Preparation of Sarulla Natural Zeolite as an Adsorbent to Pb(II) and Cd(II) Removal in Aqueous Solution

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Abstract. Sarulla natural zeolite was prepared as an adsorbent to remove heavy metals of Pb (II) and Cd (II) by batch method. Zeolite was activated with 200mL HCl 1.0N and after modification was conducted, the surface was clearer as well as the morphology, the particles were smoothly, therefore the surface area and the adsorption capability were increased. Based on mass variation of adsorbent obtained for both metals, the optimum conditions is 0.4gr, which absorption efficiencies of Pb (II) and Cd (II) were up to 40.51 % and 52.22 %, respectively. Then, Pb and Cd were adsorbed with pH maximum at 4, respectively as 41.78 % and 50.75 %. When beginning the absorption process of Pb ions, it could be immediately be absorbed with a significant amount and continued until the optimum conditions after adsorbed at 50 minutes with adsorption capability of 44.64 %. Cd metal also was absorbed slowly up to 30 minutes and absorbed with a significant amount after 50 minutes contacted time, which the absorption capability is higher than Pb as 56.92 %. The absorption capability of Cd metal was exceeded the Pb metal by using the Sarulla natural zeolite..

Keywords: Natural zeolite, sarulla, adsorption, and heavy metal

1 Introduction

The increase in human population and their needs spurred the development of the industry to grow rapidly. These rapid developments will causes environmental problems or pollution and become the main aspects that need attention, due to the amount of waste produced and disposed of by the industry into environment. Bad waste treatment induce environmental pollution by heavy metals proven to pollute the waters and the environment which impact on the community (Barchan, 1998).The presence of heavy metals in the waters will be difficult to degrade and will be absorbed in the body of the organism. Even though, those heavy metals such as Pb and Cd are classified as dangerous heavy metals and can exposed to the body by the respiratory and digestive tracts . Heavy metal poisoning of Pb and Cd cause acute and chronic poisoning. Acute metal poisoning Pb is characterized by a burning sensation of the mouth, the occurrence of gastrointestinal stimulation accompanied by diarrhea and symptoms of chronic poisoning characterized by nausea, anemia, pain in the abdomen and can cause paralysis (Csuros, 2002).

The adsorption process is one of an effective strategy to remove heavy metals content in waters. The selection of adsorbent is based on capacity, selectivity, absorption rate, does not

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contain harmful pollutants and cheap. One of the adsorbents that can be used to removal of Pb^{2+} and Cd^{2+} metal waste is zeolite (Ertan, 2005 and Gupta, 2009). The use of zeolite is based on its ability in ion exchange, adsorption and catalyst. Zeolites have very regular crystalline forms with cavities that are interconnected in all directions which causes the zeolite's surface area to be very large with suitable to be used as an adsorbent (Mohan, 2006; Treacy,2001; Salman,2017 and Kelly,2004).

Zeolite is one of mineral which found in Indonesia. Metals from industrial residues that are discharged into nature at levels that exceed the limits of waste can damage the ecosystem. Natural zeolites contained in mineral natural resources have an abundance of around 16.6 million tons which are quite large in Indonesia, especially in locations that are geographically located in the volcanic mountain range. Indonesia has a number of natural zeolite sources found in several regions such as Malang, Wonosari, Bogor and North Sumatra which have an abundance of 3,340 thousand to natural zeolites (Asalil, 2014).

Natural zeolite needs to be activated in advance to get the optimum ability in adsorb the metal waste such as lead and cadmium (Muharrem, 2017; Sabry, 2012; Peric, 2004; Milan, 2015 and Zhang, 2014). In this study, Sarulla natural zeolite was collected from Pahae sub-district, North Tapanuli regency. This zeolite has been activated or modified with hydrochloric acid and was used to adsorb Pb (II) and Cd (II) metals in nature, as a one solution to reduce the environmental pollution.

2 Material andmethod

2.1 Natural zeolite preparation

Natural zeolite was taken from Sarulla, North Tapanuli area. The natural zeolite was drilled and sieved with a 100 mesh to obtain the homogeneous zeolite grain size. The zeolite was washed with distilled water, then dried in an oven at 110^{o}C for 3 hours and a sample of Sarulla natural zeolite (SZ) would be obtained.

2.2 Natural zeolite activation

The prepared adsorbent sample of Sarulla natural zeolite (SZ) was taken as much as 100gr and activated with 200mL of 1.0N HCl solution. The mixture was stirred for 3 hours, then filtered with *Whatman* No.42. It was rinsed with distilled water again to neutral pH and dried in an oven at 120°C for 3 hours. Finally, the calcination was proceed at a temperature of 300°C for 2 hours to obtain activated Sarulla natural zeolite (ASZ).

These activated natural zeolite and prepared natural zeolite were characterized with XRD and SEM.The crystals formed were characterized by X-Ray Diffraction (XRD) Rigaku Multi Flex with Cu-Kα monochromators and morphology of crystals analyzed by Scanning Electron Microscopy (SEM) JEOL JSM-6000 F.

2.3 Determination of the optimum conditions of the adsorption process

Determination of optimum conditions was carried out in this study due to each adsorbent had different properties in the adsorption process. It was carried out by measuring three parameters, *i.e*., the mass of adsorbent, the pH of the solution of metal ion Pb(II) and Cd (II), and the contact time of adsorption.

2.3.1 The effect of adsorbent mass on metal ion adsorption process of Pb and Cd

Activated Sarulla Natural Zeolite with a particle size of 100 mesh was prepare as 0.2; 0.4 and 0.6 g. Then a 50 mL Pb metal ion solution was added with a concentration of 50 ppm with a pH of 4 solution into a 100mL Erlenmeyer. The mixture was stirred using vortex for 30 minutes. After the equilibrium the mixture was achieved, the filtered with *Whatman* No.42 and the filtrate were analyzed by AAS to analyze the Pb adsorbed concentration.

2.3.2 The effect of metal ion pH on metal adsorption process of Pb and Cd

Activated Sarulla Natural Zeolite was weighed according to the optimum mass of the adsorbent. A 50mL of Pb metal ion solution was added with a concentration of 50 ppm into a 100mL Erlenmeyer with variations in pH 2, 4 , and 6 which were arranged with citrate buffer solution . The mixture was stirred using *vortex* for 30 minutes to achieve the equilibrium. It was then filtered with *Whatman* No.42 and the metal ions which left in the filtrate were analyzed by AAS.

2.3.3 The effect of contact time on metal adsorption process of Pb and Cd

Activated Sarulla Natural Zeolite was weighed according to the optimum mass of the adsorbent. Then 50 mL of Pb metal ion solution was added with a concentration of 50ppm and the optimum pH into 100mL Erlenmeyer. The mixture was stirred with a variation contact time of 10, 30, 50 and 60 minutes. Once the equilibrium was achieved, the mixture was filtered with *Whatman* No.42 and the metal ions left in the filtrate were analyzed by AAS.
The same procedure and analysis also prepared for Cd metal ion solution

3 Results and discussion

Figure 1 shows the SEM image of Natural Zeolite Sarulla after prepared and activated. Based on SEM images, the zeolite preparation was looked coarser and there were many small flakes those suspected to be impurities. In addition, the shape not clearly seen because it was like clumping and not maximum open pore yet, which not suitable for adsorption process. After HCl activation, the zeolite was appeared to be cleaner and smoother and the porous was opened (Yousefi, 2018). After activation, the particles were smaller and smoother and the surface area was bigger which possible to increase the adsorption capability.

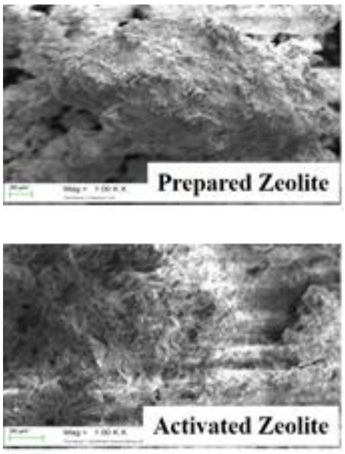

Fig. 1. SEM image of natural zeolite sarulla after prepared and activated

3.1 The effect of adsorbent mass on Pb(II) and Cd (II) adsorption

Based on the adsorbent mass, the optimum conditions were obtained with the amount of 0.4gr. Whereas, the absorption efficiency of Pb (II) and Cd (II) were found to be 40.51 % and 52.22 %, respectively. Fig. 2 shows that the absorption capacity of metal would be decreased when zeolite was optimal. Although the same adsorbent mass optimum of 4gr, however Cd was more found to be absorbed than Pb. The heavy metal sorption was attributed to different mechanisms of ion exchange processes as well as to the adsorption. During the ion-exchange process, metal ions had to move through the pores of the zeolite mass.

It also moved through channels of the lattice, and they had to replace exchangeable cations. Diffusionwas faster through the pores and was retarded when the ions moved through the smaller diameter channels. In this case, the Cd metal ion uptake could mainly be attributed to higher ion-exchange reactions than the Pb metal ion in the micro porous minerals of the zeolite samples (Sabry, 2012). However, at an adsorbent mass of 0.6, the amount of Pb ion was absorbed more than Cd ion, because the nature of Pb metal was harder than Cd, so it has the ability to fit into the larger pores compared to Cd (Mehdi, 2016).

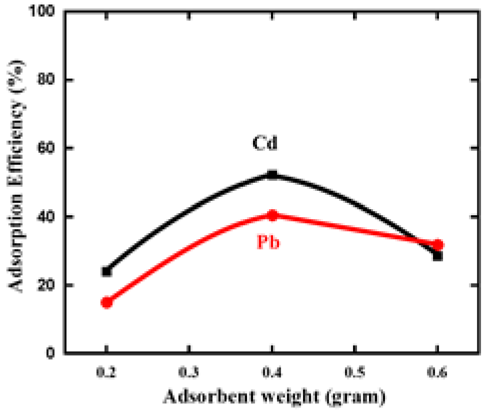

Fig. 2. The effect of adsorbent mass of Pb(II) and Cd (II) in adsorption process

3.2 The effect of pH on Pb(II) and Cd(II) adsorption

One of important parameter that determines the adsorbent's ability to absorb metal on a solid-liquid surface is pH. Therefore, the pH conditions must be kept stable during the adsorption process. The purpose of determining the optimum pH is to determine the most suitable pH where the absorption of Pb(II) and Cd (II) metal by modified zeolite reaches optimal conditions.

Adsorption of Pb (II) and Cd (II) metal ions onto the surface of the adsorbent is influenced by active sites (species) on the surface of the adsorbent. The charge of species of the adsorbent is normally affixed by the pH of the solution [16]. Fig. 3 shows the effect of pH on Pb(II) and Cd (II) metal adsorption process. It has been found that the adsorption of Pb and Cd were of 41.78 % and 50.75 %, respectively and it was reached at pH 4. The active sites of the adsorbents are protonated by H^+ ion to yield partially positive charges of the sites which were similar to those of metal ions. And these process induce the number of Cd ions absorbed atpH 4 is more than Pb. The adsorption was not carried out in alkaline conditions or pH above 6 due to metal ions of Pb^{2+} and Cd^{2+} would be formed as $Pb(OH)_2$ and $Cd\,(OH)_2$ under those conditions.

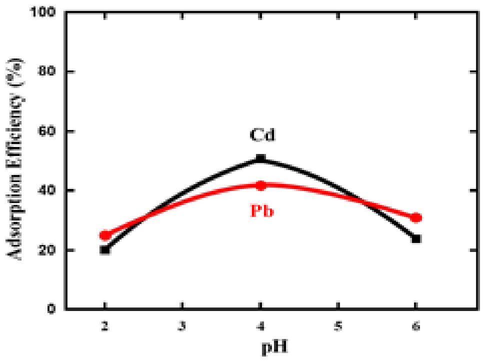

Fig. 3. The Effect of pH of Pb(II) and Cd (II) in adsorption process

3.3 The effect of contact time on Pb(II) andCd (II) metal adsorption process

The optimum contact time was determined to get the minimum time required by adsorbent to maximum absorb of Pb(II) and Cd (II). Fig. 4 shows the effect of contact time on Pb (II) and Cd (II) adsorption. At the beginning of the adsorption of Pb ions, it could immediately be absorbed at 50 minutes with the significant adsorption capability was of 44.64 % as a maximum conditions. In the other hand, Cd ion was adsorbed slightly at the beginning of adsorption and gradually increased to 30 minutes.

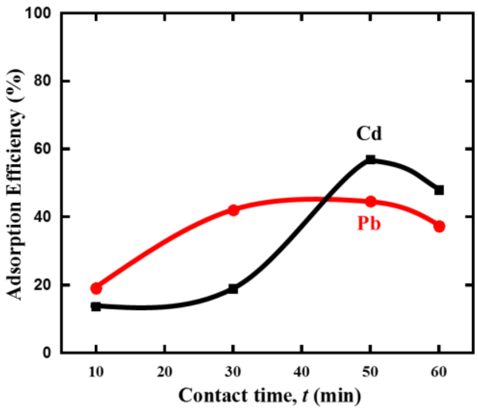

Fig. 4. The effect of contact time ofPb(II) and Cd (II) in adsorption process

However, the optimum was also found at 50 minutes contact time, but the absorption capability was found to be higher than Pb, which was 56.92 percent. It might be due to stronger interaction of Cd metal with the active site on the zeolite framework, which contributed to a greater amount of absorption than Pb metal.

Based on this study, Sarulla natural zeolite has specific properties for the absorption of Pb and Cd metal ions through ion exchange reaction.Many previous studies have shown that the amount of Pb metal ion absorption was more than Cd metal in some types of adsorbent. However, in this study, Sarulla natural zeolite could adsorbed Cd ion higher than Pbwith optimum condition for absorption of Cd was 0.4gr of mass adsorbent in pH 4 and adsorption contact time of 50 minutes.The absorption efficiencies of Cd and Pb were found to be 56.92 and 44.64 percent, respectively at the optimum conditions.

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