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Adsorption of Nickel in Nickel Sulphate Solution ($NiSO_4$) by Lapindo Mud

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Abstract

This research has been carried out to produce adsorbent from Lapindo mud through various activation process, to adsorb nickel from nickel sulfate solution. Several investigations were performed in this research such as characterization of Lapindo mud before and after activation, effect of physical, chemical and chemico-physical activation to Si/Al ratio and determine the most effective method to produce adsorbent with high adsorption rate. Lapindo mud in this research was prepared through several methods such as without activation, calcination at 500 °C for 3 hours, chemical activation with 6 N HCl under reflux for 6 hours, chemical activation with 6 N NaOH under reflux for 6 hours, chemical activation with 6 N HCl under reflux followed by calcination process and the last treatment is chemical activation with 6 N NaOH under reflux followed by calcination process. The object of this research is the Lapindo mud adsorbent ability to adsorb Ni from $NiSO_4$ solution. While activation methods and nickel concentration in this become independent variable. The reduction of nickel concentration efficiency is determined by the nickel concentration before and after adsorption process. The Si/Al ratio of Lapindo mud before activation process was 3.01 and it increase as the mud is activated. The highest Si/Al ratio was found at activation using HCl which is 7.85. Chemical activation using NaOH was found to be the best method to create the adsorbent with adsorption capacity 98.3%.

INTRODUCTION

On 29th of May 2006, first mud eruption is witnessed in Sidoarjo, Jawa Timur, Indonesa. As of May 29th, 2009, the mud is flowing at rate of 50,000 m^3 per day and recently the data reported that mud is flowing at rate of 120,000 m^3 per day. Lapindo mud in Sidoarjo is composed of 70% water and 30% solid, which might be contain contaminant that is harmful if released at high amount to the environment. Meanwhile, mud disposal is performed by flowing it to Porong and Aloo River. This act might pollute the preservation of ecosystem in the river. Therefore, finding the use of Lapindo mud would be beneficial from environmental and economic points of view.

Lapindo mud has potential to be applied as an adsorbent due to its high porosity and make it have high adsorption ability. Juniawan et al. (2013) in his research stated that Lapindo mud taken from Aloo and Porong River have porosity of 46.75 and 44.5% respectively. Meanwhile Lapindo mud also contain alumina (11%) and silica (29.8%) which can improve adsorption ability of the adsorbent. Metal compositions in Lapindo mud are shown in Table 1.

Adsorbent is a material that has ability to adsorb certain substances from gasses, liquids or solids through adsorption process. Types of adsorbent used in the adsorption process is depend on the adsorbate and adsorption ability is directly influenced by the adsorbent quality. A wide range of materials used as adsorbent are activated carbon,

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Table 1. Lapindo mud composition.

Metal	Concentration (%)
Al	11.00
Si	29.80
K	3.53
Ca	7.41
Ti	2.11
Mn	0.59
Fe	40.56
Sr	0.94
Mo	2.60

(Putra et al., 2013)

benonite, activated clay, aluminum dioxide, activated silicon dioxide, zeolite, aluminosilicate and ion exchange resin (Levine, 2002).

In order to improve Lapindo mud adsorption capability, the adsorbent need to be activated. Udyani & Wulandari (2014) stated that zeolite adsorption ability is in line with the increasing calcination temperature during activation process. Calcination temperature more than 700 °C will break zeolite structure and decrease zeolite adsorption ability Meanwhile, Calcination temperature below 200 °C will not vaporize water inside zeolite pores perfectly. Optimum calcination temperature for activation process should be take place at 500 °C as activation process performed by Gustian & Suharto (2005).

Based on this problems, in the present study the most effective activation method resulting adsorbent with high adsorption capability is investigated. This research focuses on the influence of activation method to the adsorbent characteristic and adsorption capability of Lapindo mud adsorbent. Activation methods investigated in this research were physical, chemical and chemico-physical activation.

RESEARCH METHODOLOGY

Experimental studies in this research were performed at several steps, which are Lapindo mud pretreatment, activation process, adsorption of $NiSO_4$ solution and adsorption result analysis using spectrophotometry. In pretreatment process, Lapindo mud were washed using distilled water then these were dried in the oven at 105 °C for 2 hours. These adsorbents then were sieved through 136 mesh screen. Activation processes were divided into non-activation, physical, acid chemical, base chemical, acid chemico-physical and base chemico-physical activation. Physical activation was performed with furnace at 500 °C for 3 hours. Acid and base chemical activation were performed using 6 N HCl and 6 N NaOH respectively with comparison of 100 g sample per 1 L solution under reflux condition at 90 °C for 6 hours. XRF analyses were carried out to confirm and analyze Lapindo mud adsorbent composition. BET area surface analyses were carried out to analyze pore size of adsorbent.

Aqueous Solution used in this adsorption process was $NiSO_4$. Adsorption processes were performed in an incubator shaker by using 100 g adsorbent per 100 mL $NiSO_4$ solution. The agitation speed was maintain at 100 rpm and temperature was kept at 50 °C for 60 minutes. Reduction of nickel concentrations in the end of adsorption process were analyzed using UV-VIS Spectrophotometry.

RESULTS AND DISCUSSIONS

The results of this research is Lapindo mud characteristic or its composition using XRF analysis. Lapindo mud adsorbent activations were varied by without activation, physical (calcination), acid chemical (HCl), base chemical (NaOH), acid (HCl) chemico-physical and base (NaOH) chemico-physical activation. Lapindo mud compositions for each activation process compared to clinoptilolite zeolite from literature can be seen in Table 2.

From Table 2 it can be seen that Si/Al ratio increase significantly with acid chemical and acid chemico-physical activation process. The Si/Al ratio at acid chemical and acid chemico-physical were 5.96 and 7.86 respectively. Adsorbent with base physical activation and calcination process also have slight increase in Si/Al ratio. While, lowest Si/Al ratio obtained at activation using NaOH. Lapindo mud Adsorbent compositions were then compared to clinoptilolite zeolite which has 5.20 Si/Al ratio. The Si/Al ratio can affect zeolite adsorption capacity as an adsorption. XRF result analysis showed that acid activation cause changes to the other composition such as Al and Fe resulting an increase in Si/Al ratio. This changes were occurred due to reaction between metal and HCl. The reactions are shown in equation (1) and (2).

Silica as one of components in zeolite was dissolved during base activation process (Jozefaciuk

Table 2. Adsorbent composition at dofferent activation process.

Variabel	A	B	C	D	E	F	G
Al	-	10	9.4	9.3	7.8	10	12.46
Si	28.9	30.1	**56.0**	27.7	**61.3**	31.3	**64.87**
K	3.82	3.85	4.80	3.76	4.36	2.82	2.28
Ca	8.07	7.47	3.89	8.66	3.63	9.85	1.27
Ti	2.22	2.14	4.38	2.28	4.14	2.08	-
V	0.12	0.12	0.18	0.10	0.12	0.095	-
Cr	0.11	0.10	0.13	0.1	0.07	0.094	-
Mn	0.55	0.54	0.15	0.59	0.15	0.58	0.03
Fe	**39.7**	**37.8**	18.2	**41.3**	13.1	**37.4**	0.55
Ni	0.20	0.19	0.19	0.20	0.17	0.18	-
Cu	0.17	0.16	0.18	0.18	0.16	0.16	-
Zn	0.08	0.09	-	0.09	-	0.08	-
Sr	1.1	0.99	-	1.1	-	1.1	-
Br	0.23	-	-		-	-	-
Mo	4.5	5.71	5.0	3.9	4.7	3.1	-
Eu	0.46	0.4	-	0.4	-	0.4	-
Yb	-	-	0.1	0.03	0.06	-	-
Re	0.2	0.2	-	0.3	-	0.2	-
S	-	-	0.4	-	0.2	0.3	-
Na	-	-	-	-	-	-	4.33
Ba	-	-	-	-	-	-	0.51
H_2O	-	-	-	-	-	-	13.59

A = Without activation, B = Physical activation (calcination), C = Acid activation, D = Base activation, E = Acid-physical activation, F = Base –physical activation, G = Zeolite klinoptilolit (Khaidir, 2011)

$$Fe_2O_{3(s)} + 6HCl_{(aq)} \rightarrow 2FeCl_{3(aq)} + 3H_2O_{(aq)} \quad (1)$$

$$Al_2O_{3(s)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 3H_2O_{(aq)} \quad (2)$$

& Bowanko, 2002). Silica dissolution process will change its structure as well as reduce its amount resulting reduction of Si/Al ratio. Reaction between NaOH with silica and alumina area shown in equation (3) and (4).

Physical activation using calcination process is expected to remove moisture content and remove impurities trapped inside zeolite pores and structures. This thermal treatment causes cation movements which will affect cation locations and also its pore size. Later on, this changes will influence adsorption kinetic and equilibrium (Ackley et al., 2003).

Lapindo Mud Adsorbent Brunauer, Emmett, and Teller Surface Area Analysis (BET)

BET analyses were carried out to calculate surface area, average pore radius and total pore volume. Each adsorbent from various activation process has been analyzed by using BET and the results are shown in Table 3.

The pore surface area and volume are believed affected by the increase of Si/Al ratio. Acid activation will increase adsorbent's surface area as stated by Boveri et al. (2006) and Chung (2007) that acid preparation will increase adsorbent's surface area. Adsorbent without activation has surface area of 23 m^2/g, while activation using acid, acid chemico-physical, base and base chemico-physical gave surface area of 98.099, 89.18, 53.419 and 35.06 m^2/g respectively. Slight increase of adsorbent's surface area is shown at calcination process with 23.542 m^2/g.

Adsorption Studies

Figure 1 shows that base activation give highest adsorbent adsorption capacity. It is due to hydroxide ion (OH^-) on surface of adsorbent which

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + H_2O \rightarrow 2Na[Al(OH)_4]_{(aq)} \quad (3)$$

$$SiO_{2(s)} + 2NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(l)} \quad (4)$$

Table 3. Comparison of adsorbent surface area, average pore size and total pore volume

Adsorbent	Surface Area (m^2/g)	Average Pore Size (nm)	Total Pore Volume (cc/g)
A	23	5.52644	0.0314
B	23.542	4.076	0.02388
C	53.419	4.5836	0.06121
D	98.099	5.16	0.127
E	89.18	6.10	0.136
F	35.06	4.80	0.0420

A = Without activation, B = Physical activation (calcination), C = Acid activation, D = Base activation, E = Acid-physical activation, F = Base –physical activation

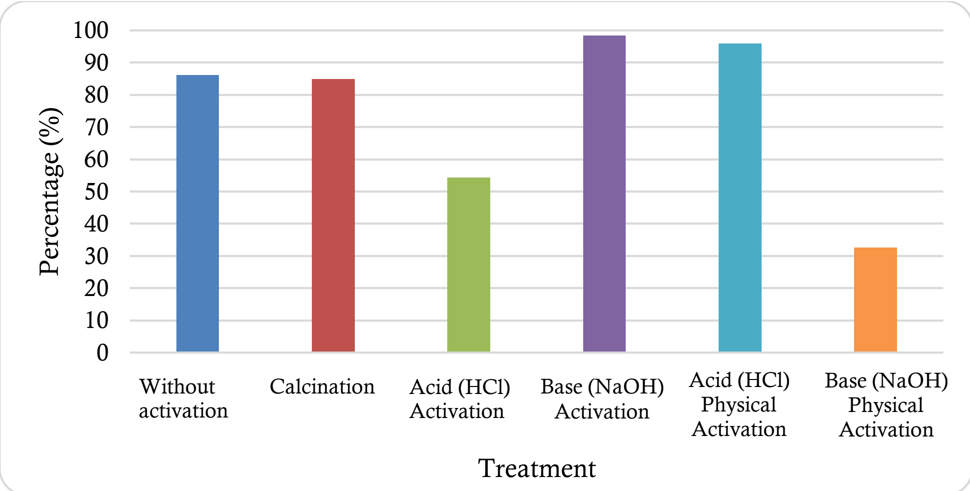

Figure 1. Adsorbance percentage

previously interact with Fe^{3+}, attract Nickel (Ni^{2+}) with positive ion leads to Nickel precipitation and become a layer on adsorbent surface. It causes decrease of Ni concentration in the solution since the Ni was restrained on the surface of adsorbent.

As shown in Table 4, adsorbent with base activation have almost 100% adsorption efficiency at different initial concentrations of $NiSO_4$. It ensures that adsorbent with base activation has high adsorption capacity.

Adosprtion Isotherm Calculation

Langmuir and Freundlich adsorption equations were investigated to model adsorption isotherm for Nickel adsorption by Lapindo mud adsorbent. The calculations were carried out by using adsorbent with highest adsorption capability, in this case adsorption isotherm calculation uses data obtained from base activation adsorbent.

Freundlich Isotherm Calculation

From Freundlich equation : $Q = k.Ce^{1/n}$ we can get the value of n and k by plotting linier graph between log Q and log Ce. Where, Q is a ratio of adsorbed component (mg) to mass of adsorbent (mg), Ce is concentration of the same adsorbent and while k and n are adsorption constants.

Figure 2 shows that nickel adsorption equation by using Lapindo mud adsorbent is y = -0.3405x - 3.827 with R^2 = 0.9576. Value of n and k obtained from the equation were n = -2.936857562 and k = 0.000148936 where each variable represent adsorption capacity and efficiency of adsorbent respectively.

Langmuir Isotherm Calculation

Langmuir equation was used to calculate maximum adsorption capacity, the equation is Ce/Q = 1/ab + (1/a) Ce. Where b is affinity

Table 4. Result analysis of UV-VIS Spectrophotometry

Initial concentration (ppm)	Data 1	Data 2	Average value	Final Concentration (ppm)	Adsorption efficiency (%)
	Absorbance				
30	0.02	0.02	0.02	0.92	96.94
34	0.02	0.0195	0.01975	0.83	97.57
38	0.019	0.019	0.019	0.55	98.55
42	0.02	0.017	0.0185	0.37	99.12
46	0.019	0.0175	0.01825	0.28	99.40

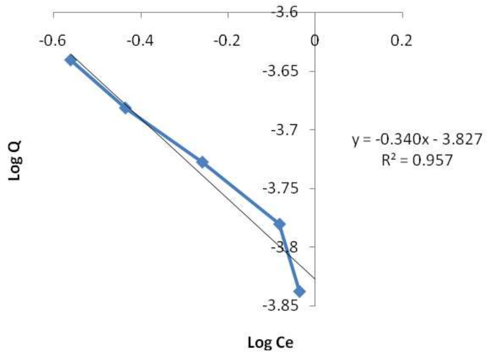

Figure 3. Graph between Log Ce vs Log Q

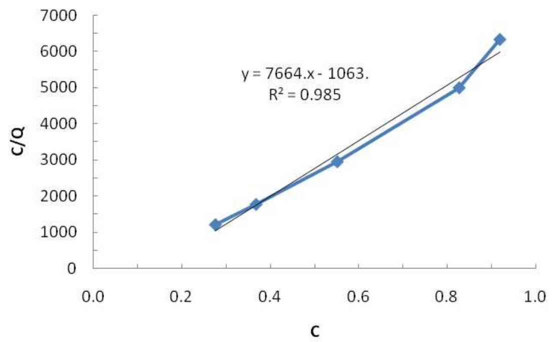

Figure 4. Graph between Ce/Q vs Ce

parameter or Langmuir constant and a is maximum adsorption capacity. Experimental results were then plotted in a graph between Ce/Q vs Ce as shown in Figure 3.

Equation of Nickel adsorption by Lapindo mud obtained from Figure 3 was y = 7664.4x - 1063.3 with R^2 = 0.9855. R^2 shows calculation accuracy between experimental data with calculation result from both calculation method. Adsorption isotherm using Langmuir model has higher R^2 compared to Freundlich model. Based on this result highest maximum adsorption capacity is obtained using adsorbent with base activation with maximum capacity 0.000151 mg nickel/mg adsorbent.

In Langmuir model, all adsorbent surface area has uniform and identical adsorption activity, no interaction between adsorbate molecules, all adsorption mechanism process also same and there is only one adsorbate layer formed on adsorbent surface.

CONCLUSION

Lapindo mud can be utilized as adsorbent for reducing nickel concentration in nickel sulfate solution. Acid chemico-physical activation using HCl was performed to improve Lapindo mud adsorbent characteristic and obtain Si/Al ratio of 7.86. While acid activation using HCl was successfully increase adsorbent pore surface area into 98.099 m^2/g. Lapindo mud with base activation using NaOH effectively reduce nickel concentration with adsorption capacity of 98.31%.

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