

Original Research Paper

The Development of Nanotechnology Bentonite as Adsorbent of Copper Metal (Cu)

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Abstract: The aims of the research to develop nanotechnology with the use of bentonite as adsorbent cooper metal (Cu). Bentonite activation treatment performed. The parameters studied in this research is a variation of the mass of bentonite, contact time and adsorption capacity. Measurements were made using AAS. Activation of bentonite using a solution of HCl 1.6 M. In experiments conducted bentonite weight variation of 0.1; 0.3; and 0.5 gr with a contact time of 30,60,90 and 120 s. The results showed that the decreased absorption of active bentonite is 96.8 and 99,7% bentonit not activated Thus discovered a new phenomenon which is not activated bentonite is have a better ability to absorb copper compared to the activated bentonite.

Keywords: Bentonite, Nanotechnology, Metal Cu, Adsorption, AAS

Introduction

Disposal of industrial waste is continuously not only pollute the environment but lead to the accumulation of heavy metals in sediments and biota (Hutagalung, 1991). Heavy metal is a metal element with a relative molecular mass larger than with other metal elements such as alkali and alkaline earth metals (Notohadiprawiro, 1993). Even low levels of heavy metals are generally toxic to plants and animals, including humans. Efforts to tackle high levels of metals can be done with the adsorption process (Sembiring *et al.*, 2009). One of the heavy metals that are harmful to the environment and the human body when the concentration exceeds a threshold that is metallic copper (Cu), because these metals are toxic and are not needed by the human body, when mankind is contaminated by heavy metals can cause high blood pressure, kidney tissue damage testibuler, lung cancer and damage to the red blood cells of kidney and liver damage and cardiovascular disorders. Cu hazardous if the concentration exceeds that of the corresponding recommended. Terms of the water quality standards that is a threshold level of Cu (II) to water class A (for drinking water) of 1.0 mg L⁻¹ of class B (for drinking water) 1.0 mg L⁻¹, class C (for fishing) 0, 02 mg L⁻¹ and class D (for agriculture, industry, hydropower) 0.2 mg L⁻¹ (Government regulation No. 20 of 1990).

To reduce the levels of Cu in the wastewater, the adsorption of Cu can be done by using the adsorbent is bentonite. Bentonite has two layers of different interlayer so that the bentonite has a high cation exchange capability, because the bentonite is a good adsorbent for absorbing organic compound or pesticide, dye and heavy metal ions (Faizal, 2014). Deposits of bentonite in Jambi province are known in three areas, namely the Bangko district with an area of 4400 hectares, Bungo Tebo = 520 hectares and Batang Hari hectare = 1350. Bentonite has been used for processing some parameters on peat water into clean water. and most likely bentonite can also be used for absorption of copper metals in the environment (Naswir *et al.*, 2015).

The method is commonly used for the management of heavy metals in the environment is a method presipitation, electrogravimetr, separation, membrane and adsorption. In a research method developed is the adsorption method, because this method has the advantage of a cheaper, simpler, easier critical operations and have a great capacity (Christidis *et al.*, 1997). The adsorbent used is bentonite. Bentonite has a good adsorption capacity, power exchange cations and anions are good. Bentonite as an adsorbent needs to be activated in advance and determined the optimum conditions before being used for the absorption process in order to work more absorbency maximal. So in this research will be to learn how efficient absorption of bentonite to

metallic copper (Cu), optimal conditions and how capacity adsorption.

Research Methodology

Materials and Equipment

Materials used in this research is the region's natural bentonite precisely Jambi Regency Tanjung area Biku Merangin, HCl, distilled, crystal $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and filter paper. The equipment used consisted of a set of glassware such as beakers, erlenmeyer, long neck flask, 200 mesh strainer, shaker, oven, grinder and measurement instruments for Copper (Cu) using Atomic Absorption Spectrophotometry (AAS).

Preparation and Activation of Bentonite

Bentonite samples taken in the area Biku Tanjung packed in sacks, then performed the sample preparation by softening and drying with hot sun, then followed by drying in an oven at 105°C for 24 h which aims to eliminate moisture (heat activation). Bentonite which has been dried crushed and pulverized to 200 mesh size nanometer. Once that is done the activation of bentonite with 500 g of bentonite with a size of 100 mesh immersed in 1000 mL of 1.6 M HCl while stirring for one hour at 100 rpm and then filtered and washed with distilled water. The resulting residue is heated to a temperature of 200°C for one hour Once dried, crushed to powder measuring nanogram to 200 mesh sieve. Activated bentonite obtained is used for the absorption of copper metal.

Preparation of Standard Copper (Cu)

In making the reagents used are crystal $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, then diluted with distilled water in a measuring cup and matched volume of 1000 mL with distilled water, then the resulting stock solution Cu 1000 ppm. Copper 1000 ppm standard solution of 2.5 mL were taken and then put in a 250 ml volumetric flask and diluted with distilled water to mark boundaries to obtain a standard solution of 10 ppm. Standard solution of 10 ppm were taken 10 mL, 20 mL, 30 mL, 40 mL, 50 mL and diluted in 100 ml volumetric flask to obtain standard solution 1, 2, 3, 4 and 5 ppm

Copper (Cu) Concentration Measurements with Mass Variation and Contact Time

Each bentonite 0.1; 0.3 and 0.5 g which has not been activated incorporated into the beaker and then added 50 mL solution of 1 ppm $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ into each glass. The solution will be stirred using a shaker speed of 200 rpm for 1 h. Variation 30, 60, 90 and 120 min. The solution is filtered to separate the filtrate and the residue. The filtrate obtained was analyzed by AAS.

Analysis Data

The concentration of the sample solution is determined by substituting the price sample absorbance (y) obtained from the data AAS through linear regression line equation $Y = ax + b$ (Miller and Miller, 1991). Copper calibration curve obtained by plotting the concentration of the copper standard solution to the absorbance. To determine the absorption efficiency of metal cadmium used the formula:

$$\% \text{ Efisiensi Absorption} = \frac{Co - Ca}{Ca} \times 100\% \quad (1)$$

note: Co = initial concentration, Ca = Concentration end.

Calculation of adsorption capacity (Q_e) Cd metal with the formula:

$$Q_e = \frac{(\text{Initial concentration} - \text{concentration end})}{\text{adsorbent mass}} \quad (2)$$

Results and Discussion

Characterization of Bentonite

Bentonite can be applied as an adsorbent for memiliki extensive surface, porous and have active sites. Bentonite is a mineral alumina silicate hydrate included in pilosilikat, or layered silicates. General chemical formula bentonite is $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. The content consists of monmorilonite bentonite, illite and quartz which 85% of its content in the form of montmorillonite (Apriliana and Dewi, 2015). Bentonite Biku Tanjung Province of Jambi contains minerals monmorillonit, quarsa, cristobalite and kaolinite as in Fig. 1 (Naswir *et al.*, 20013).

The bentonite composition of the Tanjung Biku area is determined using the SEM-EDS instrument, as listed in Table 1 (Naswir *et al.*, 2013).

Table 1: Composition of bentonite Biku Tanjung Jambi Province

| Komponen | % berat |
|-------------------------|---------|
| SiO_2 | 44.11 |
| Al_2O_3 | 33.61 |
| TiO_2 | 0.66 |
| CaO | 0.01 |
| MgO | 0.19 |
| K_2O | 0.04 |
| Na_2O | - |
| FeO | 2.22 |
| CuO | 3.85 |
| C | 14.24 |

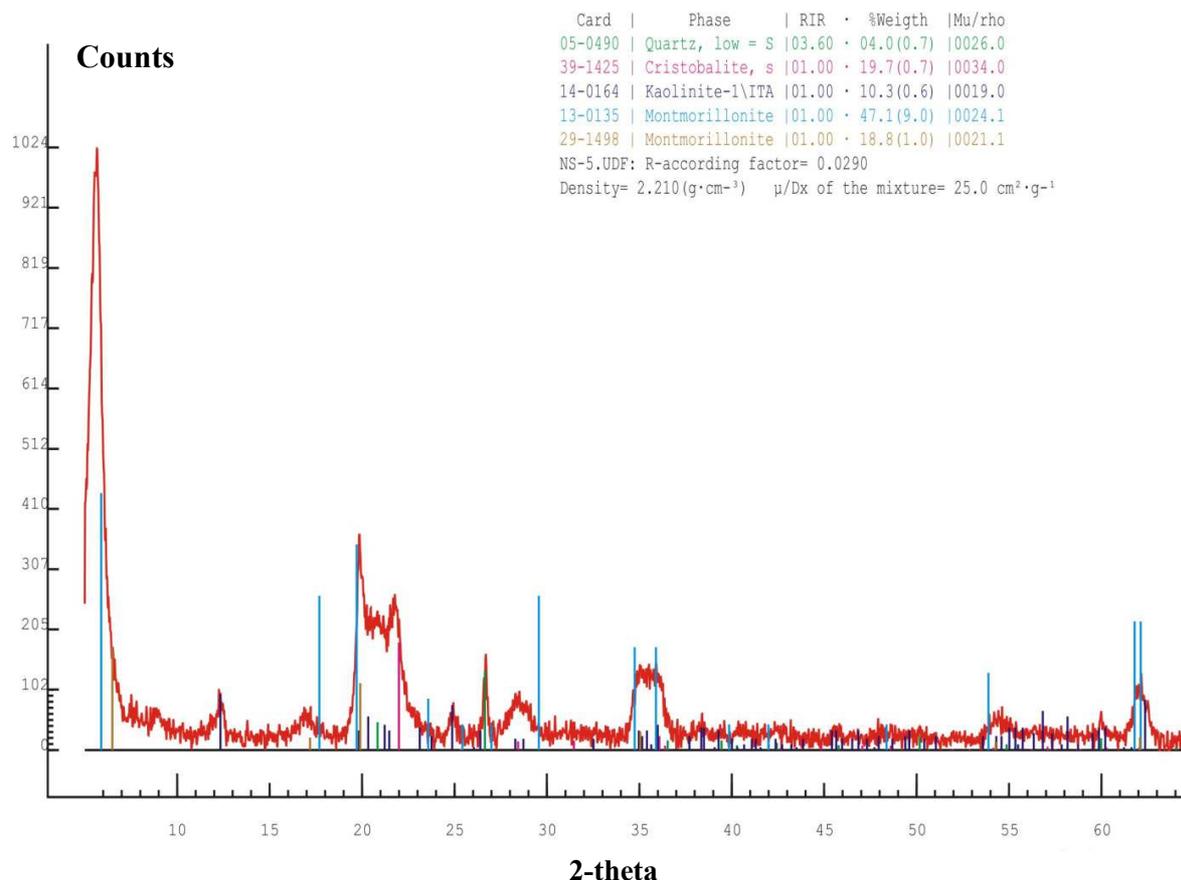


Fig. 1: Spectrum XRD Bentonit of The Biku Tanjung (Naswir *et al.*, 2013)

From Table 1 it is known that bentonite has some chemical components that cause the bentonite can adsorb, in addition to the adsorption properties of bentonite is because the particle size is very small and has a high capacity ion surface (Naswir *et al.*, 2013). Absorptive capacity will be increased if activated bentonite both physics and chemistry. Activation aims to eliminate impurity/impurities that accompany the natural clay (Prasetyowati *et al.*, 2014).

Measurement of Copper (Cu)

The resulting absorbance is directly proportional to the concentration of the standard solution ie the greater the concentration used, the absorbency also getting bigger. Having obtained the absorbent of the standard solution, then graphed the relationship between the concentration by absorbent then be produced linear regression calibration curve in getting to channel the concentration of standard solution as X-axis is plotted against the Y axis absorbency as obtained from measurement data at AAS. Standard calibration curve obtained produce regression equation $y = 0,127x$.

Measurement of Mass Variation and Contact Time

Bentonite used mass variation affects the absorption occurs, this can be illustrated in Fig. 2

From Fig. 2. The above can be seen in the treatment of active bentonite weighing 0.1 grams of Cu uptake by 96.8%, with a weight of 0.3 grams of Cu absorption amounted to 90.7%, but with bentonite which is inactive with a weight of 0.1 grams of Cu absorption of 99.7%, with a weight 0.3 grams of Cu absorption of 100%. In active bentonite is shown in the graph shows that the increased weight of bentonite absorption of Cu decreased, this is due to overly saturated HCl used in the activation (Apriliana and Dewi, 2015). According to (Ramadani and Eko, 2011), the increasing concentration of the acid will produce larger active site so that it will produce an active site that has a better adsorption capacity.

Research conducted by Bath (2012) showed that bentonite (West Java) activated by using HCl has absorption to Cu of 99.16%, while research by Ramdani by using H₂SO₄ activator showed absorption to Cu is equal to 84,11 and 90,32% (Ramadani and Eko, 2011) beside that other experts who do research on the absorption of natural bentonite to metal Cu, with good

result (Yusnimar and Drastiwati, 2005). Ion exchange reaction is a special form of chemical adsorption. Ion exchange can take place if the majority Cu adsorbent replace the existing position of positive ions in the bentonite adsorbent, so that the positive ions migrate into the liquid (Al-Jlil, 2010). This is because there is the Coulomb force between negatively charged ions contained no adsorbent with positive ions such as Cu as adsorbate, bonding can occur electrostatic bond (Apriliansa and Dewi, 2015; Komadel, 2003).

On absorption of Cu using bentonite is not yet active percent absorption efficiency of 100% with a contact

time of 30 min. This contact time is the time used by the adsorbent and adsorbate to interact directly. If the liquid phase containing the adsorbent silent, then the adsorbate diffusion through the surface of the adsorbent will be slow. It is therefore necessary agitation to accelerate the process of adsorption (Weber, 1972). According to Suarya the increased absorption of adsorbate by the adsorbent shows yet saturated adsorbent active sites by adsorbed molecules, but the weight of the adsorbate adsorbed condition have been caused by the constant saturation of active sites of the adsorbent by adsorbate molecules (Suarya, 2008).

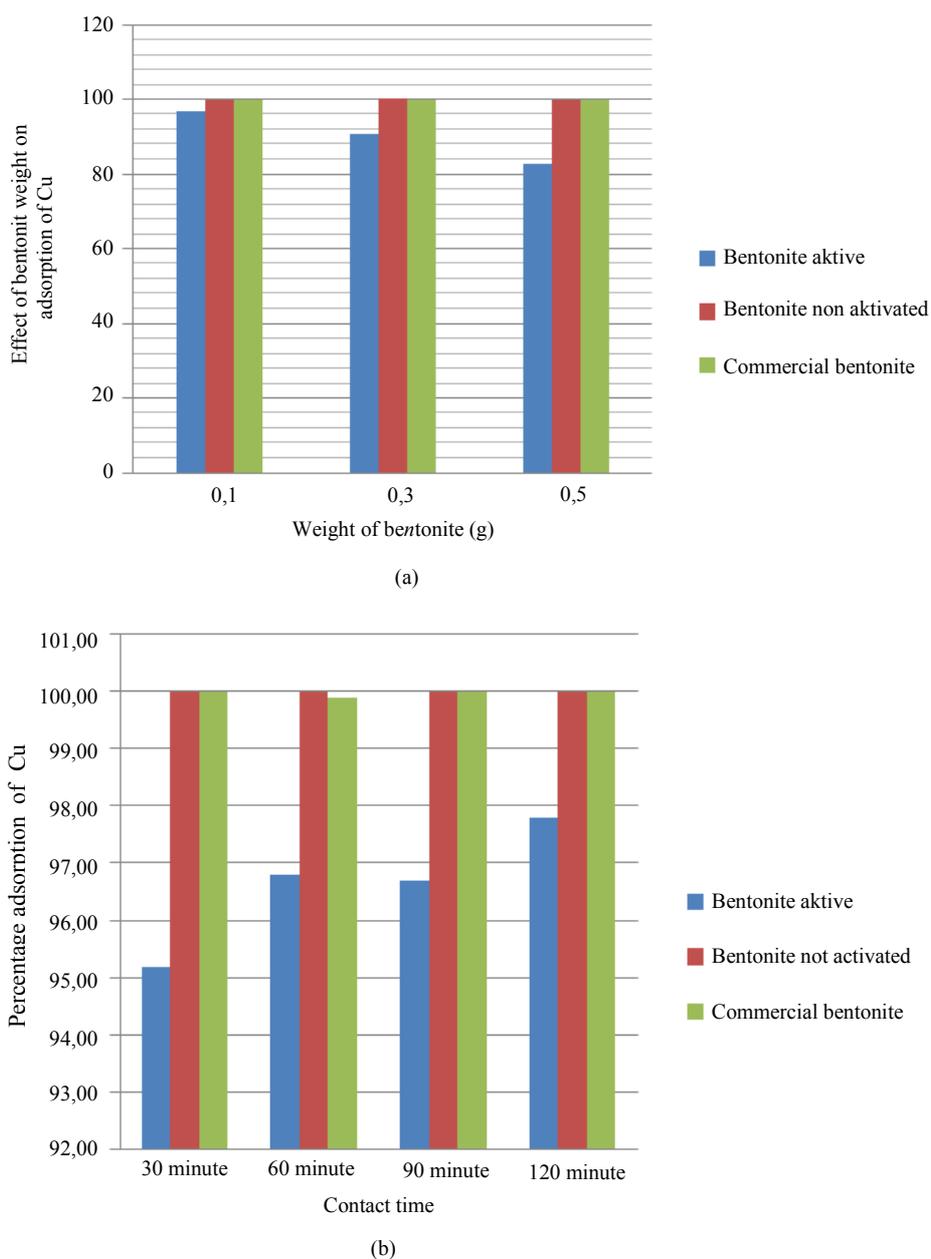


Fig. 2: Graph of weight variation (a) and contact time (b) of bentonite to the adsorption of Cu

With activation can enlarge the pores do that is by oxidize molecules adsorbent surface so that the physical and chemical changes, namely the surface area increase in size and influence on the adsorption capacity (Salamah, 2008). Activation of bentonite can be done in two ways, namely by physics and chemistry. Chemical activation is done by acid or base. The chemicals that are often used as an activator is H_3PO_4 .

$ZnCl_2$, $CaCl_2$, K_2S , HCl , H_2SO_4 , $NaCl$, Na_2CO_3 (Istighfaro, 2010). Bentonite can be used as an adsorbent for most of its crystal structure consisting of montmorillonite (smectite) with type 2: 1 i.e., $2SiO_2 \cdot AlO_3$ (Fatimah, 2014) as adsorbent and widely applied in the adsorption process. Bentonite is a mineral alumina silicate hydrate included in pilosilikat, or layered silicates. General chemical formula bentonite is $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$. The content consists of monmorilonite bentonite, illite and quartz which 85% of its content in the form of montmorillonite. The plated 2: 1 layer structure between the basic structural units results in the proximity of two oxygen atoms from the tangent tetrahedral layers, so that the basic structural units repel each other and result in the expansion of clay minerals which form the active site of an addition so that the active site is more than one layer.

For a 2: 1 layered structure the embankment between the basic structural units results in the proximity of two oxygen atoms of the tangent tetrahedral layers, so that the basic structural units repel each other and result in the expansion of clay minerals which form the active site

of an additional so-called intermediate site layer internal), The existence of sites between these layers is a special feature of the clay-coated mineral structure with 2: 1 (Sainz-Diaz *et al.*, 2001). Bentonite is masked with a large surface including nanotechnologies, a large surface formed by many fine pores in bonding. Usually the extent is about 200-1000 m^2/g of adsorbent, with a pore diameter of 0.0003 to 0.02 μ .

Adsorption Capacity

Adsorption capacity is used to describe the relationship between the adsorbent and the adsorbed substance in an equilibrium. There are two models used to determine the adsorption isotherm is Langmuir and Freundlich isotherm models. The process of absorption or adsorption by an adsorbent is influenced by many factors and also has a pattern within specific adsorption isotherms so adsorbent which absorbs a substance one with another substance would not have the same pattern of the adsorption isotherm. Cu absorption measurement results after the addition of bentonite can be summarized in Table 2.

Langmuir isotherm is based on the assumption that the adsorbent has a homogeneous surface, adsorption energy is constant in all sides, all equally adsorption process each adsorbent surface and each side of the adsorbent can only absorb one adsorbate molecule. The following chart Langmuir isotherm calculation result of bentonite active in absorbing Cu.

Table 2: Results of measurement of the concentration of Cu after treatment

| C initial | C endr | | Wight | Amount | | | |
|--|----------|--------|----------------|---------|-------------|---------|---------|
| Cu (ppm) | Cu (ppm) | Volume | bentonite (gr) | (mg/g) | | | |
| Co | Ce | (L) | M | Qe | Ce/Qe (g/L) | Log Ca | Log Qe |
| 1 | 0.032 | 0.5 | 0.1 | 0.48400 | 0.06610 | -1.494 | -0.3150 |
| 1 | 0.093 | 0.5 | 0.3 | 0.15116 | 0.61524 | -1.032 | -0.8200 |
| 1 | 0.175 | 0.5 | 0.5 | 0.0825 | 2.12120 | -0.757 | -1.0830 |
| Variation of weight bentonite aktive | | | | | | | |
| Co | Ce | | M | Qe | | | |
| 1 | 0.003 | 0.5 | 0.1 | 0.4985 | 0.00602 | -2.5228 | -0.3020 |
| 1 | 0.000 | 0.5 | 0.3 | 0.1667 | 0.00000 | -∞ | -0.7780 |
| 1 | 0.001 | 0.5 | 0.5 | 0.0999 | 0.01001 | -3.0000 | -1.0004 |
| Variation of wieght bentonite inactive | | | | | | | |
| Co | Ce | | M | Qe | | | |
| 1 | 0.002 | 0.5 | 0.1 | 0.4990 | 0.004008 | -2.698 | -0.3020 |
| 1 | 0.002 | 0.5 | 0.3 | 0.1663 | 0.012020 | -2.698 | -0.7790 |
| 1 | 0.001 | 0.5 | 0.5 | 0.0999 | 0.010010 | -3.000 | -1.0004 |
| Variation of contact time bentonite active | | | | | | | |
| Co | Ce | | M | Qe | | | |
| 1 | Ttd | 0.05 | 0.3 | 0.1667 | 0.000000 | -∞ | -0.7780 |
| 1 | Ttd | 0.05 | 0.3 | 0.1667 | 0.000000 | -∞ | -0.7780 |
| 1 | Ttd | 0.05 | 0.3 | 0.1667 | 0.000000 | -∞ | -0.7780 |
| 1 | Ttd | 0.05 | 0.3 | 0.1667 | 0.000000 | -∞ | -0.7780 |
| Variation of contact time bentonite inactive | | | | | | | |
| Co | Ce | | M | Qe | | | |
| 1 | Ttd | 0.05 | 0.5 | 0.1000 | 0.000000 | -∞ | -1.0000 |
| 1 | 0.001 | 0.05 | 0.5 | 0.0999 | 0.010010 | -∞ | -1.0004 |
| 1 | Ttd | 0.05 | 0.5 | 0.1000 | 0.000000 | -∞ | -1.0000 |
| 1 | Ttd | 0.05 | 0.5 | 0.1000 | 0.000000 | -∞ | -1.0000 |

Table 3: Results of the Langmuir isotherm of some types of bentonite and variations in time and contact time

| Variation | Type Bentonite | Result | |
|-----------------|----------------|----------------------|----------------|
| | | y | R ² |
| Massa bentonite | Aktive | $y = 14.59x - 0.525$ | $R^2 = 0.968$ |
| | In active | $y = 1.435x + 0.003$ | $R^2 = 0.189$ |
| | Commercials | $y = 1.996x + 0.012$ | $R^2 = 0.076$ |
| Contact time | Aktive | $y = 1.815x + 0.025$ | $R^2 = 0.261$ |
| | In active | 0 | 0 |
| | Commercials | $y = 10.01x$ | $R^2 = 1$ |

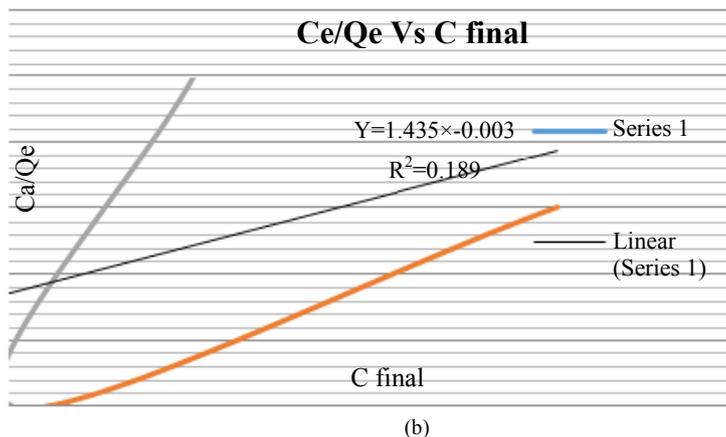
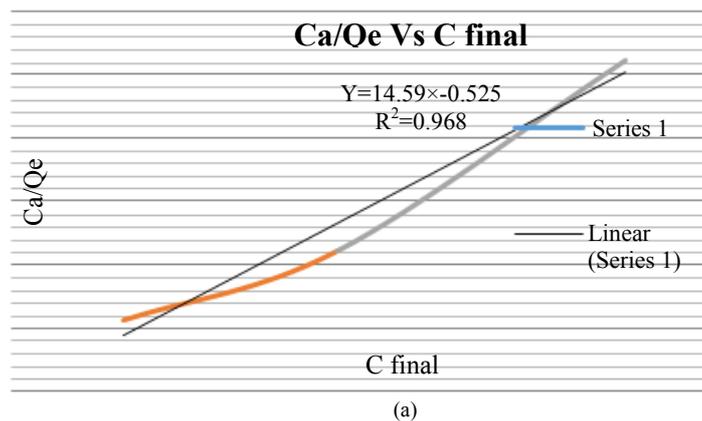


Fig. 3: (a) Langmuir isotherm bentonit active (b) Freudlick isotherm of inactive bentonite

Figure 3 shows a graph with the Langmuir isotherm active bentonite to produce a regression equation $y = 14.59x - 0.525$ and the value of $R^2 = 0.968$ and for bentonite are not actively providing the regression equation $y = 1.435x + 0.003$ and the value of $R^2 = 0.189$. Overall the regression equation obtained can be summarized in Table 2.

From Table 3 it can be seen that the regression equation resulting from variations in the mass of bentonite and bentonite variation of contact time of the active and inactive. Langmuir isotherm adsorption isotherm is a model that uses the assumption that the surface of the adsorbent have switched on any number of sites can adsorb the active site of the molecule adsorbate

and when any active sites that have been adsorbed adsorbate then the adsorbent is already unlikely to be able to adsorb again. Langmuir isotherm indicate that the adsorption process occurs chemically active sites that bentonite will interact with hydroxyl groups contained on Cu by forming hydrogen bonds.

Conclusion

The ability of bentonite that has been activated in absorbing Copper (Cu) smaller than the bentonite which has not been activated. Bentonite is not activated efficiency has 97.7% while the activated bentonite has

the absorption efficiency of 82.5% with a contact time of 30 minutes. Langmuir isotherm with the price of r close to 1 indicates that the adsorption process occurs chemically active sites that bentonite will interact with hydroxyl groups contained on Cu by forming hydrogen bonds in a single layer (monolayer)

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Author's Contributions

Susila Arita: Designed the research plan and organized the Research.

Muhammad Naswir: Design and, participated in all experiments, data collection, data-analysis and writing of the manuscript.

Irma Astriana: Data collection and participated in all experiments and Scriptwriting. discussion of the contents of the manuscript.

Nelson: Analisis data, Scriptwriting. discussion of the contents of the manuscript.

References

- Al-Jlil, S.A., 2010. Heavy metal reduction of industry waste by using bentonite and roasty clay. *Sci. Technol.*, 5: 138-145.
DOI: 10.3923/tasr.2010.138.145
- Apriliansa, P. and I.K. Dewi, 2015. Adsorption of metals Pb^{2+} and Cu^{2+} by activated bentonite base (NaOH). *J. Chem.*, 9: 235-242.
- Bath, D., 2012. Land use bentonite as adsorbent metal Cu. *Scientific J. Chem. Eng.*
- Christidis, G.E., P.W. Scott and A.C. Dunham, 1997. Acid activation and bleaching capacity of bentonites from the islands of Milos and Chios, Aegean, Greece. *Applied Clay Sci.*, 12: 329-347.
DOI: 10.1016/S0169-1317(97)00017-3
- Faizal, M., 2014. Containing Waste Water Treatment Using heavy metal composite adsorbent with Bentonite and Fe_3O_4 . *J. Chem. Eng.*
- Fatimah, I., 2014. Adsorption and catalysis using clay-based materials. Graha Science, Yogyakarta.
- Hutagalung, H.P., 1991. Sea pollution by heavy metal. Oceanology Research Center, Sea Pollution Status in Indonesia and Monitoring Techniques, LIPI, Jakarta.
- Istighfaro, N., 2010. Improved cooking oil with adsorption method using bentonite-activated carbon moringa seeds. UIN, Malang, Indoensian.
- Komadell, P., 2003. Chemically modified smectites. *Clay Miner.*, 38: 127-138.
DOI: 10.1180/0009855033810083
- Miller, J.C. and J.N. Miller, 1991. Statistics for analytical chemistry. ITB, Bandung, Indonesian.
- Naswir, M., S. Arita, M. Marsi and S. Salni, 2015. Treatment of peat water using local raw material formulations of Jambi, Indonesia. *Asian J. Chem.*, 27: 3951-3955. DOI: 10.14233/ajchem.2015.18963
- Naswir, M., S. Arita, Marsi and Salni, 2013. Characterization of bentonit by XRD and SEM-EDS and use to incease pH and color removal, Fe and organic substance in peat water. *J. Clean Energy Technol.*, 1: 313-317.
DOI: 10.7763/JOCET.2013.V1.71
- Notohadiprawiro, T., 1993. Heavy metals in agriculture. Manuscript Lecture in Palm Research Center, Medan, Indonesian.
- Prasetyowati, Yuni, Koestari and Toeti, 2014. Bentonite adsorption capacity technical as adsorbent ion Cd^{2+} . *UNESA J. Chem.*
- Ramadani and Eko, 2011. Effect of H_2SO_4 concentration and weight of natural activated bentonite and commercial. The absorption of heavy metals Cadmium (Cd) and copper (Cu) in solution Cu and Cd Standard with AAS method. Sumatera Utara University, Indonesian.
- Sainz-Diaz, C.I., A. Hernandez-Laguna and M.T. Dove, 2001. Modeling of dioctahedral 2:1 phyllosilicates by means of transferable empirical potentials. *Phys. Chem. Mineral.*, 28: 130-141.
DOI: 10.1007/s002690000139
- Salamah, S., 2008. Activated carbon manufacture of fruit leather mahogany treatment immersion in KOH solution. Proceedings of the National Seminar Teknoin, (NST' 08), Field of Chemical Engineering and Textile.
- Sembiring, Z., Buhani, Suharso and Sumadi., 2009. The isothermic adsorption of $Pb(II)$, $Cu(II)$ and $Cd(II)$ ions on *Nannochloropsis* sp encapsulated by silica aquagel. *Indo. J. Chem.*, 9: 1-5. DOI: 10.22146/ijc.21556
- Suarya, P., 2008. Clove leaf oil impurity adsorption by acid activated clay. State University of Udayana.
- Weber, W.J., 1972. Physics chemical processfor water quality control. John, New York.
- Yusnimar and Drastinawati, 2005. Utilization of bentonite as adsorbent on palm oil bleaching process. Proceedings of the National Seminar on Technology Petro-oleochemical, (TPO' 05), Riau Indonesian.