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THE EFFECT OF SARULLA NATURAL ZEOLITE MODIFICATION ON ENHANCEMENT OF PB(II) AND CD(II) CONTAMINANT ADSORPTION

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ABSTRACT

Sarulla natural zeolite was prepared as an adsorbent to remove heavy metals of Pb (II) and Cd (II) in wastewater. Natural Zeolite was activated with HCl 1N and to increase the surface area then Sarulla Natural Zeolite was modified with Phosphate (P-Zeolite). The presence of phosphate in zeolite cavity was effective to create higher surface area and pore size as main contribute to increase their adsorption amount. Surface area of modified zeolite (P_Zeolite) is 88.65 m^2/g and pore size become 100.8 A°. It is higher than zeolite before modification which surface area is 70.02 m^2/g and pore size is 50.16 A°. The optimum adsorption amount of Pb(II) is 12.28 mg/g after 30 minutes adsorption time with used 0.2g P-Zeolite. It is a significant increase if compared with Natural Sarulla Zeolite before modification which adsorbed only 5.57 mg/g by 0.4 g adsorbent mass with longer time after 50 minutes. On the other hand, the optimum adsorption of Cd(II) was adsorbed when used 0.4g P-Zeolite after 50 minutes as 7.09 mg/g. In this optimum adsorption condition, adsorption amount of Cd(II) also increased if compared with Zeolite before modification as 5.98 mg/g with used 0.2 g P-Zeolite and 30 minutes adsorption time.

KEY WORDS : Zeolite, Sarulla, Phosphate modification, Adsorption, Heavy metal

INTRODUCTION

Increasing of human needs due to population enhancement also encourage the development of industry to meet these human needs. The development of an increasingly rapid industry, it will be give high impact to induce the environmental problems when disposed of into the environment near the public habitant. The heavy metal content in this waste industry if not managed properly will greatly endanger the surrounding. The presence of heavy metals likes Pb2+, Cd2+, Cr6+, Zn2+ and Mn2+ in the waters will be difficult to eliminate, and it will be easy to absorbed in the body of the organism by the respiratory and digestive tracts. Those heavy metal poisoning of Pb and Cd can cause acute and chronic poisoning like the occurrence of gastrointestinal stimulation with diarrhea and symptoms of chronic poisoning characterized by nausea, anemia and pain in the abdomen (Barchan *et al.,* 1998).

Some methods have used to eliminate heavy metal contents in waters, but the procedures were not simple and expensive in preparation. The adsorption processes become new attractive and effective procedure to remove heavy metals content in waters with cheap in preparation and easy in application. The selection and preparation of adsorbent is also easy to arrange in enhancing capacity, selectivity, absorption speed and effectively removes harmful pollutants. One of the potential adsorbents to handling Pb2+ and Cd2+ metal waste is zeolite (Ertan *et al.,* 2005; Gupta *et al.,* 2009). Zeolite is an inorganic porous material which are used due to their ability to perform ion exchange, adsorption and catalyst. Zeolites have in order crystalline forms with high cavities and interconnected in all directions which induce the large surface area which main contributed as a potential adsorbent (Mohan *et al.,* 2006; Treacy *et al.,* 2001; Hana *et al.,* 2017; Kelly *et al.,* 2004).

Natural Zeolite is a mineral which many found in Indonesia and has potential properties as a metal adsorbent. Heavy metals which produced in an industrial residues and release into nature at levels that out of allowed specifications of waste can damage the environment. Natural zeolite contained in mineral natural resources has an abundance of around 16.6 million tons in around large in Indonesia, and mainly in locations near the volcanic range. Natural zeolite in Indonesia are found in several regions such as Malang, Wonosari, Bogor and North Sumatra which have almost 3,340 thousand tons natural zeolites (Asalil *et al.,* 2014). Natural zeolite needs to be activated in advance to get the optimum ability to adsorb the metal waste such of lead and cadmium (Muharrem *et al.,* 2017; Sabry *et al.,* 2012; J,Peric *et al.,* 2004; Milan *et al.,* 2015; Peng *et al.,* 2014).

The charge polarity of zeolites causes zeolite crystals which have an affinity for polar molecules, such as water. Water contained in pores according to the number of pores or pore volume and can be released by heating at temperatures of 300 to 400 °C. At these temperatures induces water removed from zeolite pores, then zeolites can function as absorbers of gas or liquid. Physical activation was performed to reduce a grain size, sieving, and heating at high temperatures (Ertan *et al.,* 2005). It is supposed to remove organic impurities, enlarge the pore, and increase the surface area. While chemical activation is carried out through acidification to remove inorganic impurities. This acidification will cause cation exchange with H^+. Natural zeolite with no modification are still less selective and efficient because it still contains many impurities that can interfere with the function of zeolite as an adsorbent. Therefore, it is necessary to modify natural zeolites to increase the selectivity of zeolites and improve the nature of zeolite by making pore size more uniform (Ertan *et al.,* 2005; Asalil *et al.,* 2014).

Modification of natural zeolite was carried out to obtain different cation shapes and skeletal compositions. This modification is usually carried out through ion exchange, de-alumination, and isomorphic substitution. The process of dealumination in zeolites affects the Si / Al ratio so that its physical properties are expected to also cause changes in water. Where Si- water solvent is in the form of Si (OH)4 which can enter to replace Al atoms in the zeolite framework (Ertan *et al.,* 2005). In this study, Sarulla natural zeolite was collected from Pahae sub-district, North Tapanuli regency, Indonesia. This zeolite were activated and then for to increase the surface area, Sarulla natural zeolite were modified by phosphate which are increasing to adsorbed of Pb (II) and Cd (II) ions.

MATERIALS AND METHODS

Natural zeolite preparation

Natural zeolite was taken from Sarulla, North Tapanuli area, North Sumatera, Indonesia. The natural zeolite was mashed with mortar and pestle. Then, it was sieved with a 100 mesh to obtain zeolite grain size through 100 mesh. The zeolite was washed with distilled water, then dried in an oven at 110°C for 3 hours and a sample of natural zeolite (ZS) would be obtained.

Natural zeolite activation

The prepared sample of natural zeolite (ZS) was taken as much as 100 g and activated with 200 ml of 1.0N HCl solution. The mixture was stirred with a magnetic stirrer for 3 hours, then filtered with Whatman No.42 filter paper. It was rinsed with distilled water again to neutral pH and filtered again and then dried in an oven at 120 °C for 3 hours. After that, the calcination was proceed at a temperature of 300 °C for 2 hours to obtain activated natural zeolite (ZAS). The analysis of H-Zeolite with XRD and SEM-EDS was then carried out.

Natural zeolite modification

100 g of natural zeolite were extracted in 2000 ml aquadest mixed with 13.10 g phosphoric acid. The mixture was stirred with a magnetic stirrer at 60 °C for 3 hours then filtered and dried in an oven at 120 °C for 3 hours. Then phosphoric acid modified zeolite mixed with 1500 ml saturated $NaHCO_3$ solution and stirred with a magnetic stirrer at 60 °C for 3 hours to get the form of disodium, then filtered and washed with distilled water to neutral pH. After neutral, filtered and dried again in an oven at 120 °C for 3 hours. The modified zeolite is then referred to as P-Zeolite.

Adsorbent characterization

The XRD analysis was carried out to determine the crystallinity of the adsorbent. In addition, the SEM was used to determine the morphology of the adsorbent. However, the EDS was carried out to determine the chemical composition which contained in the sample, and AAS was used to analyze the metal content of Cd (II) adsorbed by the adsorbent.

The Effect of Adsorbent Mass on Adsorption Process of Pb(II) and Cd(II)

The zeolite adsorbent with a particle size of 100 mesh was added to each 0.2g; 0.4g and 0.6g. Then a 50 ml Pb or Cd ion solution was added with a concentration of 50 ppm solution into a 100 ml Erlenmeyer. The mixture was stirred using vortex for 30 minutes. After the equilibrium the mixture was achieved, the filtered with Whatman No.42 filter paper and the metal ions which left in the filtrate were analyzed by AAS.

The Effect of Metal Ion pH on Adsorption Process of Pb(II) and Cd (II)

The zeolite adsorbent with a particle size of 100 mesh was weighed according to the optimum mass of the adsorbent. A 50 ml of Pb or Cd ion solution was added with a concentration of 50 ppm into a 100 ml. 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 filter paper and the metal ions which left in the filtrate were analyzed by AAS.

The Effect of Contact Time on Adsorption Process of Pb(II) and Cd(II)

The zeolite adsorbent with a particle size of 100 mesh was weighed according to the optimum mass of the adsorbent. Then 50 mL of Pb or Cd ion solution was added with a concentration of 50 ppm and the optimum pH into 100mL Erlenmeyer. The mixture was stirred by using a vortex with a variation of 10, 30, 50 and 60 minutes. Once the equilibrium was achieved, the mixture was filtered with Whatman No.42 filter paper and the metal ions left in the filtrate were analyzed by AAS.

RESULTS AND DISCUSSION

Due to the neutralization of negative charge with the addition of HCl at the activated zeolite still not optimum, modification of the addition of phosphoric acid will be arrange as connected of Al and O, to increasing the cavity in the framework of the zeolite structure which will affect the zeolite surface area. Then, addition of $NaHCO_3$ aims to avoid of hydrogen bonds formed in modified zeolites. The presence of hydrogen bonds will make H atoms bonded which will be difficult to be exchanged with metal ions. The scheme of modification reaction of zeolite with phosphoric acid was explained in Figure 1.

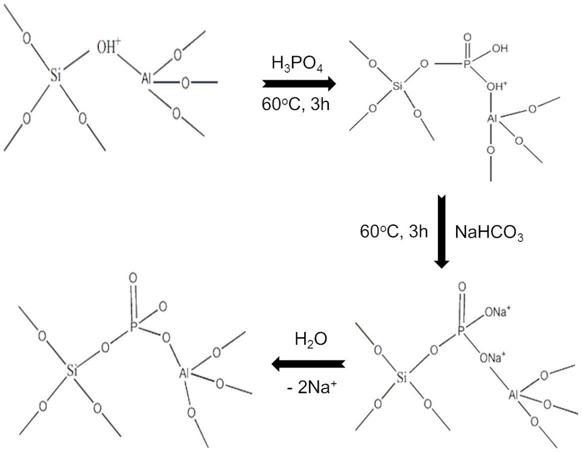

Fig. 1. The scheme of modification reaction of zeolite with phosphoric acid

Presence of phosphate ions in the zeolite cavity as connected of Al-O bond is related to the dissociation energy of the bond, where phosphate have double bonds which induce the dissociation energy is greater than Al, causing the Al bond to be easily shifted. In addition, Phosphorus (P) has a greater electron affinity in the formation of negative ions compared to Al which effect to stable negative ions formation to reacted with cathions, such as Na^+. In the purpose to stabilized the structure and obtain maximum modification conditions in zeolite cavities, cations need to be added which can be exchanged, in this case Na^+ ion derived from saturated solution of $NaHCO_3$, then was heated at 120 °C for 3 hours and then calcined at 300 °C for 2 hours to remove the remaining impurities to increase zeolite surface area and enhance metal adsorption capacity.

Figure 2 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 had not been

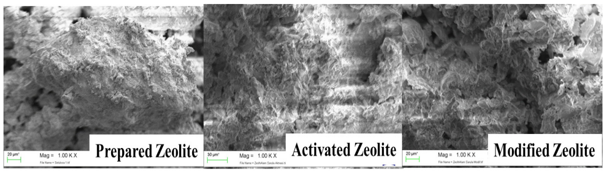

Fig. 2. SEM image of Natural Zeolite Sarulla after prepared, activated and modified

clearly seen because it was like clumping and the porch has not been opened to the maximum, so that the adsorption process could not be done. After it was activated with HCl, the zeolite was appeared to be cleaner and smoother and the porous was opened (Peng *et al.*, 2014; Mehdi *et al.*, 2016). After a cleaner surface was modified, the morphology was found to be clearer, the particles were smaller and smoother. Therefore, the surface area was got bigger and the adsorption process would be increased in big as well. EDS results (Figure 3) shows the prepared zeolite detected of impurity element, Fe, but after activation there is no element of Fe and after modification Na and P appeared which indicate the success of zeolite modification with phosphate.

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 Cd (II), and the contact time of adsorption. The adsorbent mass optimum conditions before modification were obtained that Cd(II) is higher absorbed than Pb(II). Optimum adsorbent amounts are 0.4g to adsorb of Pb(II) as 5.06 mgg^{-1} and 0.2g adsorbent to adsorb 5.98 mgg^{-1} of Cd(II). Figure 4 shows that the absorption capacity of metal would be decreased when zeolite reach optimal adsorption amount.

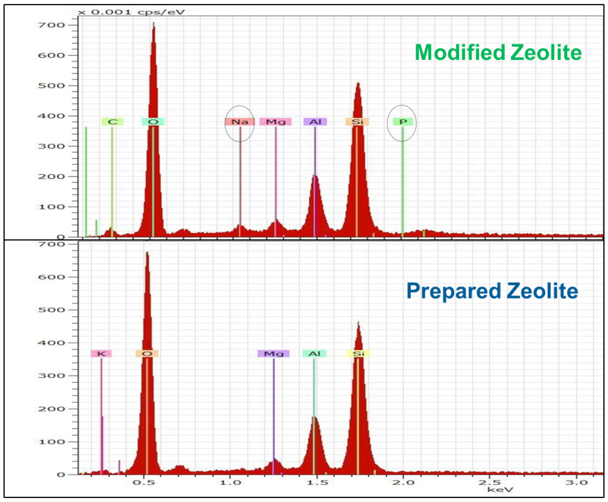

Fig. 3. EDX image of Natural Zeolite Sarulla after prepared and modified

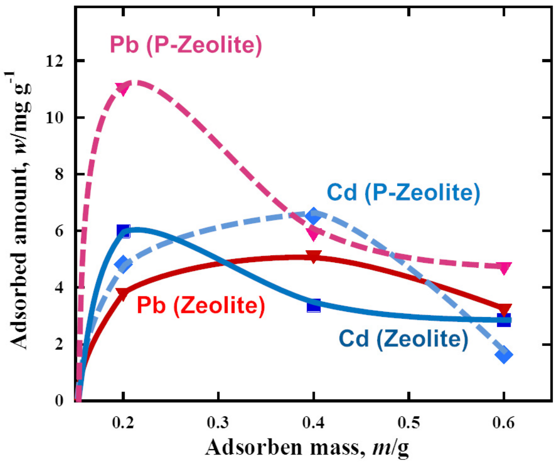

Fig. 4. The Effect of Adsorbent Mass on Pb(II) and Cd (II) Adsorption Amount.

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. Diffusion was 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 *et al.*, 2012).

However, at an adsorbent mass of 0.6, the amount of Pb(II) was absorbed more than Cd(II), because the nature of Pb metal was harder than Cd, so it has the ability to fit into the larger pores compared to Cd. This phenomena also was observed in adsorption of Pb(II) and Cd(II) at Zeolite Modification (P-Zeolite). After increase the surface area, Pb(II) was adsorbed as optimum condition with used 0.2g adsorbent and adsorbed of Pb(II) as 10.97 mgg^{-1} and it is higher than Cd(II) which optimum adsorbed at 0.4g adsorbent as 6.52 mgg^{-1}. The properties of Pb metal which are harder and have bigger molecular size than Cd have contributed to increase of Pb(II) adsorption amount (Taher *et al.*, 2018).

BET surface area, micropore volume and pore size analysis (Table 1) were supported to explain the increasing of Pb(II) adsorption amount after used modification Zeolite (P-Zeolite). Presence of phosphate was successes in enhancing the surface area as 88.65 m^2g-1 and pore size become 100.8 A°. The increasing of surface area and pore size of modified zeolite, effective to increase Pb(II) capture in modified zeolite (P-Zeolite). Interestingly, micropore volume of activated zeolite is higher than modified zeolite indicate the presence of phosphate induce smaller pore volume but create a bigger pore size with suitable to Pb(II) ion in penetrated inside the cavity of P-Zeolite.

Table 1. Pore properties of prepared zeolite, activated zeolite and modified zeolite

No	Sample Name	BET Surface Area* (m^2/g)	Pore Volume* (mL/g)	Pore Size (Å)
1	Prepared Zeolite	26.06	97	74.32
2	Activated Zeolite	70.02	176	50.16
3	Modified Zeolite	88.65	144	100.8

*micropore volume estimated by DR plot analysis and pore size by t-plot
Analysis of N_2 adsorption isotherms at 77K.

One important parameter that determines the adsorbent's ability to absorb metal ion 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 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 (Mehdi et al., 2016). Figure 6 shows the effect of pH on Cd (II) metal adsorption process. It has been found that the optimum adsorption of Pb (II) and Cd (II) were adsorbed at pH4 for all the samples (Figure 5).

Pb(II) were adsorbed in zeolite before modification and modified zeolite as 5.17 mgg^{-1} and 12.15 mgg^{-1}, respectively. In the other hand, Cd(II) were adsorbed as 2.79 mgg^{-1} in zeolite before modification and 6.19 mgg^{-1} in modified zeolite (P-Zeolite). 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. The number of Pb ions absorbed at pH 4 is higher than Cd also could explained with the similar reason as adsorbent mass examination above, then both of metal have the same properties when dilute at different pH solution.. 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 deposits of $Pb(OH)_2$ and Cd $(OH)_2$ under those conditions.

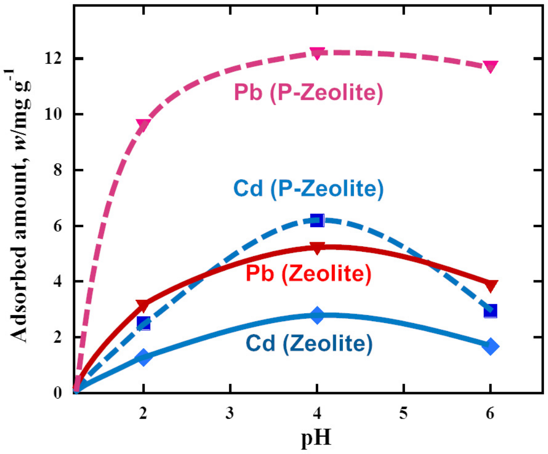

Fig. 5. The Effect of pH on Cd (II) Metal Adsorption Process

Figure 6 shows the effect of contact time on Pb(II) and Cd (II) adsorption. When starting the process of adsorption of Pb(II), it could immediately be absorbed and after 50 minutes, Pb(II) adsorbed as maximum amount as 5.57 mgg^{-1} and modified zeolite was increased the adsorption amount of Pb(II) which adsorbed only as 30 minutes as 12.28 mgg^{-1} . Whereas, at the beginning of adsorption, it was absorbed slowly up to 30 minutes for Cd metal and the optimum was also found at 50 minutes contact time, but the absorption capability was found to be smaller than Pb, which was 3.85 mgg^{-1}.

Modified Zeolite (P-Zeolite) also adsorbed higher amount of Cd(II) as 7.09 mgg^{-1} but in the same contact time in 50 minutes.

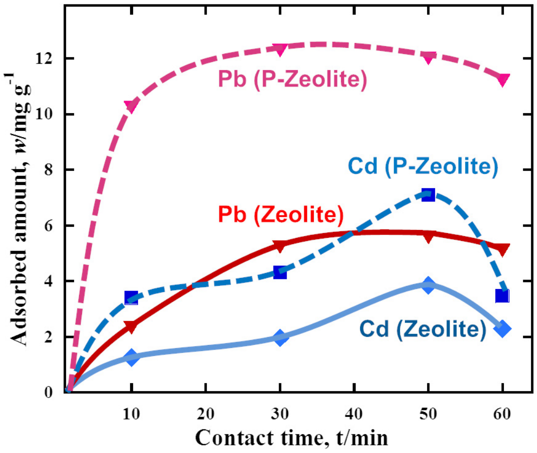

Fig. 7. The Effect of Contact Time on Cd (II) Metal Adsorption Process

CONCLUSION

In this study, Sarulla natural zeolite has specific properties for the absorption of Pb(II) and Cd(II). This adsorbent becomes the specific adsorbent for Pb(II) due to their capacity of adsorption of Pb(II) always higher than Cd(II) for both of activated and modified adsorbent. Optimum adsorption of Pb(II) in P-Zeolite is 12.28 mgg^{-1} (0.4g adsorbent, at pH 4 and 30 minutes contact time) and optimum adsorption of Cd(II) in P-Zeolite is 7.09 mgg-1 (0.4g adsorbent, at pH 4 and 50 minutes contact time). Modification of Zeolite with phosphate become a new strategy to increase adsorption capacity for both of Pb(II) and Cd(II). Presence of phosphate in zeolite cavity was effective in creating the increasing of 4 times surface area from 26.06 m^2g^{-1} to 88.65 m^2g^{-1} as main contributor to increase their adsorption capacity. The increasing of surface area and pore size of modified zeolite, effective to increase Pb(II) capture in modified zeolite (P-Zeolite). Micropore volume formation of activated zeolite is higher than modified zeolite indicate the presence of phosphate induce smaller pore volume but create a bigger pore size with suitable to Pb(II) ion in penetrated inside the cavity of P^--Zeolite.

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