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Characterization of napa soil and adsorption of Pb (II) from aqueous solutions using on column method

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ABSTRACT

This research aim to investigate and characterization Napa soil at West Sumatera, Indonesia. Napa soil is one of the biggest mineral soil in sumatera island, especially at West Sumatera. Napa soil was characterized using XRD, XRF and morphology SEM. The biggest composition in Napa soil is zeolite that can be used as adsorbant, for removal of Pb (II) from aqueous solutions by column method. The evaluated parameters were optimum pH, initial concentration, particle size and flow rate. The optimum condition was at pH=4, that is 11.146 mg/g, concentration begin optimum 250 mg/L be obtained the as big as adsorption capasity 9.195 mg/g, adsorbent heating that optimum be got to heating temperature 125^{o}C with adsorption capacity is 9,480 mg/g, the particle size that optimum be obtained to size 830-350 µm with adsorption capacity is 11.323 g/g whereas the optimum flow rate 20 drop/minute with adsorption capasity that is 11.21 mg/g. To use it equalization adsorption Langmuir to get the maximum adsorption capacity is 24.39 mg/g. This study revealed that Napa soil is a very good adsorbent to remove Pb (II) from waste water as the substitutes of more expensive synthetic material.

Keywords : Characterization, Adsorption, Napa soil, Pb(II), Zeolit

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INTRODUCTION

Napa soil is a term referring to the people of West Sumatra that kind of natural materials commonly used to treat stomach and diarhea. Napa soil is produced by the natural soil derived from the weathering of rocks feldspathic that moves away from its parent rock due to exogenous force crust. Physical characteristics of napa soil are large pores in surface and grayish white. A kind of the same soil also found in the subdistrict Lintau, district Tanah Datar and Cubadak hilly in subdistrict Limo Situjuah Nagari district 50 Kota, Solok district and local people also call it the Napa soil.

Meanwhile, degradation of environmental caused by heavy metals in industrial waste water are increasingly. Conventional methods used to remove toxic heavy metals from aquatic environment include precipitation, filtration, Oxidation-reduction, ion exchange, liquid membrane separation(1), extraction, chemical precipitation, adsorption and electro dialysis(2; 3). One of heavy metal ion is Pb (II), which the most toxic metal among heavy metals, even at low concentrations in the aquatic environment. Current USEPA drinking water standard for lead 300 µg/l when present above 0.05 mg/l in drinking water, Pb (II) is a potent neurotoxic metal(3). Lead is very toxic heavy metal. It's target organs are bones brain, blood, kidneys and thyroid glands. Presence of lead in discharge and toxic nature waters in aquatic system(4).

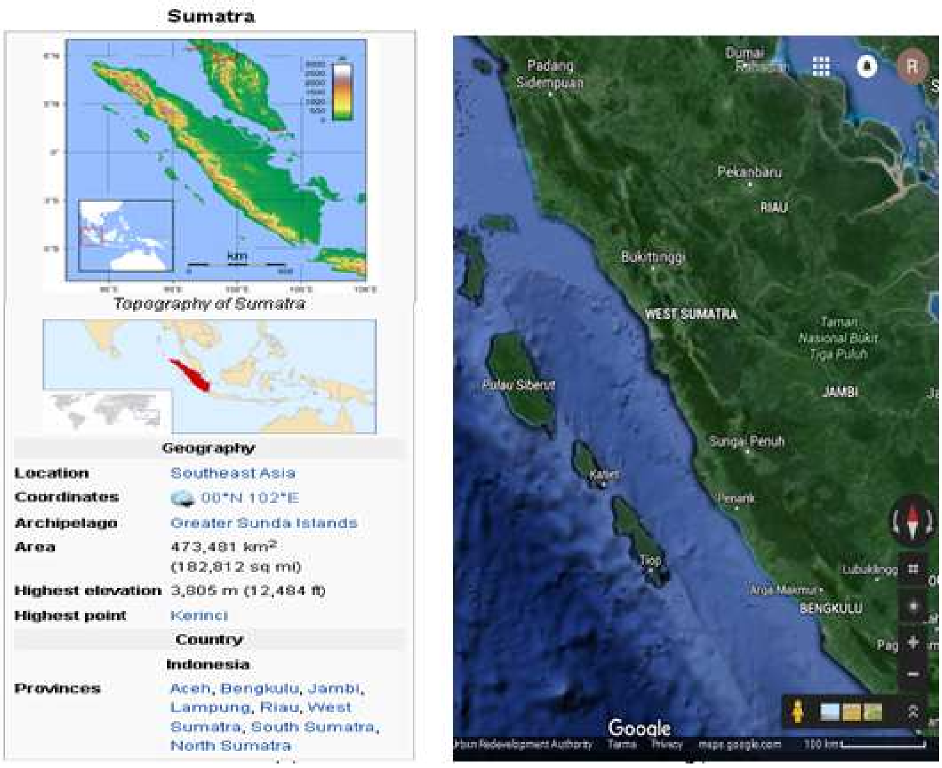
In this study, we want to investigate by XRD-XRF-SEM characterization of Napa soil and after that can investigate Napa soil were used as a adsorbent for the removal Pb (II) ions. For this purpose we would determine the optimum adsorption conditions as a function of pH, initial metal concentration ion, particle size, amount of adsorbent dose, and flow rate in the adsorption of Pb (II) by *Napa* soil with column method.

EXPERIMENTAL SECTION

Materials and Tools

Chemicals

Samples of Napa soil were collected from some districts in West Sumatera (figure 1) such as Tanah Datar, Pesisir Selatan, Solok, 50 Kota and Payakumbuh. $Pb(NO_3)_2$, HNO_3, H_2O_2, NH_3 were from Merck. Water used was double distilled water.



(a) **(b)**

Figure 1. Napa soil distribution in Sumatera Island. Topography of West Sumatera (a) and map of West Sumatera province which has contains the largest land napa (b)

Tools

The apparatus used in this research were SEM-EDX(Hitachi S-3400N), XRD, XRF analitycal balance, glasswools, and glass tools.

Preparation of Adsorbent

Soil samples of Napa in the form of granules washed with distilled water, dried in oven, until finely milled and sieved with a sieve a certain particle size, and then packed into a column in essentially placed cotton. Before use the column saturated with distilled water and ready to be contacted with a solution of heavy metals with a continuous system.

Purification of Napa Soil

Soil samples Napa in the form of crushed lumps by using a set of tools in the form of a mortar and pestle grinding into powder and sieved using a µm sieve. Napa soil that had been prepared with a size of 150 µm is taken as much as 150 gram, refluxed with 600 ml of distilled water in the distillation flask (1000 ml) for 4 hours, then was decanted. Afterwards refluxed again with 600 ml of distilled water for 4 hours, then decanted. His next dried in an oven for 3 hours at a temperature of 105^{o}C.

Preparation of Column

Preparation of equipment was needed glasses work with devices such columns. On the ground adsorbent packed column Napa which at the bottom will placed glasswool as a buffer. Before use, the column is saturated with distilled water and prepared contacted with a metal solution with continuous systems.

Metal Adsorption Experiments
Column adsorption experiments were conducted as a function of pH sorbent, dosage, particle size, initial concentration, using column sorption method.

The amount of adsorbed metal ions per gram of the Napa soil (Q, adsorption capacity) was obtained using the following (Eq.1)

$$Q = \frac{C_0 - C_f}{M} \times V \qquad \text{Equation 1}$$

Where Q is the metal uptake (mg/g)
$C_o$is the initial metal concentrations (mg/L)
C_f is the final concentrations of metal ions (mg/L)
V is the solution volume (L)
M is mass of sorbent (g)

The percentage removal (Eq. 2) of dye and amount adsorbent (in mg/g) was calculated using the following relation ships:

$$\% = \frac{C_0 - C_f}{C_0} \times 100\% \qquad \text{Equation 2}$$

Column adsorption experiments were implemented in a set of conical flask containing 10 ml of solution to investigate the effects of pH (2-6). Initial metal ion concentration (40-600 mg/L), biosorbent dosage (0.2 - 0.5 g), particle size (106-425 µm) and flow rate (1-6 ml/min). Then, the suspension was filtered and metal ion concentrations in the supernatant solution were measured by Atomic Absorption Spectrophotometer. The optimum conditions for the biosorption of Pb (II) ion were determined.

RESULTS AND DISCUSSION

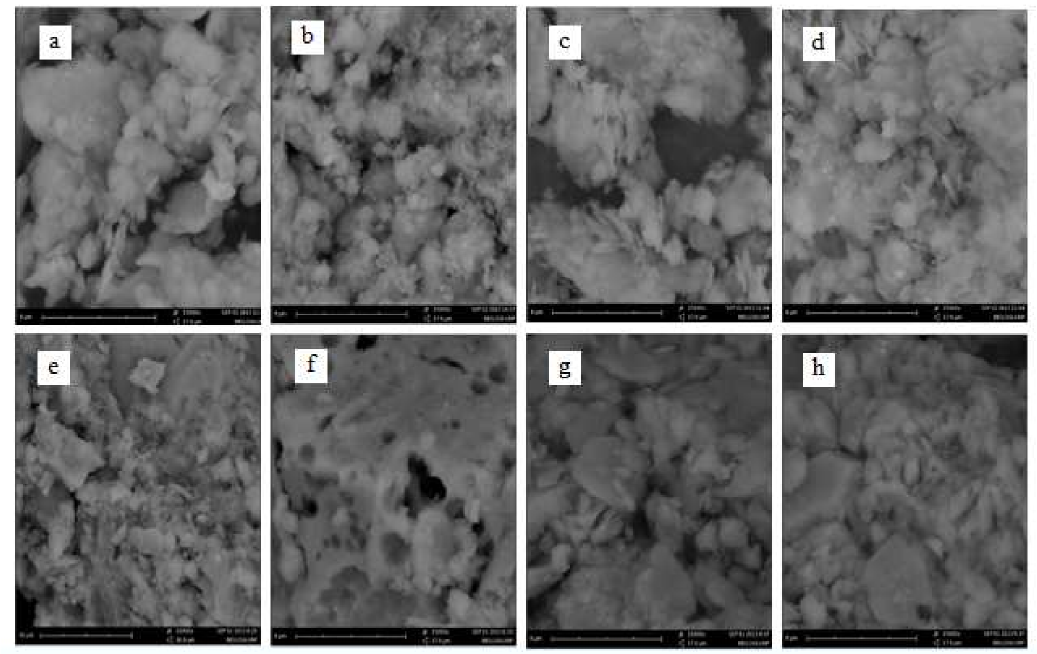


Figure 2. Scanning Electron Microscope (SEM) image of Napa soil with 15000X (times) magnification. The Napa sample was identified from South Pesisir regency (a, b) 50 Kota or Payakumbuh regency (c, d), solok regency (e, f) and tanah datar regency (g, h). All regencies was located in West Sumatera Province, Indonesia

Based on Figure 2, Scanning Electron Microscope (SEM) image of Napa soil from some regions (regencies), West Sumatera, there is a similarity pattern visible surface of the material. The a few difference of SEM image was caused by composition of metal oxide, as shown at the table 1. In Table 1 and 2 shows the composition of the oxide and mineral content of the Napa soil in various areas, and these compositions have in common that the minerals contained in the Napa soil has similarities with zeolite. The data obtained were compared with the composition of natural zeolite in the mine by the company Gravis Mining Co., the composition of the content of SiO_2, Al_2O_3, K_2O, CaO, Fe_2O_3 MgO and 65-72% respectively; 10-12%; 2.3 to 3.5%; 2.5 to 3.7%; 0.9 to 1.2% and from 0.8 to 1.9%. Date was taken from Gravis Mining Corproration, 2012, Natural Zeolit "Clinoptilolite" http://www.zeoliteproducer.com/ zeolite.html

Table 1. Composition of Napa Soil Some Regions in West Sumatra by XRF

Location of Napa soil	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	K_2O (%)	SiO_2/AlO_3
Subdistrict. Lintau, District. Tanah Datar	64.42	24.99	5976	0654	2,331	0892	2:58
Subdistrict. X Koto, District. Solok	70.43	20:52	3.67	0:40	2.70	1:26	
Subdistrict. Sarilamak, District. 50 Kota	66.21	19:42	2,982	0913	Trace	9832	3:40
Subdistrict. Situjuh, District. 50 Kota	68.70	21:24	2,168	0743	Trace	6358	3:23
Subdistrict. Batang Kapeh, District. Pesisir Selatan	51.70	41.52	2,129	3,201	0426	0156	1:24
Natural Zeolite Clinoptilolite	65-72	10-12	0.8-1.9	2.5-3.7	2.3-3.5		

Table 2. Analysis of XRD diffractogram of soil Napa 50 Kota/Payakumbuh regency (a, b), Tanah Datar regency (c), Solok regency (d) and Pesisir Selatan regency (e)

Region (Regency)	Peak [°2 Th.]	Intensity [%]	Mineral	d-spacing [A°]
a	20.8463	18.44	Quartz	4.26129
	26.6232	100.00	Kaolinite-1A, Quartz, Alumina-β	3.34831
	50.1087	11.09	Quartz	1.82049
b	20.8187	18.51	Quartz	4.26687
	265958	100.00	Kaolinite-1A, Quartz,	3.35169
	50.0770	18.82	Quartz	1.82147
c	12.3386	20.13	Kaolinite-1A	7.17374
	20.8157	20.63	Cristobalite	4.26748
	21.9676	14.54	Kaolinite-1A	4.04624
	23.6660	12.19	Kaolinite-1A	3.75958
	26.5951	100.00	Kaolinite-1A, Quartz,	3.35178
	27.9618	68.48	Cristobalite	3.19009
d	12.3427	23.23	Kaolinite-1A	7.17134
	24.8890	25.97	Kaolinite-1A	3.57753
	26.6313	96.07	Kaolinite-1A, Quartz,	3.34731
	33.2313	64.65	Hematite, Alumina	2.69605
	35.6178	100.00	Kaolinite-1A, Hematite, Alumina	2.52069
	49.4781	29.78		1.84220
e	12.3373		Kaolinite-1A	7.17450
	18.2790		Magnetite	4.85359
	20.2930	100.00	Kaolinite-1A	4.37602
	21.2207	66.38		4.18695
	24.8663	82.35		3.58075

Effect of pH solution

One important parameter that determines the ability of the adsorbent to absorb the metal on the surface of the solid-liquid is pH. Therefore, the pH conditions must be set in order to obtain good adsorption capacity. Measurement of the effect of pH on the adsorption of Pb (II) is performed by varying the pH of 2-6 with each initial concentration of 250 mg/L. Effect of pH on its capacity adsorption of metal ions Pb (II) can be seen in Figure 3. It was showed the maximum biosorption of Pb (II) occurred at pH 4 with adsorption capacity 11.146 mg/g. There was a increase (pH 2-4) and decrease (pH 4-6) in adsorption capacity with between pH from 2 to 6.

According Inglezakis et al. (2007)(5), a decrease in the adsorption of Pb (II) reflects a decrease in the amount of negative charge on the surface of the Napa soil assumed as zeolites. At low pH, silica zeolites attract the positive ions from the adsorbate. The amount of negative charge on the surface of the adsorbent decreases with increasing pH. This causes a decrease in the adsorption of Pb (II) in solution at high pH. At pH 2, the adsorption capacity is very low because the solution is too acidic, so that there is competition of H^+ ions and Pb(II) ions. Different at pH 4, many Pb(II) ions present in the solution and stuck to the surface of the adsorbent.

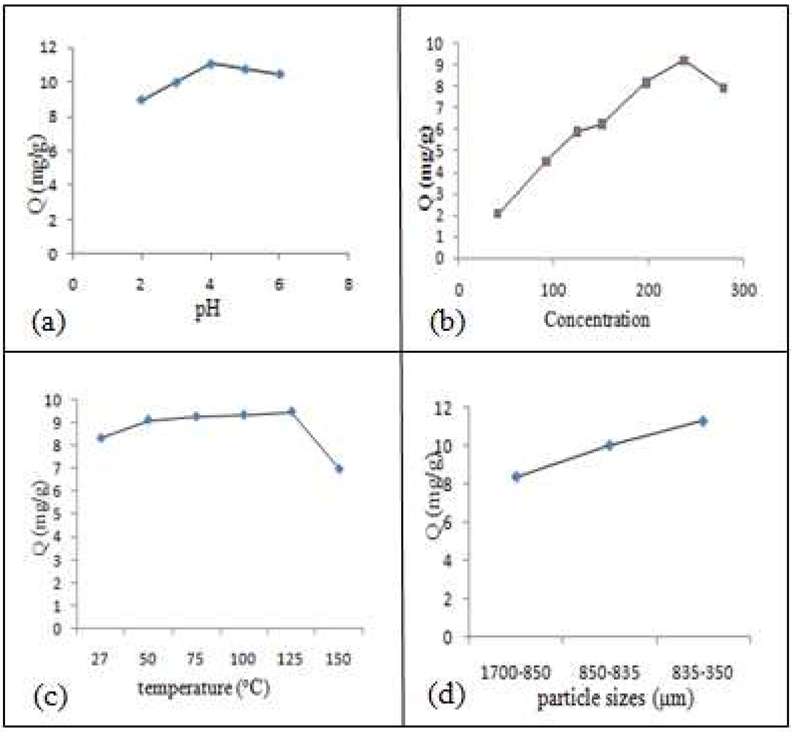


Figure 3. Effect of initial pH in Pb (II) solution on the adsorption capacity of the Napa soil adsorbent, effect of concentration (b), temperature heating (c) and Effect of particle size on Pb (II) (d)

Effect of Initial Metal Ion Concentration
Based on Figure 3, the adsorption capacity of the largest Napa soil occurs when concentration of Pb (II) ion reach between 200 ppm and 250 ppm. If initial concentration increase adsorption capacity value tends to fall because the Napa soil surface has been saturated and has undergone equilibrium.

In the metal ion concentration above the optimum concentration of metal ions adsorbed amount decreased, the initial concentration of the solution obtained optimum adsorption capacity of 9.195 mg/g, while the decline in the next concentration be 7.901 mg/g. This is probably due to all the active groups on the adsorbent has binding Pb (II) metal ions, so that there is no place for metal ions which have not been attached. There is even the possibility of blocking the active site on the adsorbent causes the metal ions that have bound to be separated again.

Effect of Adsorbant Heating Temperature on adsorption of Pb (II)
From Figure 3, the adsorption increases with temperature rise of heating the adsorbent. Absorption of the ions Pb (II) on the adsorbent soil napa increased adsorption capacity at heating temperature 50°C is 9.119 mg/g, after heating 50°C, the adsorption capacity increased less significantly by heating 125^{o}C is 9.480 mg/g, but on heating 150^{o}C, the adsorption capacity decreased sharply with the absorption capacity 6,967mg/g.

This capacity reduction due to the destruction of soil structure Napa soil (zeolite), which reduced vacuum spaces inside the zeolite and ultimately will reduce the adsorption power. Increased adsorption capacity by raising the heating temperature can be explained, because it has been breaking of hydrogen bonds between water with silanol (Si-OH) or between water with siloxane groups (Si-O-Si) in the zeolite. As a result, the release of water molecules on the surface of silica that causes an increase in surface area and pore volume so that the process of physical adsorption and chemical adsorption to become more effective and efficient.

Effect of particle size on adsorption of Pb (II)
The influence of particle size of the adsorbent for the adsorption of Pb (II) by Napa soil showed increased adsorption capacity as shown in Figure 3. The size of the particles used are in the range as follows 1700-850µm, 850-835 µm and 835-350µm. Based on data from the study showed that the absorption capacity of the adsorbent with 1700-850 mµ particle size is 8.355 mg/g, while the particle size of 835-350 µm is 11.323 mg/g.

The increase is due to the adsorption capacity of the adsorbent surface area in contact with the adsorbate increasingly widespread. The surface area of the adsorbent primarily to the availability of places adsorption.

Adsorption is a surface incident so that the amount of adsorption is proportional to the specific surface area, the more surface contact with the adsorbate it will be the greater the adsorption occurs(6).

Effect of flow rate on adsorption of Pb(II)

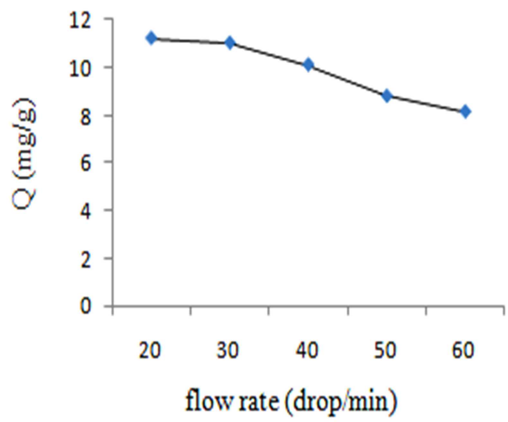


Figure 4. Effect of flow rate on Pb(II) adsorption by Napa soil

From Figure 4 shows that the uptake of land napa for Pb(II) on some variation of flow rate seen very clearly. At a flow rate of 20 drops/minute capacity of absorption is 11.213 mg/g, at a flow rate of 30 drops/min is 11.020 mg/g, whereas at a flow rate of 40, 50, and 60 drops/minute respectively is 10.108 mg/g, 8.805 mg/g, and 8.170 mg/g. At the eluent flow rate is rapid (60 drops/minute), ions Pb(II) which is absorbed much less than the flow rate of 20 drops/minute. This is because the contact time between the ions Pb(II) with an adsorbent in the column is not long enough to reach the adsorption equilibrium, so that a solution of ions Pb(II) left column before equilibrium occurs.

Mechanism of Adsorption of Pb(II) on Napa Soil adsorbent

From the results of XRD characterization, XRD and SEM, napa land classified as natural zeolite mineral. This is due, various oxides contained in the soil of Napa, among others, SiO_2, Al_2O_3, CaO and Fe_2O_3. The largest component of which is as much as 63.20% SiO_2, Al_2O_3 sebanyak16.55%, Fe_2O_3, CaO as much as 7.64% and as much as 3:34%.

Surface silica (SiO_2^+) has a high affinity for metal ions. Ion center silica (Si_4^+) has a strong affinity for electrons (easily capture electrons). Oxygen atoms bonded to the silica ion which has the properties of low alkalinity and makes the surface of the silica is a weak acid. Oxygen atoms on the silica surface is free to react with water to form a silanol group Si (OH). Other forms are also free oxide reacts with water to form hydroxide(7), such as $Al(OH)_3$, $Fe(OH)_3$ and $Ca(OH)_2$. H^+ ions in the form of hydroxide will be weakened and easily separated and lead metal ions to be bonded and strongly adsorbed(8).

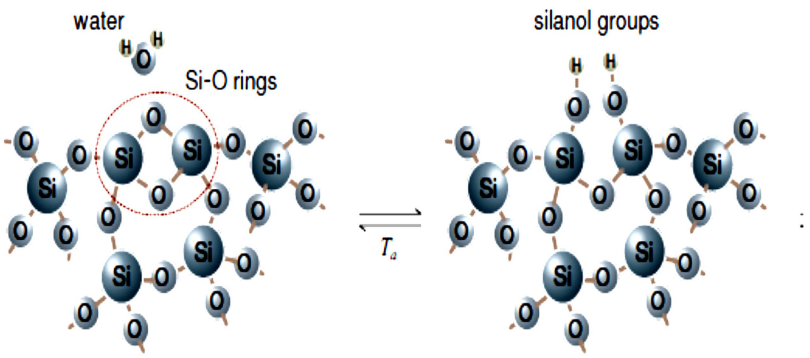


Figure 5. Structure and reactions of the ring pebentukan silanol siloxanes

The presence of negative charge of the release of H^+ atoms of Si(OH) will cause interactions between positively charged metal with active sites on the surface of the adsorbent that is negatively charged. At the same time, the surface ligand will compete with OH^- in binding metal cations, that will lead to an increase in metal adsorption by soil napa. PH effect on metal species in solution. Metal ions in solution before it is adsorbed by the adsorbent first undergo hydrolysis, produces protons and hidrokso metal complexes such as the following reaction:

$M^{2+}_{(aq)} + H_2O_{(l)} \rightarrow M(OH)^{+}_{(aq)} + H^{+}_{(aq)}$

Where M^{2+} is Pb^{2+}

In the process of absorption using a zeolite, the existing Pb^{2+} ions in the solution will be absorbed by the surface of the zeolite pores and bersubtitusi with H^{+} cations existing on the surface of the zeolite, as in the following reaction :

$\text{Zeolites-H}^{+} + Pb^{2+} \rightarrow \text{Zeolite-Pb}^{2+} + H^{+}$

Pearson theory suggests the principle HSAB (Hard and Soft Acid Bases) by classifying according to the Lewis acid-base properties of hard and soft. Strong acidic cation will interact strongly with the ligands strongly alkaline. Otherwise weak acid cation which will interact strongly with the ligand that is a weak base. Between lead ions is acid. The OH group in silanol and aluminol including strong acids. Another view states that the metal cation will be attracted by the particles of diatomaceous soil, because of the negative charge on the surface of the soil.

Adsorption Isotherm

From Figure 6 shows that the adsorption of Pb (II) by adsorbent napa land that gives linearity to Langmuir isotherm 84.9% and 76.5% for the Freundlich isotherm. Adsorption pattern is determined by comparing the linearity of the curve shown by the price of R_2 (Suardana 2008) [19]. Based on these results, napa land allegedly adsorbent adsorption followed Langmuir isotherm types. Langmuir approach assumes adsorbate adsorbed form a single layer, surface adsorbate same binding power, there is no lateral interchanges between adsorbate molecules, and molecules adsorbed adsorbate is localized, meaning that these molecules do not move on the surface.

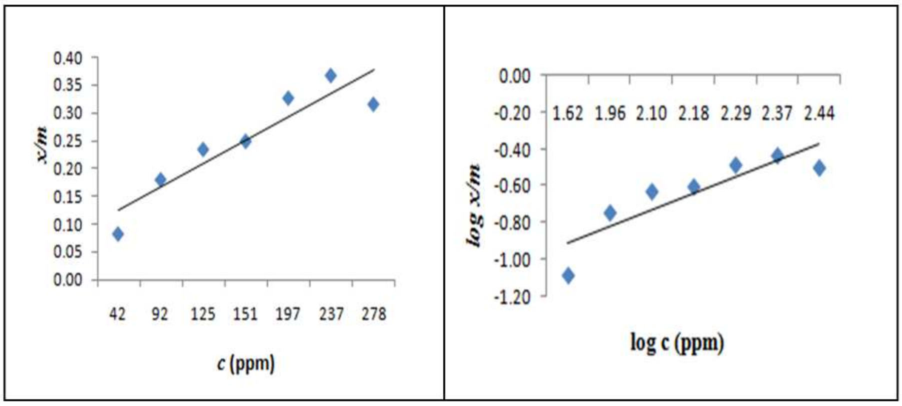


Figure 6. Adsorption Isotherm of Langmuir (a) and Freundlich (b) for ion Pb(II) on column method

Maximum Absorption Capacity Determination of Pb(II) on Napa soil

By using the Langmuir adsorption isotherm equation (Eq. 3) so we can determine the maximum absorption capacity of the soil napa for Pb(II).

$$\frac{C}{x/m} = \frac{1}{(x/m)_{mak}k} + \frac{1}{(x/m)_{mak}} \qquad \text{Equation 3}$$

x/m is adsorbed metal milligrams per gram of dry materials; k is the equilibrium constant (affinity constants uptake); C is the concentration of free ions when the equilibrium (mg/L); (x/m) mak was milligrams metals absorbed in the saturated state (capacity of maximum absorption), the plot of data C/(x/m) versus C produces a straight line, then the constant affinity uptake (k) and a capacity of maximum absorption (x/m) mak can be determined by the slope and intercept. And k values (x/m) makyang obtained for Pb(II) ion are respectively 0.488 and 24,39mg/g.

CONCLUSION

The results demonstrate that Napa soil are an effective adsorbent to remove Pb (II) from aqueous solution. Pb(II) was removed in coulomb experiments. Adsorption process was affectifed by pH 4, temperature heating at 125^{o}C, initial concentration 250 mg/L, particle size 830-350 µm and 20 drop/min flow rate with adsorption capacity 24.39 mg/g. The equilibrium data fitted well to Langmuir isotherm with R^2 = 0, 849 and affinity constant for adsorption is 0.488 (Fig 6). The study revealed that Napa soil adsorbent could be used as on adsorbent for the removal of other heavy metals on large scale.

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