Characterization of the γ,α-alumina and its adsorption capability to adsorb nickel (ii) and magnesium (ii) from nickel sulfate as a result of solvent differences

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Abstract. This study discusses the characteristics phase of the alumina mixture, namely the γ, α-alumina as well as its ability to adsorb the nickel (II) and magnesium (II) from nickel sulfate due to solvent differences. The γ, α-alumina was synthesized under acidic conditions (pH = 5) from poly aluminum chloride that was calcined at 800 °C by the sol-gel method. The particle size of γ, α-alumina is 15.65 μm; BET specific surface area of 104.12 m² g⁻¹; mesopores volume of 0.284 mL g⁻¹; and a shape type of IV isotherm curve. Such the characteristic belongs to an adsorbent. The solution of nickel sulfate as Solution (b) has a bigger total adsorption capacity than that of the Solution (a), namely 16.46 mg L⁻¹ and 2.49 mg L⁻¹ respectively. The alkaline buffer formation as the ammonium hydroxide and ammonium chloride in Solution (a) may result in reducing the adsorption capability of the γ,α-alumina. The magnesium concentration of nickel sulfate in Solution (a) is smaller than that of the nickel one, namely 118.36 mg L⁻¹ for the Mg and 486.64 mg L⁻¹ for the Ni. However, the Mg is still more adsorbed around 29.96 mg L⁻¹ compared to the Ni (19.80 mg L⁻¹).

Keywords: alumina, gamma, alpha, adsorption, sol-gel and mesopores.

1. Introduction
Alpha alumina is reported to have a hexagonal crystal structure with the R-3c space group, specific surface area around 15.396 m² g⁻¹, pore volume of 0.0453 mL g⁻¹ but do not have hysteresis isotherm curve [6]. The alpha alumina has transformed at temperature 1050 °C, but the presence of precursors containing chlorine and carbon in the gel performs a promoting effect on the initial formation of alpha alumina at 950 °C [13].

Gamma alumina owns a cubic crystal structure with the Fd-3m space group. Its specific surface area BET is 96-196 m² g⁻¹. Its mesopore volume is (0.294-0.327 mL g⁻¹) and its surface is formed from agglomeration of spherical sub-particles [6]. Figure 1 shows the three-dimensional structures of the gamma and alpha alumina, while Figure 2 is the isotherm curve of the gamma and alpha alumina.
Figure 1. Three-dimensional structure of the gamma (a) and alpha alumina (b) derived by fitting the High Score Plus Program. The red ball is the oxygen while the blue ball refers to the aluminum [6].

Figure 2. The isotherm curve of 111-μm gamma alumina GA-800 and alpha alumina GA-1100 [7].

Gamma alumina has been widely used as the adsorbent of the orange-G [3], adsorbent for acrylic acid from aqueous environment [9], adsorbent for water de-fluoridation [4]; adsorbent for Cr6+, Ni2+, Cd2+ and Pb2+ [12] and for catalyst supports with bimetallic Ni-Pt [2]. It is widely used in several chemical processes, such as hydrogen production, oil hydrogenation, petroleum refining, automotive emissions control, etc. [1]. This study used the γ, α-alumina as an adsorbent for magnesium (II) and nickel (II) from nickel sulphate.

Physisorption refers to the phenomenon of gas molecules adhering to a surface at a pressure less than the vapor pressure. The attractions between the molecules being adsorbed and the surface are relatively weak and definitely not covalent or ionic. Enhancement of the amount of gas molecules on the surface of a solid is caused by the van der Waal forces [5]. IUPAC recommends classifying pores according to their size, namely macropores (the pores with widths more than 50 nm); mesopores (the pores of internal width between 2 and 50 nm) and micropores (the pores with internal diameters of less than 2 nm.) [16]. Table 1 shows the classifications of physical adsorption isotherms and Figure 3 exhibits the form of the isotherm.
Table 1. Classifications of physical adsorption isotherms [5]

| Type | Interpretation |
|------|----------------|
| I    | Characteristic of a chemisorption isotherm or physisorption on a material that has extremely fine pores (micropores) |
| II   | Characteristic of a material, which is not porous, or possibly macroporous, and has a high energy of adsorption |
| III  | Characteristic of a material, which is not porous, or possibly macroporous, and has a low energy of adsorption |
| IV   | Characteristic of a material, which contains mesoporosity and has a high energy of adsorption. These often contain hysteresis attributed to the mesoporosity |
| V    | Characteristic of a material, which contains mesoporosity and has a low energy of adsorption. These often contain hysteresis attributed to the mesoporosity |
| VI   | Characteristic of a material, which contains multiple pore size |

Figure 3. The isotherm curves of physical adsorption [5]

There are several methods to prepare the gamma alumina such as mechanical synthesis, vapor phase reaction, precipitation, combustion, and sol-gel methods [14]. [10] and [2] made a gamma alumina from aluminum chloride under acid conditions by a sol-gel method. In this research, the γ,α-alumina consist of phase alumina (68.30% gamma and 31.70% alpha) will made from the aluminum chloride under acid conditions of pH=5 using a sol-gel methods [6]. The nickel sulfate as a source of nickel and magnesium will be dissolved using different solvents to find out the effect of different solvents on the adsorption ability of γ,α-alumina as an adsorbent.

Adsorption of nickel and magnesium by the gamma alumina from laterite samples had been conducted by [6], with a ratio of the magnesium was higher than that of the nickel, namely 229.73 mg L⁻¹ and 22.71 mg L⁻¹ respectively. The adsorption conditions were carried out under alkaline condition (pH = 10). Magnesium-nickel adsorption was carried out with the inverse composition of the magnesium, namely smaller than that of the nickel in a concentration form of the nickel sulfate sample, in terms evaluating whether the abundance of one cations has an effect or not to the adsorption strength of the γ,α-alumina as an adsorbent.
2. Methodology

2.1 Dissolution of nickel sulfate
Nickel sulfate will dissolve in two different ways, namely:

- Dissolution by hydrochloric acid and ammonium hydroxide
  As much as 1.0000 g of nickel sulfate sample are weighed, then dissolved with 20 mL hydrochloric acid and heated on a hotplate at 80 °C, after dissolved nickel sulfate is diluted with distilled water to a volume of 100 mL, then ammonium hydroxide is added to pH = 10 and put into a volumetric flask 250 mL. This nickel sulfate is called Solution (a). The nickel and magnesium concentrations of Solution (a) are characterized by the atomic absorption spectrophotometers (AAS) Variant 240FS.

- Dissolution by distilled water and ammonium hydroxide
  The nickel sulfate sample is then dissolved with distilled water, heated on a hotplate at 80 °C. After the nickel sulfate dissolve, then is added the ammonium hydroxide of pH = 10 and put it into a 250-mL volumetric flask. This nickel sulfate is called Solution (b). The nickel and magnesium concentrations of Solution (b) are characterized by the AAS Variant 240FS.

2.2 Synthesizing the γ,α-alumina by sol-gel methods
Poly aluminum chloride (PAC) is dissolved with distilled water at 800 °C, then the ammonium hydroxide is added until pH 5-5.5 to get the precipitate aluminum hydroxide (Al(OH)3). The precipitate is dried at 250 °C and milled using a ring mill at speed of 700 rpm for 8 minutes, then calcined in a tube furnace at 800 °C [7]. The alumina is characterized by particle size analyzer (PSA), X-ray diffraction (XRD Shimadzu/7000 Maxima-X) and surface area analyzer Quadra orb SI. The sample is coded as γ,α-alumina. It consists of phase alumina (68.30% gamma and 31.70% alpha).

2.3 Adsorption of Nickel (II) and Magnesium (II)
Solution (a) and (b) are pipetted 50 mL to a 200 mL beaker glass and then are added 1 g of γ,α-alumina, then stirred for 2 hours. The precipitate is filtered using a Whatman filter paper No. 40. The filtrate is pipetted 5 mL then put into a 250 mL volumetric flask, and then 10 mL hydrochloric acid is added. Concentration of nickel and magnesium are measured by AAS Variant 240FS.

3. Results and Discussion
Solution (a) composition detected by AAS is shown in Table 2.

| Element | Total Quantity (mg L⁻¹) |
|---------|------------------------|
| Ni      | 486.4                  |
| Mg      | 118.36                 |

Nickel sulfate dissolved completely in hydrochloric acid. To get adsorption condition, the ammonium hydroxide was added until the pH reached 10 and the Solution (a) was still clear (no Ni and Mg precipitations occurred). The Ni and Mg did not precipitate in the excess alkaline conditions. Nickel in the presence of excess ammonium hydroxide dissolved as the hexa ammine nickel (II) ions performing a deep blue complex formation of [Ni(NH₃)₆]^{2+}. Magnesium was not precipitated but still soluble in the presence of chloric acid and excess ammonium hydroxide.
Reactions between HCl and NH4OH produced NH4Cl and prevented precipitation of the Mg (OH)2 [15].

Dissociation of the completely ionized ammonium salt increased but the hydroxyl ions decreased due to the common-ion effect. As a result, the hydroxyl ions reduced a lot and resulted the Mg still available within the solution. The presence of ammonium salt would reduce the hydroxyl ion and the constant of Mg (OH)2 solubility product was not exceeded [15].

Dissolution of nickel sulfate as Solution (b) produced nickel and magnesium (Table 3). The Ni sulfate dissolved when the 80 °C-aquadest was added, followed by NH4OH addition until the pH reached 10. The Ni still dissolved as a dark blue complex compound of [Ni (NH3)6]²⁺ although its concentration reduced from 486.64 to 426.73 mg L⁻¹. Yet, such a decrease did not affect compared to the magnesium concentration that decreased from 118.36 to 8.03 mg L⁻¹. The reason is that the nickel sulfate solution does not have ammonium salt. Without the ammonium salt, the Mg precipitates as a white Mg(OH)2. Less Mg (OH)₂ occurs due to its small solubility value, i.e. 9 m g⁻¹ [11].

| Element | Total quantity (mg L⁻¹) |
|---------|------------------------|
| Ni      | 426.73                 |
| Mg      | 8.03                   |

Making the alumina sample was conducted at pH = 5 – 5.5 (acid condition) as the study used a poly aluminum chloride – the material that has acid condition. It is more economy to get the precipitate of aluminum chloride if the sample condition is also in acid condition by adding less NH4OH. The alumina as either oxide or hydroxide has a pH between the value of pHpzc and pHiep, namely from 5 to 9.6 [8]. Such a condition enables to make the alumina in the acid or alkaline conditions. The aluminum oxide dried at 250 °C was ground in the ring mill at 700 rpm for 8 minutes and then was calcined at 800 °C. Particle size analyzer showed that the alumina had 15.65 µm in size.

**Figure 4.** XRD Diffractogram (a) gamma alumina standard γ,α-alumina d ICSD 98-006-6559; (b) alpha alumina standard ICSD 98-007-5559, dan (c) γ,α-alumina.

XRD analysis (Figure 4) showed the results that the alumina sample had a mixed phase as gamma alumina (68.30%) with a typical broad peak of gamma alumina and alpha alumina (31.70%).
with a typical sharp peak. The gamma alumina retains the Miller indices of 022, 113, 004, and 044 while the alpha alumina exhibits the Miller indices of 012, 104, 113, 110, 024, 116, 214, and 030 [6]. Table 4 shows the Miller indices, 2θ and relative intensity of gamma and alpha alumina using the HighscorePlus program.

Table 4. Refinement data for the values of Miller indices, 2θ and relative intensity of gamma and alpha alumina using the HighscorePlus program

| Phase | Miller indices | 2θ (º) | Relative intensity (%) |
|-------|----------------|--------|------------------------|
| Gamma | 022            | 31.99  | 12.96                  |
|       | 113            | 37.71  | 15.24                  |
|       | 004            | 45.88  | 23.36                  |
|       | 044            | 66.92  | 26.53                  |
| Alpha | 012            | 25.55  | 61.20                  |
|       | 104            | 35.13  | 97.03                  |
|       | 113            | 37.71  | 15.24                  |
|       | 110            | 37.74  | 45.46                  |
|       | 024            | 52.52  | 50.15                  |
|       | 116            | 57.47  | 100.00                 |
|       | 214            | 66.47  | 39.96                  |
|       | 030            | 68.15  | 30.77                  |

Previous studies show that the alpha alumina did not occur at 800 °C, but at 1000 °C for 111.0 μm particle size of the alumina [7]. In this study, the alpha alumina was formed at 800 °C. Smaller alumina particle size (around 15.65 μm) is supposed to be the cause. Reducing the size to a smaller one will reduce the sintering and crystallization temperatures due to its surface energy content, and then it converts some of the gamma alumina to the alpha one. Another possibility is the alpha alumina phase formed from the particles size is smaller than 15.65 μm, because only 31.7% of the alpha alumina is formed at the 800 °C calcination temperature.

Results of characterizing the γ,α-alumina by surface area analyzer is shown in Table 5. The table shows that the BET specific surface area of the γ,α-alumina has 104.12 m² g⁻¹ and the mesopores volumes of 0.284 mL g⁻¹. This indicates that the γ,α-alumina has the ability to be adsorbent. The γ,α-alumina had mesopores volume of 0.284 mL g⁻¹. The micro-pore volume of γ,α-alumina has a smaller value, namely 0.052 mL g⁻¹. The γ,α-alumina had an average pore radius of 54.58 Å, which means that its pore diameter is 10.916 nm. Such the pore diameter belongs to the mesopores category, because the size of pore diameter is in the mesopores range, namely 2-50 nm [5].

Table 5. Characterization of alumina γ,α-alumina by Surface Area Analyzer

| Sample      | BET Specific surface area (m² g⁻¹) | Pore volume at P/P0=0.99 (mL g⁻¹) | Micro-pore volume (mL g⁻¹) | Total pore (mL g⁻¹) | Average pore radius (Å) |
|-------------|-----------------------------------|-----------------------------------|---------------------------|---------------------|-------------------------|
| γ,α-alumina | 104.12                            | 0.284                             | 0.052                     | 0.336               | 54.58                   |

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adsorbent. The γ,α-alumina had mesoporous volume of 0.284 mL g⁻¹. The micro-pore volume of γ,α-alumina has a smaller value, namely 0.052 mL g⁻¹. The γ,α-alumina had an average pore radius of 54.58 Å, which means that its pore diameter is 10.916 nm. Such the pore diameter belongs to the mesoporous category, because the size of pore diameter is in the mesoporous range, namely 2-50 nm [5].

Based on Figure 5, the γ,α-alumina curve belongs to the type IV physical adsorption curve (a), namely a typical adsorption for mesopores with particle sizes above 4 nm which leads to the formation of hysteresis. The pore filling based on the type IV occurs as monolayer, multilayer and capillary condensation [5].

![Figure 5. Isotherm curve of physical adsorption γ,α-alumina resulted from surface area analyzer](image)

The adsorption of Ni (II) and Mg (II ) by γ,α-alumina from the nickel sulfate solution was carried out under pH = 10. The filtrate was then measured by the AAS to determine the concentration of non-adsorbed nickel and magnesium that may still left within the nickel sulfate filtrate in either Solution (a) or (b). The adsorbed concentration was obtained by subtraction the initial concentration of nickel and magnesium in Solution (a) and (b), before and after the γ,α-alumina addition. Result of the AAS is shown in Table 6.

![Table 6. Results of the AAS tests for Solution (a) and (b) after alumina addition](table)

| Solutions (a) dan (b) + γ,α-alumina | Nickel sulfate solutions |
|----------------------------------|-------------------------|
|                                  | solution (a) | solution (b) |
| Filtrate concentration/non-adsorption (mg L⁻¹) | 466.84 | 88.40 | 105.48 | tt |
| Adsorption concentration (mg L⁻¹) | 19.80 | 29.96 | 321.25 | 8.03 |
| Adsorption capacities (mg L⁻¹) | 0.99 | 1.50 | 16.06 | 0.40 |
| Adsorption percentage (%) | 4.07 | 25.31 | 75.28 | 100.00 |

Based on Table 6, the γ,α-alumina as an adsorbent is able to adsorb nickel and magnesium within the nickel sulfate solution at pH = 10. The difference of nickel sulfate solvent affects the
ability of alumina γ,α-alumina as an adsorbent. Nickel adsorption by alumina γ,α-alumina produced a greater adsorption capacities and percentage in Solution (b), namely 16.06 mg L⁻¹ and 75.28%, but in Solution (a), the adsorption is smaller, namely 0.99 mg L⁻¹ and 4.07%. Based on Table 1 and 2, it is known that the nickel content in both solutions have not too different in concentration, namely 486.6386 mg L⁻¹ and 426.7346 mg L⁻¹.

Based on the capacity value and adsorption percentage that have significant differences, such a condition is supposed to be the presence of Cl⁻ within the solution. According to [4], if the pH value is bigger than the pHpzc, the adsorbent surface will have a negative charge. As a result, it prefers a cation condition. In this research, the adsorption is carried out under an alkaline condition (pH = 10), to adsorb the Ni (II) and Mg (II) as cations. Based on the nickel concentration in Solution (a) before adsorption (486.6386 mg L⁻¹), it is possible to have a nickel adsorption capacity of 16.06 mg L⁻¹, however, as the Solution (a) contains chlorine and ammonium hydroxide, it will form ammonium chloride as an alkaline buffer solution. The formation of this buffer solution may inhibit adsorption capacities of the nickel, namely of 0.99 mg L⁻¹.

In Solution (b), all Mg (II) is adsorbed by the γ,α-alumina because the concentration is very small, namely 8.0348 mg L⁻¹. As a result of dissolution process by the ammonium hydroxide, the Mg was precipitated in Solution (b). An adsorption capacity of the Mg in Solution (a) is 1.50 mg L⁻¹. Solution (a) has smaller adsorption capacities for the Ni and Mg than that of Solution (b). It is possibly because in Solution (a), an alkaline buffer is formed and affects the adsorption under alkaline conditions of pH = 10. The amount of magnesium which is not adsorbed is 88.4020 mg L⁻¹. Without interference from the formation of the alkaline buffer, all magnesium can be more adsorbed by the γ,α-alumina, if compared to the adsorption capacity value of the γ,α-alumina in Solution (b).

The composition ratios of the magnesium and nickel in Solution (a) from nickel sulfate are 118.36 mg L⁻¹ and 486.64 mg L⁻¹ respectively, an opposite to magnesium and nickel composition from laterite, namely 229.73 mg L⁻¹ and 22.71 mg L⁻¹ [6]. This comparison is to find out whether the abundance one of cations will affect the adsorption capability of an adsorbent. The Mg composition in Solution (a) is smaller than that of the Ni, but the Mg adsorption is bigger than that of the Ni of γ,α-alumina. Its concentrations are 29.96 mg L⁻¹ and 19.80 mg L⁻¹ respectively. In the previous studies, [7] states that in laterite solution contains the Mg composition bigger than that of the nickel, the Mg is adsorbed bigger than that of the Ni of γ,α-alumina, namely 186.79 mg L⁻¹ and 2.20 mg L⁻¹ although the ratio of Mg concentration within the solution is smaller or bigger than the Ni as the effect of alkaline condition. Based on the hard-soft acid base (HSAB) concept, the OH⁻ tends to react more with the hard acid (Mg²⁺) than the borderline acids (Ni²⁺).

4. Conclusion
The γ,α-alumina has been successfully made from poly aluminum chloride in an acidic condition at pH=5-5.5 by a sol-gel method at calcination temperature of 800 °C. The γ,α-alumina have particle size of 15.65 μm; BET specific surface area of 104.12 m² g⁻¹; mesopores volume 0.284 mL g⁻¹ and type IV isotherm curve. Adsorption capacities of γ,α-alumina in solution (b) greater than solution (a) because of an alkaline buffer (NH₄Cl) formation in the solution (a), then the adsorption ability of γ,α-alumina will be reduced. Adsorption of magnesium is bigger than that of the nickel in solution (a), namely 29.96 mg L⁻¹ and 19.80 mg L⁻¹. Total adsorption capacity of γ,α-alumina occurs in solution (b) is 16.46 mg L⁻¹. Adsorption of nickel and magnesium in a solution under alkaline conditions (pH = 10) shows that the magnesium will be more adsorbed than the nickel and it is not influence by the greater or smaller concentrations of magnesium in the solution.
5. **Acknowledgement**

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6. **References**

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