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The development of nanotechnology bentonite as adsorbent of metal Cadmium (Cd)

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Abstract. Cadmium (Cd) is a heavy metal that is toxic to the environment. Cadmium in the environment can be derived from natural processes such as weathering of living creatures and plants or animals from mining and industrial waste. To overcome the heavy metal pollution in the environment can be used adsorption method. The adsorbent used in the study is bentonite. The purpose of this study was to determine the absorption efficiency bentonite to the metal cadmium. Bentonite samples from the area of Jambi Province. Bentonite is divided managed bentonite inactive, active bentonite and bentonite are processed in the industry. The parameters studied in this research are a variation of the mass of bentonite, contact time and adsorption capacity. Measurements were made using Spectrometry Atomic Absorption (AAS). The results showed that the activated bentonite not have the absorptive capacity of the metal cadmium that is better than the activated bentonite. Efficiency absorption cadmium metal bentonite with a mass of 0.5 g and a contact time of 120 minutes was 90.5%, while benoit activated with HCl efesiensinya only 32.70%.

1. Introduction

Industrial development and technology are increasingly rapidly, causing pollution and environmental damage also intensified because of uncontrolled pollutants that enter the environment such as heavy metals. Environmental pollution is a world problem, heavy metals including the most important pollutants. Industrial progress has led to an increase in pollutant emissions into ecosystems. Metals tend to accumulate in water and move up through the food chain and certain concentration pads can cause contamination in fish such as metals Zn, Cr, Cd, and Pb [1]. Research on soil contamination showing average concentration of Cu, Cr, Co, Pb and Zn is higher than the background level of the earth's crust [2]. The same is also done in research in the Islamic urban area of Shahr Iran [3]. Heavy Metal Contamination and Mobility at the Mine [4]. Research of metals in Vegetables in urban areas in India shows that the highest Zn deposition rate followed by Cu, Cd and Pb, and atmospheric deposition can increase the levels of heavy metals in vegetables and harmful to consumers [5].



Heavy metals into the aquatic environment will experience precipitation, dilution and dispersion, then absorbed by the organisms that live in these waters. The deposition of heavy metals in the waters occurs because of a hydroxyl anion carbonate and chloride. Heavy metals have properties that easily bind to organic matter and settles in the bottom waters and sediments together with levels of heavy metals in sediment is higher than in water [6]. Among the heavy metal contaminants are interesting to study is the metal cadmium 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 cell damage red blood kidney and liver damage, and cardiovascular disorders. Aquatic life would be threatened if the heavy metal polluted river, lake or sea [6], [1]. Cadmium metal content should not exceed 0,01ppm on waters 0,003mg / L for drinking water quality Heavy metals that enter aquatic systems, both in rivers and seas will be removed from the water bodies through three processes, namely precipitation, adsorption, and absorption by aquatic organisms [4]. The heavy metals present in the aquatic environment will undergo precipitation, dilution and dispersion, then be absorbed by the organisms living in the waters. The deposition of heavy metals in the waters occurs because of a hydroxyl anion carbonate and chloride. Heavy metals have properties that easily bind to organic matter and settles in the bottom waters and sediments together with levels of heavy metals in sediment is higher than in water [5].

Among the heavy metal contaminants are interesting to study is the metal cadmium 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 cell damage red blood kidney and liver damage, and cardiovascular disorders. Aquatic life would be threatened if the heavy metal polluted river, lake or sea [6], [1]. Cadmium metal content should not exceed 0,01ppm on waters 0,003mg / L for drinking water quality.

The method is commonly used for the management of heavy metals in the environment is a method presiptasi, electrogravimetri, 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 [7] [11]. 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 absorbennya maximal [8] [10].

2. Research Methodology

2.1. Tools and materials

The tools used in this research are measuring cup, flask, a long neck, a sieve of 100 mesh, erlenmeyer, cup, oven, shaker, stir bar, cup crucible, mortal, and the instrument used was spectrophotometry Atomic Absorption (AAS), HCl, solution of Cd (NO₃)₂.

2.2. Preparation and Bentonite Activation

Before bentonite was first activated bentonite preparation by reducing the size of bentonite and drying in the sun, then bentonite was heated in an oven at 105°C for 24 hours. Bentonite that has been dried and crushed until mashed to 150 mesh. Then do the activation by soaking using 1.6 M HCl solution while stirring for 1 hour with a speed of 100 rpm then filtered and washed with aquades. The resulting residue is heated to 200 °C for 1 hour. After drying, crushed until smooth and sieved with 150 mesh size [8], [9], [10].

2.3. Preparation of Calibration Curve

The standard calibration curve for the determination of cadmium metal was made by using Cd (NO₃)₂ solution, a standard solution concentration of 0.6 ppm; 1.2 ppm; 1.8 ppm; 2.4 ppm and 3 ppm. Absorbance measurement using AAS instrument. The calibration curve was obtained by making a curve between the concentration on the uptake of each Cd²⁺ concentration.

2.4. Determination of bentonite absorption

Weighed bentonite with a weight variation of 0.1; 0.3 and 0.5 grams were added to the cup and 50 ml of Cd²⁺ 1 ppm solution was added, stirring with shaker at 200 rpm for 1 hour, with variations of 30, 60, 90 and 120 minutes. The solution is filtered to separate the filtrate and the residue. The obtained filtrate was analyzed by AAS.

2.5. Data analysis

Cadmium concentration measurement using optimization result, the determination of levels of cadmium from the regression equation cadmium standard calibration curve obtained by using the formula: $Y = bx + a$. Determine the absorption efficiency of metal cadmium is used formula:

$$\% \text{ absorption efficiency} = \frac{C_o - C_a}{C_a} \times 100 \%$$

Note: C_o = initial concentration, C_a = end concentration

Calculation of adsorption capacity (Q_e) metals Cd with formula

$$Q_e = (\text{Initial Concentration} - \text{End Concentration}) / \text{Adsorbent Mass}$$

Langmuir isotherm graph is calculated the equation:

$$\frac{C_a}{Q_e} = \frac{1}{b} C_a + \frac{1}{Kb}, \text{ and created curve } C_a/Q_e \text{ (g/L) Vs } C \text{ end (mg/L)}$$

3. Results And Discussion

3.1. Standard Calibration Curve of Cd metal

The calibration curve metal cadmium (Cd) is made by measuring the concentrations of a standard solution of 0.6 ppm; 1.2 ppm; 1.8 ppm; 2.4 ppm and 3 ppm. The measurement results produce a calibration curve with a linear equation obtained = 0,231x + 0.082 with a correlation coefficient of 0.989.

3.2. Measurement of Mass Variation and contact time

Bentonite used mass variation affects the absorption occurs, it can be illustrated in **Figure 1**.

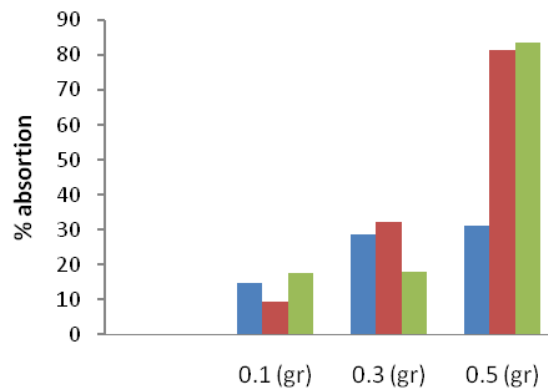


Figure 1. Graph of effect of mass of bentonite on cadmium metal absorption; (■) Active bentonite, (■) Inactive bentonite, (■) Commercial bentonite

From the pictures above can be explained that the ability of bentonite that is not activated (red curve) has a better ability of activated bentonite (blue curve) to absorb the metal cadmium. The test results showed that the absorption of bentonite activation with a mass of 0.5 grams only absorbed by 31.20%. While bentonite inactive on the mass of 0.5 grams able to absorb cadmium amounted to 81.60%. An increase in the absorption of the metal cadmium from the mass of 0.3 grams to 0.5 grams of saturated show yet active sites of the adsorbent by adsorbate molecules, then the weight of larger adsorbent adsorbate adsorbed amount has increased not so significantly or tend to remain, it shows their limit of adsorbent in adsorbing metals Cd [12].

The high ability to absorb metal cadmium bentonite is caused by ion exchange reaction, in which a number of cadmium ion mass of fluid move its position to the surface of bentonite [13] The reaction of ion exchange is a special form of chemical adsorption. Ion exchange can occur if part of cadmium ions replace the existing position of positive ions in the bentonite adsorbent, so that the positive ions migrate into the liquid. This is because there is the Coulomb force between negatively charged ions contained in the adsorbent with a positive ion of adsorbates [14].

Activation is done chemically bentonite. Chemical activation is done by using mineral acids, because the mineral acid will increase the absorption and dissolve impurities that cover the pores of the adsorbent, impurities in the form of carbonate [9], [15]. Soaking with hydrochloric acid, which causes the oxides of aluminum, calcium, iron and magnesium which had been filled pores become soluble and pore becomes vacant, then the surface of bentonite will bind H^+ ions from the acid [16]. The existence of H^+ ions on the surface of bentonite will cause bentonite to become active because it has the H^+ active. H^+ is what will serve as the ion exchange when the adsorption process based on ion exchange. When the adsorption process is trapping in the pore, the H^+ ions will be forced out. The adsorption process of metal (cation) in the bentonite is generally an ion exchange reaction. In this study, activation of bentonite using HCl, the goal is to exchange the cations present in the pores of bentonite with H^+ ions by releasing ions Al^{3+} , Fe^{3+} and Mg^{2+} so as bentonite become more active [8][10][11].

In the graph Figure 2 also shows that the activated bentonite ability to absorb cadmium lower than bentonite not activated, this is due to the possibility of high concentrations of hydrochloric acid at the time of activation of bentonite. Where the factors that affect the activation process is the concentration of activators and mesh size. So with a concentration of 1.6 M HCl causes dealumination, where H^+ ions will replace Al^{3+} . Dealumination process causes damage octahedral layers which resulted in the collapse of the framework of Si-Al on bentonite thus affecting the adsorption capacity of bentonite. In addition to the

high concentration of H^+ ions are exchanged into interlayer layer and a layer of bentonite lattice more and more, so the more soluble Al^{3+} ions. This resulted in damage to the lattice structure of bentonite which led to the decline of surface area and absorptive capacity of bentonite. Bentonite has an adsorption properties because it has a high ion exchange capacity. Adsorption is a process of clotting substance that is dissolved in the solution from the surface of the adsorbent substance or object, causing an interaction between the substance with an adsorbent. The adsorption process can be described as the process of molecules leaves the solution and stick to the surface of the adsorbent substances [15], [17].

3.3. Contact time

Time contacting done varies starting from 30 minutes, 60 minutes, 90 minutes and 120 minutes against active bentonite and bentonite inactive. The effect of contact time on the adsorption of cadmium can be illustrated in **Figure 2**.

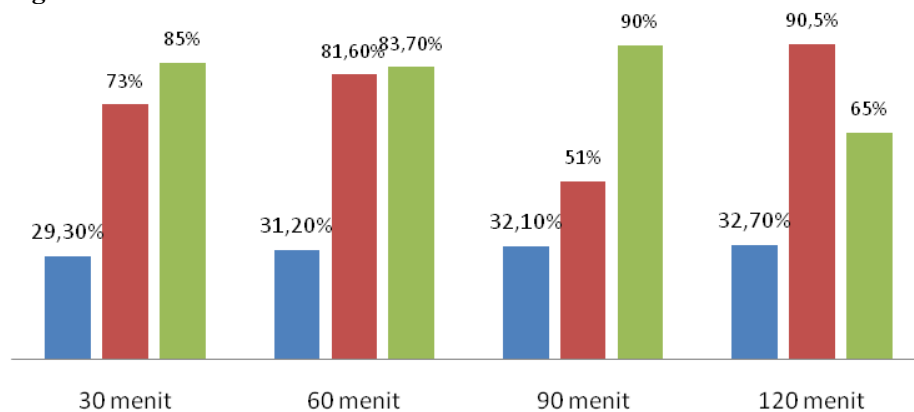


Figure 2. Graph of the effect of contact time on the absorption of metals Cd (■) Active bentonite, (■) Inactive bentonite, (■) Commercial bentonite

From **Figure 2** can be explained that the active bentonite (blue images) at the contact time of 30 minutes, the metal Cadmium is absorbed by 29.30% and increases the contact time of 60 and 120 minutes, but the increase is not too significant even snoring constant. This is because the surface of the adsorbent has been saturated because the pores of the adsorbent has been met by the previously adsorbed metal so that the ability of the adsorbent to absorb adrorbat relatively constant. These events showed the limits of the adsorbent to adsorb metals Cadmium [9]. The purpose of activation of the contact acid is to exchange cations Ca^+ contained in Ca-bentonite into H^+ ions and release ions Al, Fe, and Mg and impurities other on the lattice structure, so physically bentonite becoming active [8]. [10],[18] . For bentonite inactive (red images), at the time of contacting 30 minutes to 60 minutes to increase quite well that the percent absorption by 73% to 81.60% and in the minutes to 120 percent more absorption rose again to 90%.

3.4. Adsorption capacity

This adsorption isotherm is used to describe the relationship between the adsorbent and the substance teradsorb in an equilibrium. From the adsorption isotherm equation can be seen in the form of capacity isotherm characteristics and mechanism of adsorption process. Graphs obtained from the adsorption isotherm calculation show the relationship between the amount of adsorbent with a unit weight of the adsorbent and the adsorbate amount at the time of equilibrium.

Table 1. Results of Adsorption Capacity Calculation Langmuir and Freundlich Active Bentonite on mass variations

C initial Cd (ppm)	C end Cd (ppm)	Cd (L)	Volume (L)	Bentonite Weight (gr)	Adsorption Amount (mg/g)	Ca/Qe (g/L)	Log Ca	Log Qe
Co	Ca			M	Qe			
1	0,145	0,5	0,1	0,1	8,55	0,016	-0,838	0,931
1	0,285	0,5	0,3	0,3	2,383	0,098	-0,545	0,377
1	0,688	0,5	0,5	0,5	0,624	1,102	-0,162	-0,204

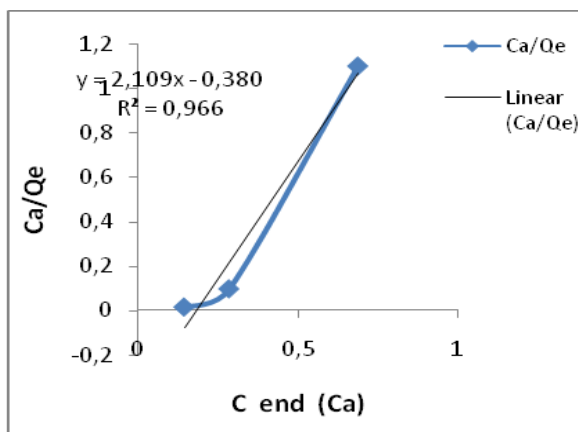


Figure 3. Langmuir Isotherm Graph

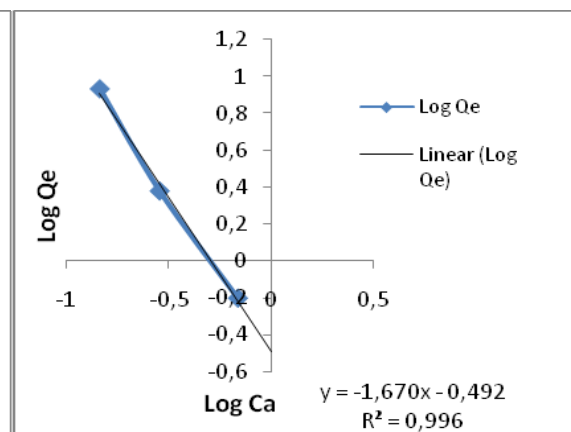
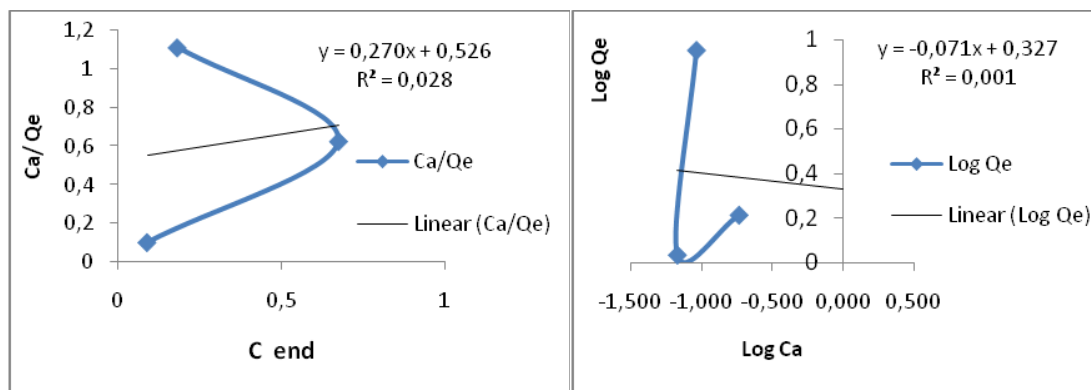
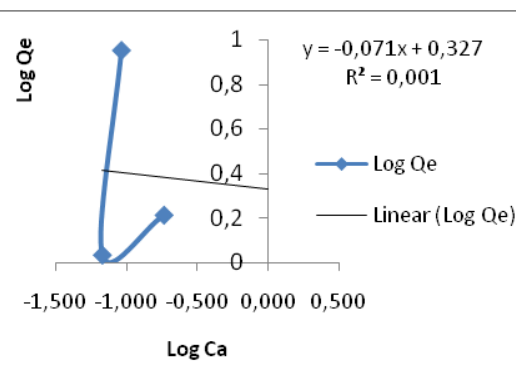


Figure 4. Freundlich Isotherm Graph

From the picture above, Langmuir isotherm graph showing the Ca / Qe Vs C by the end of bentonite is active on the variation of the mass obtained by the linear regression equation $y = 2,109x - 0,380$ and r price is 0.966. Results perhitungan adsorption capacity of bentonite inactive in **Table 2**.

Table 2. The adsorption capacity of langmuir bentonite is inactive

C initial Cd (ppm)	C end Cd (ppm)	Cd (L)	Volume (L)	Bentonite Weight (gr)	Adsorption Amount (mg/g)	Ca/Qe (g/L)	Log Ca	Log Qe
Co	Ca			M	Qe			
1	0,092	0,5	0,1	0,1	9,08	0,10	-1,036	0,95
1	0,676	0,5	0,3	0,3	1,08	0,625	-1,17	0,033
1	0,184	0,5	0,5	0,5	1,632	1,112	-0,735	0,212

**Figure 5.** Langmuir Isotherm Grap**Figure 6.** Freundlich Isotherm Grap

From the picture above, obtained Langmuir isotherm graph showing the Ca / Q_e Vs C by the end of bentonite is not yet active on the variation of the mass obtained by the linear regression equation $y = 0,270x + 0,526$ and r price was 0.028. Langmuir isotherm results to variations in time and contact time can be summarized in **Table 3**.

Table 3. Isotherms Langmuir of several types of bentonite

Variation	Type bentonite	Results	
		y	R ²
Mass	Active	$y = 2,109x - 0,380$	$R^2 = 0,966$
	Inactive	$y = 0,270x + 0,525$	$R^2 = 0,028$
	Comercial	$y = 1,200x - 0,096$	$R^2 = 0,538$
Contact time	Active	$y = 29,36x + 20,96$	$R^2 = 0,835$
	Inactive	$y = 1,108x - 0,081$	$R^2 = 0,978$
	Comercial	$y = 0,062x + 0,515$	$R^2 = 0,003$

From **Table 3** the results of the Langmuir isotherm shown that bentonite is active in the variation of the mass showed a better linear regression value with $r = 0.966$. For a variation of contact time, the value of regression, linear better seen in bentonite not activated with the value of $r = 0.978$. If the regression value close to 1, the accuracy of calculation results can be justified or if repetition would have almost the same results. Langmuir isotherm indicates that the adsorption process occurs chemically active sites that bentonite will interact with hydroxyl groups contained on Cd by forming hydrogen bonds. The adsorption process according to the Langmuir isotherm indicate that the interaction between Cd with bentonite surface is limited to the formation of a single layer (monolayer).

From the curve isotherm adsorption Langmuir above, there are several curves obtained linearity is not good that the bentonite is not yet active variation of mass with the value of regression $R^2 = 0.028$, the bentonite commercial variation of mass with the value of regression $R^2 = 0.538$ and bentonite commercial varied contact time with the value of regression $R^2 = 0.003$. While on active bentonite mass variations, active bentonite and bentonite is not yet active contact time varying values obtained regression is $R^2 = 0.966$; 0.835 and 0.978 . This indicates that prices are of Langmuir isotherm close to 1. It is assumed that

the interaction between Cd with bentonite can take place either chemically through hydrogen bond formation

4. Conclusion

Unactivated bentonite has a better capability in the absorption of Cadmium metal. Inactive bentonite has a capacity of up to 90.5 % while the activated bentonite has only 32.70 % absorption efficiency in the absorption of cadmium metal. Contact time and bentonite mass effect on the absorbance of bentonite in cadmium metal absorption, the best contact time is 60 minutes with a mass of 0.5 gram. In this condition a maximum absorption of bentonite. Langmuir isotherm is an adsorption isotherm, which describes the chemical process. Cadmium adsorption by bentonite being followed Langmuir isotherm models are active bentonite mass variations, active bentonite and bentonite is not yet active on the variation of contact time with the linear regression coefficient obtained is $R^2 = 0.966; 0.835$ and 0.978 .

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