resource that is easy to get for use in various purposes. Seawater has many mineral deposits, one of which is MgCl₂. This research aims to synthesize Mg/Al-NO3 hydrotalcitelike with Mg raw material from seawater, characterization and test the adsorption capacity to Cu²⁺ and Cr⁶⁺ metals. Mg/Al hydrotalcite-like synthesis with NO3 interlayer was performed on a 2: 1, 2,5: 1, 3: 1-mole ratio with pH 10 for 1 hour coprecipitated. Characterization of Mg/Al-NO₃ Hydrotalcite-like using Atomic absorption spectrophotometry (AAS), X-Ray Diffraction (XRD), XRF(X-ray fluorescence spectrometry), Surface Area Analyzer (SAA). The hydrotalcite-like adsorption power application was tested against Cu²⁺ and Cr⁶⁺ metals. The results showed that Mg/Al-NO₃ Hydrotalcite-Like formed at d003, d006, and d110 were 8,55, respectively; 3,86; and 1,51 Å according to the ICDD Hidrotalsit Mg/Al-NO₃ standard, and the area covered by SAA was 132,081 m²/ g, with compositions tested by XRF on $\ensuremath{\text{Mg}}(OH)_2$ and Al(OH)₃ were 11,5 g/ml and 20,3 g/ml, respectively. Hidrotalsit Mg/Al-NO3 adsorption Cu2+ occurred of 3.63 mg/g at 30 min contact time and Cr^{6+} metal of of 0,75 mg/g at contact 60 minutes.

Keywords: adsorbent, synthesis, hydrotalcite, seawater

I. INTRODUCTION

Seawater is a renewable resource that is easily available for use in various purposes. Indonesia is an archipelagic country surrounded by the sea with an area of waters reaching two-thirds of the land area, which is one of the factors that support seawater to be utilized in the field of scientific research. Seawater has a lot of mineral content, besides salt, there are also chemicals such as MgCl₂. hydrotalcite from magnesium originating from the artificial sea which contains the main compounds NaCl, Na₂SO₄, MgCl₂, and CaCl₂ [6].

Mineral Hydrotalcite is a double-layered hydroxide that has a negatively charged layer with cations on the interlayer[4]. Anionic clays such as hydrotalcite are less abundant in nature than cationic clays, but anionic clays are easily synthesized. The hydroxide layer has a brucite-like structure and is known as the double hydroxides layer [2] with a general formula $[M^{2+}_{1-x}M^{3+}x(OH)_2]^{x+}$ [A_{n-b}/n].mH₂O, where M^{2+} and M^{3+} is metal pollution such as copper (Cu²⁺) in an aquatic environment that can pose a danger to health in humans, animals and plants. If the

copper metal content in the aquatic ecosystem exceeds the maximum concentration limit, a metal bioaccumulation process can occur in living things. Cu metals in the form of metalloproteins can show reduced oxidation activity, from Cu^{2+} to Cu^+ which can change the structure and function of proteins in living organisms. When Cu enters and accumulates in the human body in high concentrations it can be toxic and result in damage to the liver and kidneys through strong bonds with metallothionein residues [16].

Adsorption is the most effective method for reducing heavy metal pollutants. Adsorbent material has been widely developed in minimizing heavy metal contamination in the water is hydrotalcite. Hydrotalcite has a memory effect (can be regenerated) [12] and has low toxicity. This study utilizes magnesium from Tidung Island sea water as a raw material for making hydrotalcite Mg/Al-NO3 with NO₃ interlayer. Magnesium from seawater was then added by Al (NO₃)₃.9H₂O, by comparing variations in the mol ratio of Mg and Al using the coprecipitation method and its application used as an adsorbent of metal ions Cu^{2+} and Cr^{6+} . The purpose of this study was to determine the characteristics of hydrotalcite Mg / Al-NO₃ using SAA, XRD and XRF and determine the adsorption capacity of metal ions Cu²⁺ and Cr⁶⁺ by Hydrotalcite Mg /Al-NO_{3.}

II. MATERIALS AND METHODS

A. Materials

The material used in this study is sea water from Tidung Island Beach which was taken on, $Al(NO_3)_3.9H_2O(p.a)$, $Na_2NO_3(p.a)$, $NaHCO_3$ (p.a), $Na_2CO_3Aquadest$, NaOH, Cr^{6+} logam (p.a), $CuSO_4(p.a)$, $HNO_3(p.a)$, APDC (*Ammonium Pyrrolidine Dithiocarbamate*) (p.a), MIBK (*Methyl Isobutyl Keton*)(p.a), $Na_2SO_4(p.a)$, $AgNO_3(p.a)$, gas N_2 , HCl (p.a), dan NaOH (p.a).

B. Instrumentation

The tools used in this research are Whatman no.2 filter paper, thermometer, hot plate, Erlenmeyer, centrifuge, a set of glassware, stirrer, stirrer, oven, pH meter, desiccator, volumetric pipette, drop pipette, three-foot flask, AAS Shimadzu instrument AA-7000, SAA Autosorb-1, and Shimadzu XRD-600 X-Ray diffractometer.

C. Procedure

Analysis of Mg²⁺ and Ca²⁺ in seawater with AAS Seawater is filtered using filter paper on the water pump with water volume 1 L. The filtered sample water is placed in a 1 L measuring cup, set the pH of the sample with 1N HNO₃ as much as 20 drops or with 1 N NaOH up to pH 3. Then the sample is concentrated by heating using hot plate until the volume becomes 500 ml. Then poured into Erlenmeyer and cooled to 30°C. The sample was added 5 ml APDC, then homogenized. Added MIBK (Methyl Isobutyl Ketone), shaken for 30 seconds and allowed to stand until two layers formed, the water phase was removed and the organic phase was collected into the test tube. If foam or emulsion is formed Na₂SO₄ is added. Then the filtrate was tested using AAS. Impurity of Ca²⁺ from Sea Water [6]. 100 mL of sea water is added with a solution of 0.001 M Na₂CO₃ and 0.002 M NaHCO₃, stirred for one hour at 700C. Ca content analyzed by AAS.

• Synthesis of Hydrotalcite Mg / Al-NO₃ from Seawater [5]

A total of 250 mL of a mixture of 0.1 M NaNO₃ and 1 M NaOH was added slowly to a reactor containing 50 ml of a mixture of Al (NO₃) $3.9H_2O$, and a magnesium solution of seawater, with variations in the Mg /Al 2 mole ratio : 1; 2.5: 1; and 3: 1 to pH 10. The solution is stirred for 1 hour at 700C, left for 12 hours then washed using distilled water until free of chloride, white solids are dried using an oven at $60^{\circ}C$ for 6 hours.

• Characterization of Mg / Al-NO₃ Hydrotalcite

The hydrotalcite crystal structure was characterized using Xray diffractometer (XRD) and scanned every 0.020 / second with an angle range of $2\Theta = 100$. Determination of the surface area of the material was analyzed using the Surface Analyzer Area (SAA) and the composition of the hydrotalcite sample was Fluorescence analyzed using X-Ray Spectrometry (XRF).

• Determination of Cu²⁺ metal adsorption capacity with time variations.

A total of 0.1 g of Mg /Al-NO₃ hydrotalcite was put into a beaker glass containing 20 ml of a solution of Cu^{2+} metal ion concentration of 20 mg / L with a variation of time 0, 15, 30, 45, and 60 minutes at optimum pH 5 which was regulated by addition of 0.05 M NaOH and 0.05 M HCl, then stirred at a speed of 200 rpm at 25^oC for 1 hour. The solution was filtered with filter paper and added 1 drop of concentrated HNO₃ solution, then analyzed using AAS. The same procedure is also performed on Cr⁶⁺ metals.

III. RESULTS AND DISCUSSION

A. Analysis Mg^{2+} and Ca^{2+} in Sea Water

Testing of the levels of Mg^{2+} and Ca^{2+} found in Tidung Island seawater was carried out in two ways, namely treatment-free test results obtained at 1.481% and 0.129%. While the levels of Mg^{2+} and Ca^{2+} with

treatment and treatment using additional Na₂CO₃ or NaHCO₃ solution to reduce Ca²⁺ levels - each level of Mg²⁺ and Ca²⁺ was obtained at 0.905% and 0.098%. Ca²⁺ ions have a large influence as impurities in the synthesis of hydrotalcite, because calcium can form bicarbonate salts, and settles as white deposits similar to Mg deposits, so that before the synthesis it is necessary to remove Ca²⁺ ions. The Ca²⁺ ion in this study can be reduced by adding a mixture of Na₂CO₃ and NaHCO₃ to sea water [6].The solution of sodium bicarbonate derived from a mixture of sodium carbonate (Na₂CO₃) and sodium bicarbonate (NaHCO₃) will react with CaCl₂ to form bicarbonate salts with the reaction equation as below.

$$CaCl_2 + 2NaHCO_3 \longrightarrow Ca(HCO_3)_2 + 2NaCl_2$$

The decrease in Ca²⁺ levels in this study was 0.031% and Mg²⁺ of 0.576%. The results of this study are different from the research which states that sedimentation in this way can precipitate 3% of Mg²⁺ and 96% ions of Ca²⁺ from total metal ions in sea water [6]. This can be caused because in this study using pure seawater, while sea water used in the study is a mixture of dolomite seawater, so that the calcium content can be deposited 96% [6].

• Synthesis of Hydrotalcite Mg / Al-NO₃⁻[1]

Mg/Al-NO₃ hydrotalcite was synthesized by coprecipitation method with NO₃ interlayer. hydrotalcite synthesized by comparison of variations in the mg ratio of sea water and Al 2: 1; 2.5: 1; and 3: 1. The Ca²⁺ content in seawater is kept to a minimum, this is to avoid the formation of impurities when the synthesis takes place. The pH of the solution is maintained at pH so that Al³⁺ ions do not form deposits of Al(OH)₃. Conversely, if the pH of the solution is less than pH 10, there will be precipitation of compounds other than hydrotalcite Mg/Al-NO₃.

The stability of hydrotalcite Mg / Al-NO₃ is influenced by the size of the constituent cation radius, so that the structure of Mg / Al-NO₃ becomes unstable if the cation radius M₂ is + <0.06 nm. The results of empirical calculation of hydrotalcite Mg/Al-NO3 from seawater are $[Mg_{0.691}Al_{0.31}(OH)_2(NO_3)_{0.31.0.5}(H_2O)]$. This is in accordance with the results of calculations obtained [11], with hydrotalcite Mg / Al-NO₃ synthesized from pure compounds namely $[Mg_{0,686}Al_{0,313}(OH)_2(NO_3)_{0,31.0,848}(H_2O)].$ Empirical calculations show no significant difference in the ratio of Mg /Al and nitrate anions between hydrotalcite Mg / Al-NO3 from pure compounds with hydrotalcite Mg/Al-NO3 from seawater.

B. Characterization Test of Mg / Al-NO₃ Hydrotalcite Using X-Ray Diffractometer (XRD)

Synthesis of hydrotalcite Mg/Al-NO₃ was characterized using X-ray Diffractometer (XRD). This

analysis aims to identify that the main compounds synthesized are Hydrotalcite Mg / Al-NO₃.

Three peaks in the Hydrotalcite Mg /Al-NO₃ sample with a comparison of the mole variation in this study had different d-spacing. The d-spacing includes d₀₀₃ peaks namely Mg (OH)₂, d₀₀₆ peaks namely Al(OH)₃, and peak d110 namely NO₃. Mole variation of 2: 1 Hydrotalcite Mg/Al-NO₃ has three peaks of d-spacing, respectively 8.30; 3.80; and 1.50. Molecular variation of 2: 1, Hydrotalcite Mg/Al-NO₃ has three spikes d-spacing 003, 006, and 110 which are not the same as Mg/Al hydrotalcite-like ICDD standard in Figure 1. A mole of variation 2.5: 1 has three d-spacing peaks respectively 8.55; 3.86; and 1.51 Å, wherein moles variation 2.5: 1 has the same d-spacing as the standard ICDD Mg / Al hydrotalcitelike. 3: 1-mole variation has three shoots of d-spacing respectively 8.22; 3.97; and 1.50 Å where in moles of 3: 1 d-spacing is not the same as Mg / Al hydrotalcitelike ICDD standard.

Figure 1. Difraktogram of $Mg/AlNO_3$ hydrotalcite from sea water (a) $Mg / Al NO_3$ hydrotalcite 2: 1 (b) $Mg / Al NO_3$ hydrotalcite 2.5: 1 (c) $Mg / Al NO_3$



hydrotalcite-like 3:1

Table 1. *Value* of reflection of the field synthesized by Hydrotalcite Mg / Al-NO₃ from seawater

Value of reflectio ns the	Mg/Al hydrotalc ite	Hidrotalsit Mg/Al- NO ₃ 2:1	Hidrotalsit Mg/Al- NO ₃ 2,5:1	Hidrotalsit Mg/Al-NO ₃ 3:1 (Å)
mea	ICDD (Å)	(A)	(A)	
d ₀₀₃	8,59	8,30	8,55	8,22
d ₀₀₆	3,79	3,80	3,86	3,97
d ₁₁₀	1,52	1,50	1,51	1,50

Hydrotalcite Mg/Al-NO₃ has three main peaks which are special features of a layered structure on Hydrotalcite Mg/Al-NO₃ namely 003, 006, and 110 [3]. The special three-peak d-spacing value in the sample is a comparison of mole variation and d-price Standard spacing is shown in Table 1. Table 1 shows the d-spacing of Hydrotalcite Mg/Al-NO₃ by the ICDD standard in the ratio of mole variations to 2.5: 1. This identified that Hydrotalcite Mg/Al-NO₃ was formed at a ratio of 2.5: 1.

The results of the study for Mg/Al hydrotalcitelike with the NO₃ interlayer have d_{003} of 9.03. Hydrotalcite Mg /Al-NO₃ from seawater in this study had d_{003} of 8.55 [10]. The low intensity of d^{003} formed can be made possible due to the presence of remaining calcium ions, and precursors in sea water that might react, thus inhibiting the formation of hydrotalcite-like, which results in very low crystallization of Hydrotalcite Mg/Al-NO₃ [3]. The synthesis process shows that metal hydroxide compounds have been formed, these metal hydroxide compounds are Mg(OH)₂ and Al(OH)₃ compounds which have peaks of 2Θ in a row around 19° and 20° . The possibility of Al (OH)₃ settles first because it has a smaller solubility value compared to $Mg(OH)_2$ or Ca(OH)₂ which is supported by XRF results data which shows the composition of the content of Hydrotalcite Mg/Al-NO₃ constituents [1].

The cause of the emergence of unwanted new peaks in the Hydrotalcite Mg / Al-NO3 sample is also influenced by the presence of mother liquid when left for 24 hours [4]. Hydrotalcite Mg/Al-NO₃ which was left for a long time in water produced a higher crystallization rate compared to hydrotalcite Mg / Al-NO₃ which was left in the mother liquor [9]. This condition is possible to be influenced because in a solution that is left to stand for 24 hours, the mother liquor is still left so that it causes the development of fine particles blocked by larger particles.

C. Analyzed the Content Contained in the Sample with a Ratio of 2.5: 1 Using XRF

Table 2. The results of the analysis of levels of Mg (OH)₂ and Al(OH)₃ using XRF

	Mg(OH) ₂	Al(OH) ₃
Concentrations (g/ml)		
	11.5 g/ml	20.3 g/ml

Table 2 shows that in the synthesized sample Hydrotalcite Mg/Al-NO₃ contained the main components of reducing Hydrotalcite Mg/Al-NO₃ namely Mg(OH)₂ and Al (OH)₃ in the amount of 11.5 g / ml and 20.3 g / ml, so that the mole ratio of Mg / Al ratio is obtained. The component of Al(OH)₃ in this study has the largest amount, compared with the results of a study which states that the main component of the largest constituent is Mg (OH)₂ of

20 g /m [7]. It can be assumed that the deposition of the hydrotalcite $Mg/Al-NO_3$ phase that occurs is imperfect.

D. Surface Area Analyzer (SAA)

To determine the surface area, Hydrotalcite $Mg/Al-NO_3$ was analyzed by Surface Area Analyzer (SAA) by the BET method (Brunauer, Ermet, and Teller). The results of the analysis can be seen in Table 3.

Table 3. Data on the Results of Surface Analysis ofHydrotalcite Mg /Al-NO3

No	Ratio	Parameters		
	Mg:Al	Surface Area	Radius	
		m^2/g	Á	
1	2:1	85,557	1,1255	
2	2,5:1	132,081	9,884	
3	3:1	283,504	7,6553	

The results of the analysis in Table 3 show that the specific surface area of Hydrotalcite Mg/Al-NO3 for a ratio of 2: 1 is 85.557 m²/g. The ratio of 2.5: 1 has a surface area of 132.081 m $^{2}/g$, and for a ratio of 3: 1 it has a surface area of 283.504 m²/g. This significant difference allows for the presence of other impurities found in the synthesis of Hydrotalcite Mg/Al-NO₃.Hydrotalcite Mg/Al-NO₃ with a mole ratio of 2.36: 1 and using the BET method has a surface area of 186.8 m²/g [13]. Mg/Al-NO₃ hydrotalcite from seawater can be classified as mesopore, because it has a radius of 10-100 Å, and has a surface area of 40-240 m²/g, wherein that area are other microcrystalline regions, such as Al $(OH)_3$ and Mg $(OH)_2$ [15]. The similarity of surface area hydrotalcite-like data from seawater in this study is in the variation ratio of 2.5: 1 with the results of previous studies namely at ratio 2.36: 1. Identify that hydrotalcite-like Mg /Al-NO₃ is formed [13].

E. Determination of Hydrotalcite Mg / Al-NO₃ adsorption capacity with time variation



Figure 2. The adsorption capacity of Mg/Al-NO₃ hydrotalcite with time comparison

Based on Figure 2 it is known that the adsorption capacity occurs very quickly in the 30 minutes for Cu^{2+} metal ions. This is indicated by the reduction in

the amount of Cu^{2+} metal ions absorbed by the surface of Hydrotalcite Mg/Al-NO₃ and has reached the equilibrium point because there is no change until 60 minutes. Whereas Cr6+ metal ions were adsorbed very fast at 60 minutes but at 45 minutes there was a slowdown of Cr⁶⁺ metal ion adsorption, because the surface-active side of hydrotalcite Mg/Al-NO₃ had not experienced saturation point during precipitation reaction[10]. This is supported by the results of adsorption efficiency which can be seen in Figure 3.



Figure 3. per cent adsorption of Cu^{2+} and Cr^{6+} by Mg /Al-NO₃ with time variations

Figure 3 shows that the maximum per cent adsorption for Cu^{2+} of 99.9% occurs at 30 minutes contact time which is indicated by the achievement of an equilibrium point. Whereas in Cr^{6+} there was a fluctuation in per cent adsorption from contact time of 15 minutes to 60 minutes. This is due to the process of adsorption and desorption. The longer the contact time of adsorption, the higher the surface adsorption ability of Hydrotalcite to Cu^{2+} metal ions and Cr^{6+} metal ions which is characterized by a reduction in the concentration of Cu^{2+} and Cr^{6+} metals [8].

IV. CONCLUSION

The optimum mole ratio for synthesizing Hydrotalcite Mg / Al-NO3 from seawater is at a mol ratio of 2.5: 1 at pH 10 with a temperature of 700C within 1 hour. The characteristic Hydrotalcite Mg/Al-NO3 from seawater has a surface area of 132,081 m2/g, according to the surface area of hydrotalcite previous studies amounted to 40-240 m2/g and has a pore radius of 10-100Å in the ratio 2.5: 1.

Hydrotalcite Mg /Al-NO3 with a variation of 2.5: 1 has d-spacing 8.55; 3.86; and 1.51 Å, d-spacing is in accordance with the ICDD hydrotalcite-like standard, which shows that Hydrotalcite Mg / Al-NO3 has been formed. Hydrotalcite Mg/Al-NO3 has an adsorption capacity for Cu2+ metal is 3.56 mg / g for contact time of 30 minutes at 3.63 mg / g and for Cr6+ metal is 0.021 mg / g for contact time 60 minutes of 0.75 mg / g.

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