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Effectiveness Study of Drinking Water Treatment Using Clays/Andisol Adsorbent in Lariat Heavy Metal Cadmium (Cd) and Bacterial Pathogens

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Abstract. Water is a natural resource that is essential for all living creatures. In addition, water also caused of disease affecting humans. The existence of one of heavy metal pollutants cadmium (Cd) in the body of water is an environmental problem having a negative impact on the quality of water resources. Adsorption is one of the ways or methods that are often used for the treatment of wastewater. Clay and allophanic soil were used as Cd adsorbent by batch method. Ceramic filter was used to reduce Cd concentration in the ground water. This study aims to determine the effect of the composition of clay and Allophane, activation temperature and contact time on the adsorption capacity of Cd in the model solution. The optimum adsorption condition and the effectiveness of drinking water treatment in accordance with Regulation of the Minister of Health using clay/Andisol adsorbents in ensnare heavy metals Cd and bacterial pathogens. Identification and characterization of adsorbent is done by using NaF, Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), specific surface area and total acidity specific. The Cd metal concentrations were analysed by atomic absorption spectroscopy. Adsorption isotherms determined by Freundlich and Langmuir equations. Modified water purification technology using ceramic filters are made with a mixture of clay and Andisol composition. The results showed samples of clay and Andisol containing minerals. The optimum condition of adsorption was achieved at 200 °C of activation temperature, 60 minutes of contact time and the 60:40 of clay:Andisol adsorbent composition. Freundlich isotherm represented Cd adsorption on the clay/Andisol adsorbent with a coefficient of determination (R^2=0.99) and constant (k=1.59), higher than Langmuir (R^2=0.89). The measurement results show the water purification technology using ceramic filters effectively reduce *E. coli* bacterial and Cd content in the water.

1. Introduction

Water is a vital necessity for human sustainability. Heavy metals are one of the toxic and dangerous pollutants since it is not degraded in nature [1, 2]. Cadmium (Cd) is a heavy metal resulted from rocks and soil erosion, volcanic eruptions, mining activities and industrial waste (leather, textiles, batteries, paint and pesticides) [3, 4]. At high concentrations and in the long term, heavy metals can cause health risks for humans and ecosystems.

Various methods have been developed by the researchers to improve water quality [4-6]. Adsorption method has been developed as a method of reducing heavy metals due to it is more effective, simpler and cheaper than other methods [4, 7]. Sorption is the process of centralization of adsorbate molecules or ions on the adsorbent surfaces, either physics or chemistry.

Andisol soil is soil that occurs from the weathering of volcanic rocks that are scattered throughout its existence Indonesia, especially in Lawu, Dieng, Merapi, Merbabu and Wilis Mountains [8]. Allophane adsorbent has good characteristics, such as porosity, absorption and high cation exchange. Many studies have utilized allophane as adsorbent with relatively high effectiveness [9, 10]. Allophane and clays can be combined since they have similar characteristics as adsorbent. Clay is an aggregate of minerals that form of land consisting mainly of hydrous aluminium silicates, having active sites on the surface, hard and stiff when dry, and stable at high temperatures [8,11-12].

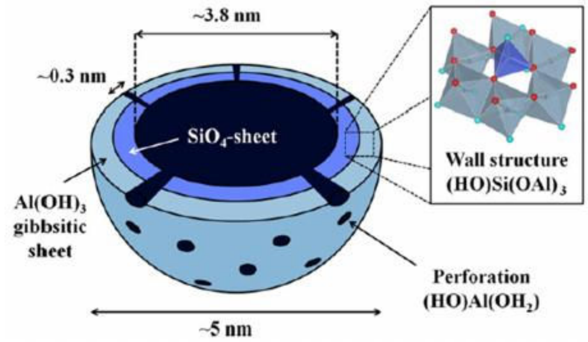

Figure 1. Structure Allophane [13]

Clay samples can be obtained from Bekonang, Mojolaban, and Sukoharjo, meanwhile Andisol can be obtained from Cemoro Sewu, Lawu Karanganyar. Andisol and clays further developed for the manufacture of ceramic filters to reduce the cadmium levels in water. Development of the main ceramic filter made from clay, is expected to result in a reduction of pollutant physical, biological and chemical that more effectively in order to obtain clean water that can be tolerated for drinking water; simple because its operation does not require any special skills; materials are used locally available and easy to obtain and inexpensive [1, 12, 14-16]. Muhdarina et al. [17] examined the manufacture of ceramic membranes as a water purifier. Porous ceramic membrane plays a major role in water purification because of its properties, which is stable at high temperatures, high mechanical strength and easy regeneration. Agmalini et al. [1] used a ceramic membrane made from clay and coal fly ash to improve the water quality of the swamp. The ceramic filter can be made by mixing clay with sawdust, bark rice [21], leaf tea, powdered coffee, or organic materials other combustible [16] to increase the flow rate. In this study studied the physical and chemical parameters such as pH, TDS, cadmium concentration and flow rate, as well as reduce *E. coli* bacteria.

The purpose of this study was to determine the effect of the composition of clay and Andisol, activation temperature and contact time on the capacity of adsorption of metal ions Cd in the solution of the model, determine the optimum conditions adsorbent mixture of clay and Andisol as adsorbent metal ions Cd in the solution of the model and determine the effectiveness of the filter ceramics for the reduction of Cd metal ions in water, and reduce coli bacteria.

2. Materials and Methods

2.1. *Materials*

Clay was obtained from Bekonang, Sukoharjo, Central Java. Andisol soil was obtained from Cemoro Kandang, Lawu Mountain, Central Java. Distilled water was obtained from the Chemistry Laboratory of Universitas Sebelas Maret. The Cd standard solution, HNO_3 (Merck), NaF (Merck), Ammonia (Merck) were used in this research.

2.2. *Preparation of Adsorbent*

2.2.1. *Clay*

The clay used in this study came from the area of Bekonang, Sukoharjo, Central Java. The clay obtained is cleaned, dried with aerated at room temperature, and crushed until smooth. Clay was then sieved with a 150 mesh sieve. The powder that passed 150 mesh was soaked in distilled water, filtered, and dried at a temperature of 105 °C for 4 hours [42].

2.2.2. *Andisol Soil*

Andisol soil used in this study came from Cemoro Sewu, Lawu, East Java. Andisol soil obtained was cleaned, washed with distilled water and dried with aerated in the open air, then crushed until smooth. Furthermore, Andisol soil was sieved with a 150 mesh sieve. The powder that passed 150 mesh was soaked in distilled water and filtered, then dried at a temperature of 105 °C for 4 hours [42].

2.2.3. *Identification*

Identification and characterization of Adsorbent were done with NaF test, XRD, FTIR, SAA, AAS, total acidity test specific.

2.3. *Adsorbent Activation*

Activation adsorbent was done chemically and physically. Chemical activation was only performed for Andisol soil, as many as 50 grams of Andisol soil is added to 250 mL of NaOH with a concentration of 3 M. Then the mixture was stirred at 70 °C with stirring time for 5 hours, then cooled. Once the mixture is cool then filtered and washed with distilled water until the neutral pH condition or equal to pH solvent. After that, the Andisol soil was dried in an oven for 4 hours at a temperature of 105 °C [42]. Subsequently, adsorbent was made with composition variation between clay and soil Andisol, namely 0: 100, 20:80, 40:60, 50:50, 60:40, 80:20 and 100: 0 wherein the mixing of the clay and the soil is done in a way Andisol stirring for 1 hour. After that, the solid phase is filtered and washed with distilled water several times, followed by drying in an oven for 4 hours at 105 °C. Each composition of the mixture was physically activated at temperature variations of 100, 200 and 400 °C for 3 hours.

2.4. *Performance Test of Adsorbent*

Cd metal ion adsorption process was carried out by the batch method of immersion. About 0.05 g of a mixture of clay and Andisol soil was added into 15 mL of 8 ppm Cd solution. Then, it was stirred at a constant speed (150 rpm) at room temperature for 30, 60 and 90 minutes. Afterward, it was filtered and measured by Atomic Absorption Spectroscopy (AAS) to determine the concentration of Cd metal ion that is not adsorbed by adsorbent.

2.5. *Determination of Sorption Isotherm*

A total of 0.05 g of optimum adsorbent was added into 15 mL of Cd solution with variations concentration by 15, 20, 25 and 30 ppm and then stirred at the optimum time. The sorption results was filtered with Whatman paper #40, then measured by AAS to determine Cd metal ion that is not adsorbed. The results are then analysed by the Langmuir and Freundlich isotherm models.

2.6. *Making Ceramic Filter*

The process of making ceramic filter was made by craftsmen of pottery in Bayat, Klaten by adjusting the composition of raw materials. As for the stages of manufacture are that dry mixing is performed between clay, Andisol soil and flour powder with a weight ratio of 2:3:1. The mixture was added with water and stirred to form a clay mixture. The mixture was printed in gypsum cylindrical mold with a inside diameter of 4 cm, the outside diameter of 5 cm, thickness of 0.5 cm and a length of 20 cm. Material was removed from the mold and dried at room temperature for 7 days. The, it was burnt on a wood stove for 12 hours.

2.7. *Ceramic Filter Performance Test*
The ground water was drained from the tank through a PVC pipe with the aid of a pump. The water was passed through ceramic filter, activated carbon granules, carbon block, then to osmosis membranes and the last pass of activated carbon powder. The flow rate was measured at intervals of 10 minutes. Water filtrate is collected and measured the TDS and pH. The Cd metal ion content was measured by AAS and compared with commercial water filter and control (untreated well water).

3. Result and discussion
3.1. *Identification of Adsorbent*
3.1.1. *The NaF Test*
The existence of allophane soil can be identified by NaF test. NaF test was done by measuring the pH of 1 g of soil in 50 mL of 1 N NaF solution for 2 minutes. The soil pH value greater than 9.4 indicates a high allophane content in soil samples [30]. The NaF can react quickly when added to the soil sample containing allophane. The fluoride (F) group can react with aluminum (Al) and break down the structure of soil aggregates so that it will release OH^- ions [31]. The NaF test results of Andisol soil samples showed that the pH value of 10.88 indicates that the Andisol soil contains allophane adequate.

3.1.2. *FTIR Characterization*
The FTIR characterization was employed to determine and evaluate as well as compare the functional group each raw materials. The FTIR spectra of Andisol Soil and Clay reveal in Fig. 2 and 3. The characteristic of each functional group shows in Table 1.

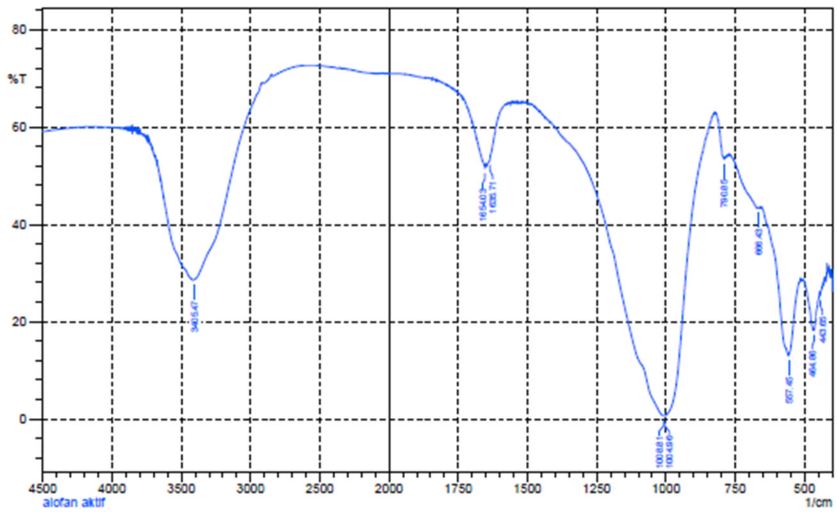

Figure 2. FT-IR spectra of Andisol Soil

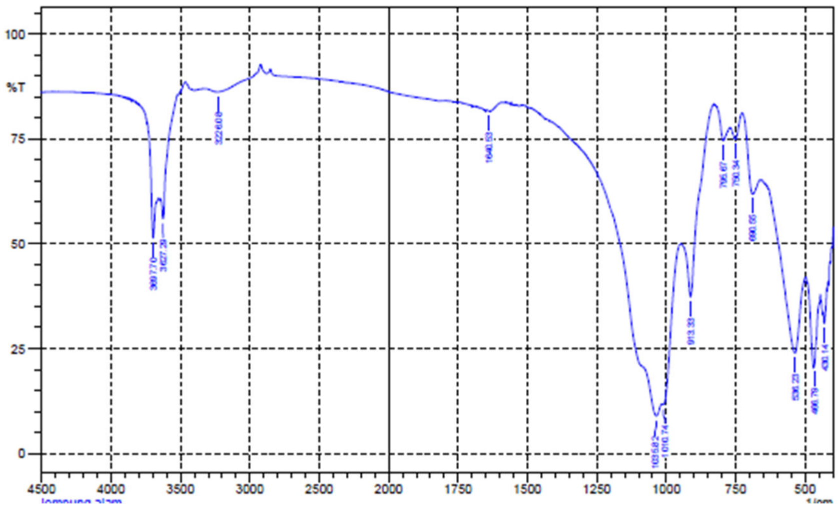

Figure 3. FT-IR spectra of Clay

Table 1. Data from the analysis of the functional group clays and Andisols

Functional Group	Wave number (cm^{-1})		
	reference	**Clay**	**Andisol**
Stretch–OH	3700-3000 [1] 3455[2]	3697.71-3226.08	3405.47
Bending Vibration H-O-H	1640 [3]	1640.53	1654.03
O-Si-O or O-Al-O	973. 11 [2]; 1039.60 [1]	1035.82 1010.74	1008.81 1004.96
Bending Vibration Si-O or Al-O	470.60 [1] 485. 58 [2]	795.67 750.34	790.85
Kaolinit	3600-3800[5] 1030 [4]	3627.29; 3697.7; 1010.74; 1035.82	1004.96; 1008.81
Gibsit	3400-3500 [5]; 1030; 974 [7]	1010.74; 1035.82	3405.47; 1004.96; 1008.81
Felspar	647 [4]	690.55	666.43
Allophane	3400; 1640; 1040; 670; 470[2]; 430 [7]	1640.53; 1035.82; 690.55 430.14; 466.79;	3405.47; 1635.71;1654.03; 1008.81; 1004.96 443.65; 464.86;

3.1.3. *XRD Characterization*

The XRD characterization is employed to evaluate the presence of chemical and minerals in the Andisol or Clay samples revealed from the specific 2θ showed in Fig. 3. Based on the analysis of Fig. 2, 3 and 4, as well as Tables 1 and 2, it can be concluded that adsorbent Andisol and clay contain minerals identified by the diffraction peaks at d /(A) the characteristics. Minerals in clays and Andisol adsorbent are allophane, feldspar, gibsit, kaolinite and montmorillonite. The presence of those minerals was revealed by the presence of their characteristic of both functional group and basal spacing at specific 2θ which it was already explain in Table 1 and Table 2.

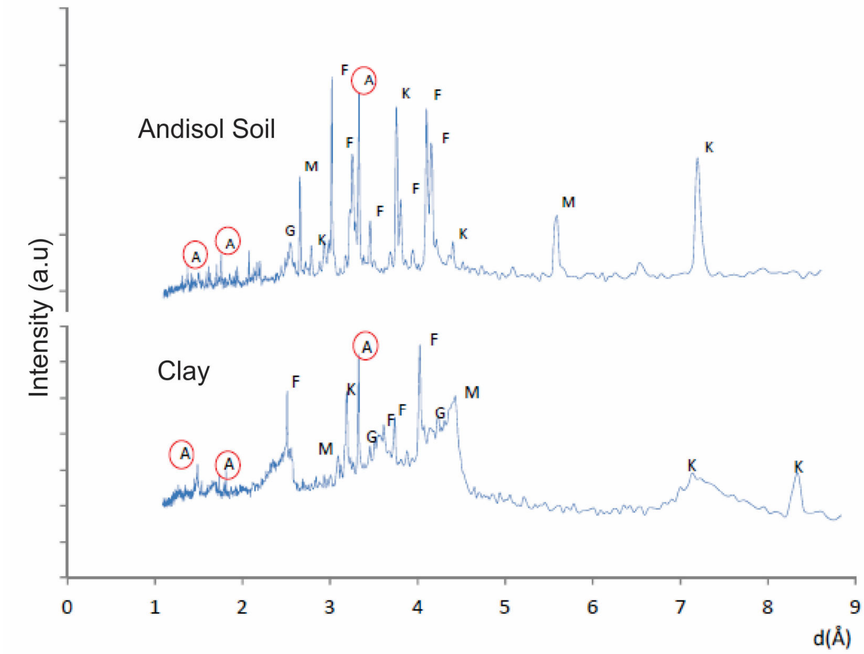

Figure 4. XRD diffractograms of Andisol Soil and Clay

Table 2. Results of XRD analysis clay soil and Andisol

Materials	**d (Å)**		
	Reference	**Clay Sample**	**Andisol Sample**
Allophane	3.30; 2.25; 1.80; 1.40 (1)	3.33; 1.81	3.29; 1.74; 1.36
Feldspar	4.00-4.20; 6.30-6.45; 3.80-3.90; 3.73-3.75; 3.64-3.67; 3.44-3.48; 3.00-3.25 (2) 3.27; 3.23; 3.59; 3.76; 3.44; (3)	4.03; 4.22; 3.74; 3.61; 3.20	4.04; 3.71; 3.70; 6.47; 3.22; 3.19; 2.98
Gibbsite	4.34; 4.83; 3.30 (2) 4.85; 4.36; 2.45; 2.38 (4)	3.45;	2.53; 3.41
Kaolinite	7.10-7.20; 4.45-4.46; 4.35-4.36; 4.17; 4.12; 3.84; 3.56-3.58 (2) 8.91; 4.65; 4.14; 3.81; 3.51 (5)	8.34; 7.14;	7.09; 3.76; 3.89; 4.34
Montmorillonite	12.00-15.00; 5.90 (2) 15.00; 1.49; 2.53; 1.29; 4.05 (6)	2.51; 1.49	5.48; 2.62

3.2. *Performance Test of Adsorbent*

Andisol/clay adsorbent has a high affinity for metal ions because they have active sites of Si-OH, Al-OH and -OH capable to provide electronegative charge on their surfaces allowing the exchange of cations in the process of adsorption of metal ions in the Cd solution [25, 37]. Sorption ability of silicate minerals derived from the number of negative charge on the structure of silicate minerals. The negative charge is neutralized by the positive charge of adsorbate, for example heavy metal cations [46]. Adsorption data results in Fig. 5 show that the adsorption of metal ions decreases with increasing of clay percentage in the mixture of clay and Andisol. The Reduction of Andisol/clay adsorbent ability can be explained by the data of surface area and acidity number of each adsorbent.

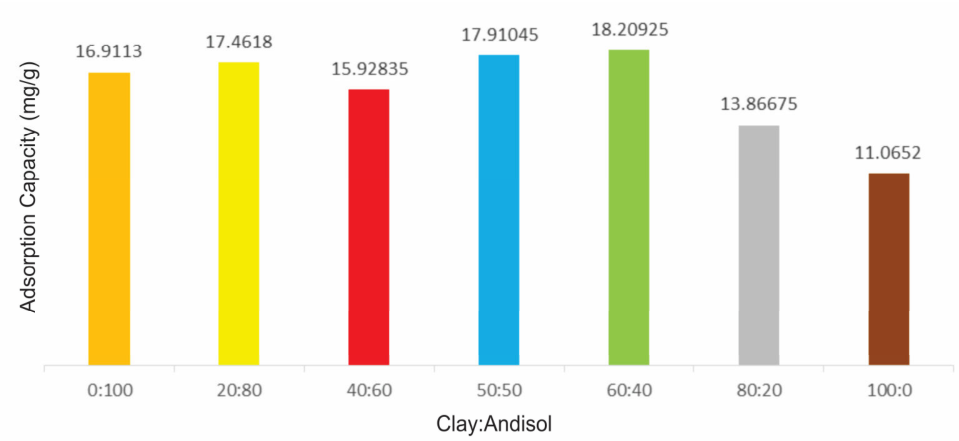

Figure 5. Comparison of adsorption capacity between various adsorbent.

The surface area is one of the decisive factors in the sorption process since the surface area provides the size of the area on the surface of adsorbent in the adsorption process of the Cd metal ion. So, the larger of the adsorbent surface area will produce greater adsorption capacity [36]. Clay has a surface area of 56.54 m^2/g, while the Andisol soil has a much larger surface area, which is 257.84 m^2/g. The surface area data of both Andisol and clay show in Table 3. Adsorbent with composition ratio 0:100, or 100 percent of the Andisol shows the highest sorption capacity compared to other adsorbent composition.

The measurement results show Andisol soil acidity has a larger value, i.e. 4.18 mmol/g compared to clay and the mixture, that are 2.65 and 3.47 mmol/g, respectively (see Table 3). The greater the number of acidity means adsorbent able to provide more active sites on the surface as a medium in the process of adsorption of the metal ion Cd. [13].

Table 3. Surface area and acidity of Andisol and Clay

Sample	Surface Area (m^2/g)	Acidity (mmol/g)
Andisol	257.84	4.18
Clay	56.54	2.65

Adsorption capacity of adsorbent calcined at 100 °C and 200 °C higher than the adsorbent calcined at 400 °C as shown in Fig. 6. The Increasing of calcination temperature is able to free the water molecules trapped in the matrix of clay and Andisol leaving a porous cavity structure and increase the surface area of adsorption. The calcination temperature that is higher than the optimum temperature damaged the adsorbent structure and consequently decreased the surface area so that the adsorbent media limited [27]. The results of this study are also consistent with the results of Wicaksono et al. [49] that they calcined bentonite at 120 and 400 °C. Bentonite adsorption ability was tested by conducting adsorption process against methylene blue solution. The results showed that the bentonite with a calcination of 120 °C was able to absorb the methylene blue and better than the bentonite which is calcined by 400 °C.

Adsorption capacity of Andisol/clay adsorbent increased with the long of contact time. When adsorption has reached the maximum, adsorption capacity was reduced by increasing contact time. At a temperature of 100 and 200 °C, all compositions of adsorbent adsorption capacity increased with increasing of contact time by 30 to 60 minutes and decreased when the contact time of 90 minutes.

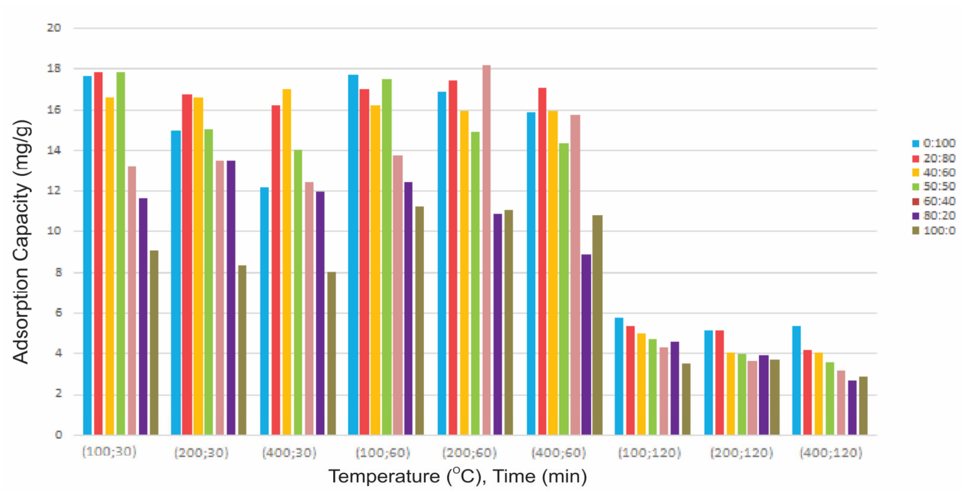

Figure 6. Effect of temperature and contact time toward adsorption capacity of various composition of Andsiol/clay adsorbent

At the contact time of 60 minutes, most of the active sites on the surface of clay and Andisol has been occupied by metal ions Cd and has been occured repulsion between adsorbed metal ions Cd and metal ions in solution to occupy the active sites. The repulsive force and the competition among the Cd metal ions caused reduction of metal ion adsorption capacity of Cd^{2+} [9, 14]. With increasing contact time, the more hydrated cations formed with a radius larger than the radius of Cd metal ions thus blocking the process of adsorption [29]. Longer contact time is not always followed by a rise adsorption capacity. When the contact time has reached saturation point, there will be events desorption, the metal ions Cd will be released back into solution due to an excessive contact between metal ions Cd in solution and adsorbed ion [44, 20].

3.3. *Adsorption Isotherm*

Langmuir isotherm equation is determined using the equation ${}^{c}/_{Q} = {}^{1}/_{(k.Q_{max})} + {}^{c}/_{Q_{max}}$ and Freundlich isotherm using equation $\log Q = \log K + {}^{1}/_{n} \log c$ with each is made curve c vs. c/Q and log c vs log Q as shown in Fig 7a and 7b, respectively. Based on the fitting linier, the linearity of Freundlich isotherm has a value of $R^2 = 0.9914$, higher than the Langmuir isotherm, i.e. $R^2 = 0.8872$. Thus, it can be concluded that the type of isotherm in this study followed the Freundlich model.

Freundlich isotherm model explains that the adsorption occurs on more than one surface (multilayer) and adsorbent have heterogeneous surfaces with a different binding energy [3; 18]. Cd metal ion adsorbed into Andisol/clay adsorbent is physical sorption. This sorption type is suitable for sorption mechanisms that require regeneration process.

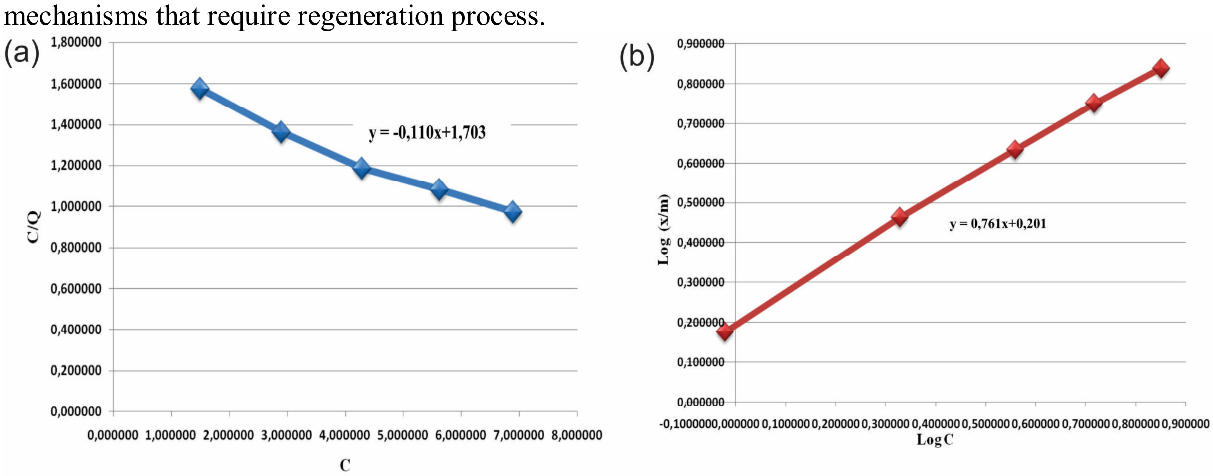

Figure 7. (a) Langmuir and (b) Freundlich isotherm adsorption models.

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3.4. *Performance of Filter Purifier*
One of the drinking water treatment processes is utility of a ceramic filter. The ceramic filter is able to reduce physical, chemical and biological pollutants in order to obtain clean water that can be used for drinking water [43, 19, 47, 21, 26, 17, 51, 35, 11]. Muhdarina et al. [26] explains in their research on special properties of porous ceramic membranes, such as the high temperature stability, mechanical strength and easy in terms of regeneration.

The ingredients for making a ceramic filter can be vary, but as a main ingredient is clay because of its ability to be shaped and resistant to high temperatures. Other ingredients combine to improve the effectiveness of the performance of the ceramic filter, such as Andisol soil and flour. Andisol soil is added as a mixture for the manufacture of filters since its cationic exchange capacity is higher to adsorb heavy metals [33, 23, 10], but this material is difficult to set up and less resistant to high temperatures. Starch powder is used to increase the flow rate or discharge of water. At high combustion temperatures flour powder will be burned and left the room in a filter so that these spaces will be used as a water molecule. The measurement results in Table 5 shows that the ceramic filter is effective in reducing dissolved solids (94%) and lower Cd concentration in water wells (98.9%), higher than a commercial filter, ie 93.1% (TDS) and 93.8 % (Cd).

4. Conclusion
Composition of clay and Andisol, calcination temperature and contact time affect the adsorption capacity of Cd metal ions in solution models. The optimum conditions of Andisol/clay adsorbent to adsorb Cd metal ions in solution models are the composition of Andisol:Clay (60:40), the calcination temperature of 100 °C and a contact time of 60 minutes. The ceramic filter of Andisol/Clay mixture is effective to reduce the metal ion content of cadmium in water by 98.9% and bacterial pathogens that produce potable water.

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