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 hydrotalcite-like 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 h coprecipitated. Characterization of Mg/Al(NO₃)₂ 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)₂ Hydrotalcite-Like formed at d003, d006, and d110 were 8,55, respectively; 3,86; and 1,51 Å according to the ICDD Hydrotalcite Mg/Al-NO₃ standard, and the area covered by SAA was 132,081 m²/g, with compositions tested by XRF on Mg(OH)₂ and Al(OH)₃ were 11,5 g/ml and 20,3 g/ml, respectively. Hydrotalcite Mg/Al-NO₃ adsorption Cu²⁺ occurred of 3,63 mg/g at 30 min contact time and Cr⁶⁺ metal 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 [M²⁺₁,M⁺₄ x(OH)₄]⁺[Aₓ/₅,M/₅]⁺mH₂O, where M²⁺ and M⁺ 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 Cu²⁺ 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 Cu²⁺ and Cr⁶⁺. 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-NO₃.

II. MATERIALS AND METHODS

A. Materials

The material used in this study is sea water from Tidung Island Beach which was taken on, Al(NO₃)₃.9H₂O(p.a), Na₂NO₃(p.a), NaHCO₃ (p.a), Na₂CO₃Aquadest, NaOH, Cr⁶⁺ logam (p.a), CuSO₄(p.a), HNO₃(p.a), APDC (Ammonium Pyrrolidine Dithiocarbamate) (p.a), MBK (Methyl Isobutyl Ketom) (p.a), Na₂SO₄(p.a), AgNO₃(p.a), gas N₂, 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-6000 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 Na₂SO₃ is added. Then the filtrate was tested using AAS. Impurity of Ca²⁺ from Sea Water [6]. 100 ml of seawater is added with a solution of 0.001 M Na₂CO₃ and 0.002 M NaHCO₃, stirred for one hour at 700°C. 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) 3.9H₂O, 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 700°C, left for 12 hours then washed using distilled water until free of chloride, white solids are dried using an oven at 60°C for 6 hours.

- Characterization of Mg / Al-NO₃ Hydrotalcite

The hydrotalcite crystal structure was characterized using X-ray diffractometer (XRD) and scanned every 0.020 / second with an angle range of 2θ = 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 analyzed using X-Ray Fluorescence 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 Cu²⁺ 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°C 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 Cr²⁺ metals.

III. RESULTS AND DISCUSSION

A. Analysis Mg²⁺ and Ca²⁺ in Sea Water

Testing of the levels of Mg²⁺ and Ca²⁺ 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 Mg²⁺ and Ca²⁺ 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.

$$\text{CaCl}_2 + 2\text{NaHCO}_3 \rightarrow \text{Ca(HCO}_3\text{)}_2 + 2\text{NaCl}$$

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 hydroxide 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 10 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 M⁺ is < 0.06 nm. The results of empirical calculation of hydroxide Mg/Al-NO₃ from seawater are \([\text{Mg}_{0.686}\text{Al}_{0.31}\text{OH}(\text{NO}_3)_{0.31}\text{(H}_2\text{O})]\). This is in accordance with the results of calculations obtained [11], with hydrotalcite Mg / Al-NO₃ synthesized from pure compounds namely \([\text{Mg}_{0.686}\text{Al}_{0.31}\text{OH}(\text{NO}_3)_{0.31}\text{(H}_2\text{O})]\).

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 hydroxide Mg/Al-NO₃ was characterized using X-ray Diffractometer (XRD). This
analysis aims to identify that the main compounds synthesized are Hydrotalcite Mg / Al-N03.

Three peaks in the Hydrotalcite Mg / Al-N03 sample with a comparison of the mole variation in this study had different d-spacing. The d-spacing includes d_{003} peaks namely Mg (OH)_2, d_{006} peaks namely Al(OH)_3, and peak d_{110} namely NO_3. Mole variation of 2: 1 Hydrotalcite Mg/Al-N03 has three peaks of d-spacing, respectively 8.30; 3.80; and 1.50. Molecular variation of 2: 1, Hydrotalcite Mg/Al-N03 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 hydrotalcite-like. 3: 1-mole variation has three shoots of d-spacing 003, 006, and 110 which includes d_{003} peaks namely 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-N03 constituents [1].

The cause of the emergence of unwanted new peaks in the Hydrotalcite Mg / Al-N03 sample is also influenced by the presence of mother liquid when left for 24 hours [4]. Hydrotalcite Mg/Al-N03 which was left for a long time in water produced a higher crystallization rate compared to hydrotalcite Mg / Al-N03 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

<table>
<thead>
<tr>
<th>Concentrations (g/ml)</th>
<th>Mg(OH)_2</th>
<th>Al(OH)_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.5 g/ml</td>
<td>20.3 g/ml</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 shows that in the synthesized sample Hydrotalcite Mg/Al-N03 contained the main components of reducing Hydrotalcite Mg/Al-N03 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/m² [7]. It can be assumed that the deposition of the hydrotalcite Mg/Al-N03 phase that occurs is imperfect.

**D. Surface Area Analyzer (SAA)**

To determine the surface area, Hydrotalcite Mg/Al-N03 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 of Hydrotalcite Mg/Al-N03**

<table>
<thead>
<tr>
<th>No</th>
<th>Ratio</th>
<th>Surface Area</th>
<th>Radius</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg:Al</td>
<td>m²/g</td>
<td>Å</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2:1</td>
<td>85,557</td>
<td>1,1255</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.5:1</td>
<td>132,081</td>
<td>9,884</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3:1</td>
<td>283,504</td>
<td>7,6553</td>
<td></td>
</tr>
</tbody>
</table>

The results of the analysis in Table 3 show that the specific surface area of Hydrotalcite Mg/Al-N03 for a ratio of 2:1 is 85.557 m²/g. The ratio of 2.5:1 has a surface area of 132.081 m²/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-N03 Hydrotalcite Mg/Al-N03 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-N03 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-N03 is formed [13].

**E. Determination of Hydrotalcite Mg / Al-N03 adsorption capacity with time variation**

Based on Figure 2 it is known that the adsorption capacity occurs very quickly in the 30 minutes for Cu²⁺ metal ions. This is indicated by the reduction in the amount of Cu²⁺ metal ions absorbed by the surface of Hydrotalcite Mg/Al-N03, 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-N03 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 2. The adsorption capacity of Mg/Al-N03 hydrotalcite with time comparison**

**Figure 3. per cent adsorption of Cu²⁺ and Cr⁶⁺ by Mg /Al-N03 with time variations**

Figure 3 shows that the maximum per cent adsorption for Cu²⁺ of 99.9% occurs at 30 minutes contact time which is indicated by the achievement of an equilibrium point. Whereas in Cr⁶⁺ 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 Cu²⁺ metal ions and Cr⁶⁺ metal ions which is characterized by a reduction in the concentration of Cu²⁺ and Cr⁶⁺ metals [8].

**IV. CONCLUSION**

The optimum mole ratio for synthesizing Hydrotalcite Mg / Al-N03 from seawater is at a mol ratio of 2.5:1 at pH 10 with a temperature of 70°C within 1 hour. The characteristic Hydrotalcite Mg/Al-N03 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 10-100 Å in the ratio 2.5:1.

Hydrotalcite Mg /Al-N03 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-N03 has been formed. Hydrotalcite Mg/Al-N03 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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