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The influence of high energy milling to the adsorption of Cd(II) and Zn(II) ions on activated zeolite

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Abstract. Natural zeolite is believed to be able to effectively reduce heavy metal levels in water. However, due to the weakness of natural zeolites which have a low surface area and impurity so that the adsorption ability of heavy metals becomes less optimal. Increasing the surface area by using high energy milling is expected to optimize the ability of adsorption. In this study, the particle size of natural zeolite was reduced by using high energy milling then activated with HCl and NH_4Cl. The adsorption process was carried out by mixing activated zeolite and activated zeolite milling(activated zeolite fine powder) in a solution of metal ions Zn(II) and Cd(II). SEM-EDX analysis showed a change in surface morphology size on activated zeolite milling and GSA indicated an increase in surface area from 69.48 m^2/g to 97.9 m^2/g. Activated zeolite tends to having a little bigger in ability of adsorption to Cd(II) ions and Zn (II) ions than activated zeolite milling in highest variation of concentration, 800 ppm. In optimum contact time of adsorption, activated zeolite could adsorp Cd(II) ions shorter nevertheless longer to Zn(II) ions than activated zeolite milling. Both of the zeolites have ability to adsorp Zn(II) ions more than Cd(II) ions.

1. Introductions

Heavy metals are a group of pollutants because they cannot be decomposed (non degradable) in the open environment. As for dangerous heavy metals such as zinc (Zn) and cadmium (Cd). Generally, heavy metals become contaminants in water which are influenced by various industrial activities such as the battery industry, iron pipe industry, or electronic industry [1]. The toxicity of metal zinc and cadmium can affect humans when accumulated in excessive amounts. The effects on humans are very serious including reduction in bone density, and death [2].

Adsorption is a process that can reduce the levels of heavy metals effectively [3]. The adsorption process can be affected by the surface area, the greater the surface area, the adsorption process is expected to increase. One of the materials that can support the adsorption method is natural zeolite. Large abundance and low prices are the hallmarks of natural zeolite [4]. However, the disadvantage of natural zeolites is that they have impurities and a small surface area, so an increase in surface area and cleaning of natural zeolites from various impurities is needed to optimize the adsorption ability of zeolites. Some treatments that can be done are by modification and activation [5,6,7,8]. Modification of natural zeolites can be done using a tool that is high energy milling [9]. The use of high energy milling tools can reduce particle size without significantly changing the chemical bond structure [10]. Smaller particle size can increase the surface area so that it is expected to increase the adsorption ability.

2. Methods

This study has several stages of treatment including the milling of natural zeolite with HEM which was analyzed using SEM-EDX and GSA. The decreasing of metal ions concentration were analyzed by AAS.

2.1 Tools and materials

2.1.1. Tools. The tools used are a set of standard laboratory glassware, collision tools, stirrers, watch glass, petri dish, analytic balance, oven, 100 mesh sieve, Milwaukee digital meter pH, AAS (Atomic Absorption Spectrometry) Perkin Elmer AAS 400 type, SEM (Scanning Electron Microscopy) type JEOL JED 2300 and GSA (Gas Sorption Analyzer) Quantachrome type NOVAwin.

2.1.2. Materials. The material used were Wonosari natural zeolite, Whatman no. 42, Merck 1 M HCl solution, Merck 1 M NH_4Cl solution, aquadest, powder $CdSO_4.8H_2O$ P.A, powder $ZnSO_4.7H_2O$ P.A

2.2 Experimental

2.2.1 Treatment of high energy milling on natural zeolite. Natural zeolite was sieved with a 100 mesh sieve. Making zeolite fine powder(zeolite milling) was done by top down method using high energy milling (HEM-E3D) by grinding the starting material (natural zeolite) into a milling tool. The ratio used was 1: 5. Every time doing the milling, 5 grams of zeolite with 10 grinder balls weighing each 2.5 grams were included in the HEM-E3D jar. The milling process lasted for 30 minutes at a speed of 700 rpm.

2.2.2 Activation of zeolite. 100 grams of natural zeolite was soaked with 500 mL of 1M HCl solution for 24 hours, filtered and washed with distilled water to neutral pH and heated in an oven at 100°C for 4 hours. Then soaked with 250 mL 1M NH4Cl for 24 hours. Drying using an oven at 100oC for 4 hours.

2.2.3 Activation of zeolite milling. Zeolite milling of 150 grams was soaked with 500 mL of 1M HCl solution for 24 hours, filtered and washed with distilled water to a neutral pH and heated in oven at 100°C for 4 hours. Then soaked with 250 mL 1M NH_4Cl for 24 hours. Drying using an oven at 100°C for 4 hours.

2.2.4 Characterization. Activated zeolite and activated zeolite milling were characterized using GSA to determine surface area, pore size, total pore volume, SEM-EDX to determine surface morphology.

2.2.5 Adsorption of Zn(II) and Cd(II) metal ions on Zeolite Activated and Zeolite Milling Activated. Activated zeolite and activated zeolite milling as much as 0.5 g were added to 25 ml of Zn(II) and Cd(II) solutions with concentration variations of 100, 150, 200, 300, 400, 500, 600, 800 ppm then shaking out using shaker with 1 hour. Continued filtering using filter paper, the filtrate was analyzed using AAS. The same treatment for contact time variations is done with an initial concentration 150 ppm and a time variation of 1 minute, 5 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes, and 90 minutes.

3. Results and discussions

3.1.Preparation of natural zeolite

Natural zeolite in the form of rock is crushed using mortar to become a powder, then sieved using a sieve with a size of 100 mesh sieve (150 μm). The purpose of this sifting is to obtain a smaller and uniform particle size. The smaller the particle size used, the milling process becomes more effective and efficient[11]. The structure of the sieve hole is expected to get the same particle size or less than 150 μm.

After the sieving process is done, the formation of zeolite particle size becomes smaller, using HEM-E3D. The principle of this tool is the collision between the sample and the ball in the grinding container. Collisions occur because of the kinetic energy in the balls obtained from the movement in the grinding container[12]. The faster movement will provide greater energy so that the collision that occurs will be stronger.

3.2.Activation natural zeolite and zeolite milling

In this study, natural zeolite and zeolite milling were activated chemically by soaking on 1M HCl acid for 24 hours. The use of HCl aims to remove metal oxides and dust or soil material which can cover the zeolite pores so that the pores in the zeolite are expected to become more open. The concentration of HCl used should be not too high, so that the nature of zeolite crystals is still maintained[11]. After soaking with HCl, the natural zeolite is washed with distilled water. The washing is done by replacing aquadest that have soaked zeolites repeatedly. It is expected that the remaining unwanted cationic metals and impurities will be wasted. This washing process stops being marked with pH in the immersion container to be neutral. Zeolites were dried using oven heating at 100ºC for 4 hours.

The zeolite activation then is soaking using 1M NH_4Cl. Immersion with NH_4Cl aims to replace the balancing cation on the natural zeolite framework with NH_4^+ ions[13]. Zeolites were washed again with distilled water, followed by drying using an oven at 100ºC for 4 hours.

3.3.Characterization of zeolite activated and zeolite milling activated

3.3.1. SEM and EDX. SEM data provides information on surface shape and size of activated zeolite and activated zeolite milling, while EDX provides information on the composition of constituent elements in zeolite activation and zeolite milling activation.

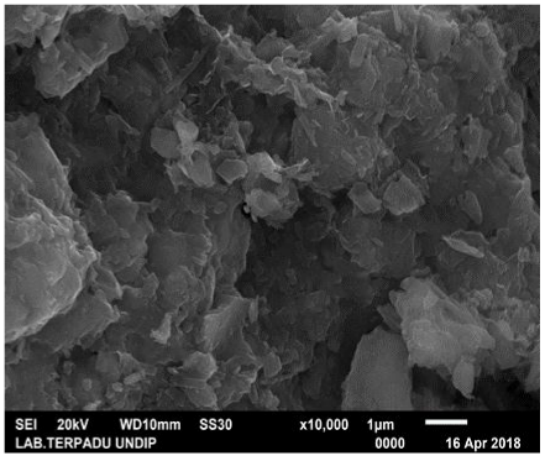

Figure 1. Results of SEM characterization on activated zeolite

In Figure 1 can be seen the results of the analysis using SEM on the zeolite activation, that overall still has a form of irregular spherical surface. Besides that, the zeolite activation tends to have an uneven particle size, there are still relatively large particles. The size of zeolite activation is in the range 1-3 μm.

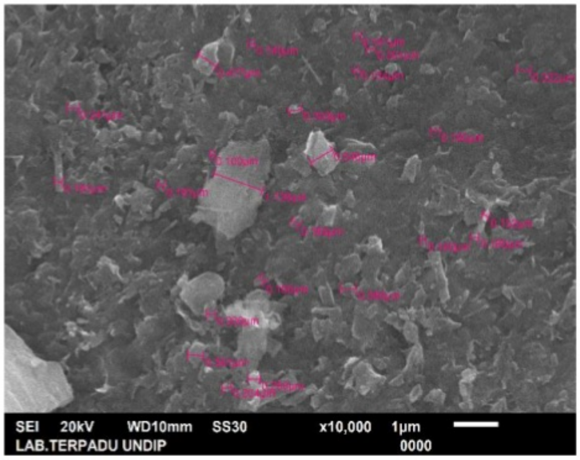

Figure 2. Results of SEM characterization on activated zeolite milling

In Figure 2 shows the results of SEM are different when compared with Figure 1, it can be seen that the high energy milling treatment has an effect on the particle shape in zeolites. With milling treatment at a speed of 700 rpm and for 30 minutes it can be seen that morphology shows a significant difference in particle size even though it still shows irregular bulb shape. It can be seen that the milling process is able to make zeolite into a smaller particle size compared to zeolite activation, particle size with a range of 0.2-1.5 μm.

Characterization using EDX provides information about the element content on the surface of the zeolite activation and zeolite milling activation. EDX results from activated zeolite and activated zeolite milling are presented in Table 1. Calculation of element content percentage in EDX analysis uses percent (%) of atoms, because suppose that percent of atoms show the number of atoms on the zeolite surface. Then it is possible that percent (%) weight is obtained from the number of atomic weights in zeolite samples.

Table 1. Result of EDX analysis

Element	AZM		AZ	
	% Mass	% Atom	% Mass	% Atom
Si	31.77	20.21	24.49	15.79
Al	1.14	0.76	5.43	3.64
O	56.02	62.57	55.20	62.48
C	11.07	16.47	10.78	16.26
Ca	-	-	0.73	0.33
K	-	-	1.21	0.56
Fe	-	-	1.61	0.52
Total	100	100	100	100

This is evidenced by the data that has been presented in Table 1. It can be seen that the content of Ca, K, Fe on activated zeolite is 0.33%, 0.56%, and 0.52%. In contrast to the activated zeolite milling that the Ca, K and Fe metals were not detected. It is suspected that this is influenced by the activation process and the shrinking of particles in the zeolite which has been given milling treatment. The particle size possessed by activated zeolite milling results in more effective removal of impurities.

3.3.2. Characterization using GSA. The working principle of GSA is based on the process of adsorption of N_2 gas from porous surface solids. Table 2 shows that the surface area of activated zeolite milling on activated zeolite has increased by 28.42 m^2/g. Activated zeolite has a surface area of 69.48 m^2/g and activated zeolite milling has a surface area of 97.9 m^2/g. This change is due to the smaller particle size after the milling process so that the number of particles in the activated zeolite milling is more than the activated zeolite since having the same mass. This also happened with the preceding research with high energy ball milling treatment able to increase the surface area of zeolite[14]. In this research the total pore volume also tend to increase, which is initially activated zeolite of 1.32 x 10^{-1} cc/g to 1.57 x 10^{-1} cc/g in activated zeolite milling.

Table 2. Result of BET analysis on specific surface area, specific pore volume and pore diameter

Sample	Surface Area (m^2/g)	Total Pore Volume (x10-1 cc/g)	Average Pore Size (Å)
Activated Zeolite	69.48	1.32	37.6
Activated Zeolite Milling	97.9	1.57	31.57

There is a decrease in the average pore size in activated zeolite milling compare with activated zeolite. The activated zeolite has an average pore size of 37.6 Å and activated zeolite milling is 31.57 Å, it is suspected that the particle size in activated zeolite milling has a smaller size compared to activated zeolite. The smaller particle size, it will relatively give a pore size to the material decreasing [15].

3.4.Adsorption of metal ions on zeolite activated and zeolite milling activated

Adsorption test on activated zeolite and activated zeolite milling was assessed through the influence of concentration and contact time variation on metal ions Cd(II) and Zn(II).

3.4.1. Effects of variation concentration adsorption Cd(II) dan Zn(II) metals ion. Figure 3 shows the adsorption ability of activated zeolite milling and activated zeolite on Cd(II) metal ion that the increasing concentration of metal ion, the adsorption ability of the two adsorbents become greater. In activated zeolite milling, the highest adsorption ability is up to 19.05 mg/g, whereas in the activated zeolite is 19.12 mg/g, both at 800 ppm on concentration variation. Both materials performed almost similar adsoption ability to Cd(II) although activated zeolite milling has larger surface area than activated zeolite. That is probably because of the soft acid character of Cd(II) and hard base character of O atoms in zeolite stucture. In general soft acids prefer to bind to soft bases and hard acids prefer to bind to soft bases according to Pearson concept(1963)[16]. In this case, the differences between Cd(II) and O atoms in that character suppose to influence the adsorption ability.

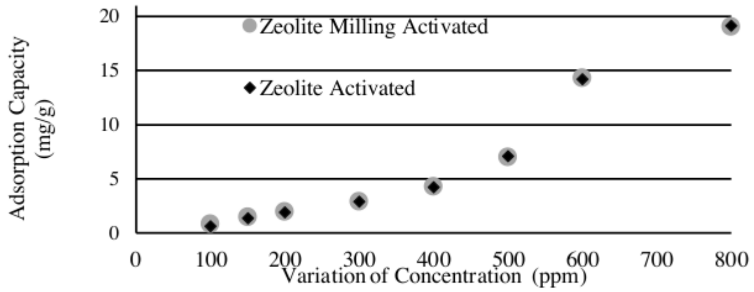

Figure 3. The ability of adsorption to Cd(II) metal ion

Figure 4 shows the adsorption ability of activated zeolite and activated zeolite milling of Zn(II) metal ion. It is seen that along with the increase in the concentration of metal ion, the adsorption ability of both adsorbents are greater. The highest adsorption ability is obtained at a concentration of 800 ppm on both adsorbents. The ability of adsorption of metal ions in activated zeolite milling is 39.52 mg/g, while the activated zeolite is 39.6 mg/g. Treatment using high energy milling tools is done to reduce particle size so as to increase surface area. The large surface area of the adsorbent can increase the adsorption ability so that the adsorbent can accommodate more adsorbates compared to the smaller surface area[17]. However, based on the experimental results presented in Figure 3 and Figure 4, activated zeolite milling that has been given milling treatment does not have a significant effect on the adsorption ability compared to activated zeolite.

The pore size of an adsorbent can affect the amount of adsorbate that can be absorbed by the adsorbent. As pore size increases, the amount of adsorbate that can enter the pore will be greater[3]. The BET results in table 1 show that the pore size possessed by zeolite milling activation has decreased compared to activated zeolite which is 6.03 Å. While the pore volume shows an increase in activated zeolite milling, although the increase is not too significant, that is equal to 0.25 x 10^{-1} cc/g.

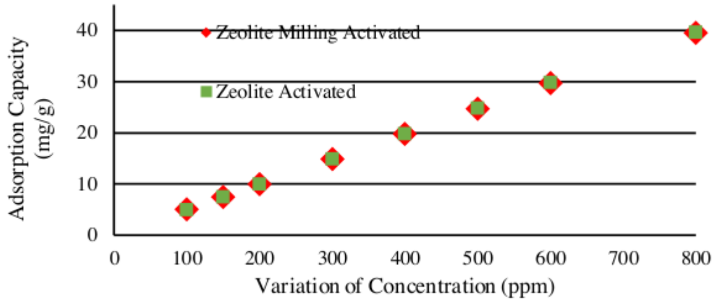

Figure 4. Adsorption ability of Zn(II) metal ion

Zeolite particles which have a size below 10 μm can be more easily agglomerated. Agglomeration is a process of clumping on small particles forming larger particles. Especially in wet conditions, the surface of zeolite particles will be easier to bind with other particles, thus forming a larger particle size [18]. It is possible that this occurs in activated zeolite milling because based on the results of SEM in Figure 2 the size of the surface morphology is in the range 0.2 - 1.5 μm. Smaller sizes compared to activated zeolites make the potential for agglomeration in activated zeolite milling easier to occur. The larger particle size can reduce adsorption ability because the surface area for contact between adsorbents and adsorbates is reduced[16]. It is suspected that this is what causes the difference in adsorption ability in activated zeolite milling to be insignificant compared to activated zeolite.

3.4.2. Effects of contact time adsorption metals Ion Cd(II) and Zn(II). Figure 5 shows the adsorption ability of activated zeolite milling and activated zeolite in metal ion Cd(II). As the contact time of the two adsorbents increases, the adsorption ability also increases. However, after passing the optimum point, the adsorption ability in both adsorbents tends to decrease. At activated zeolite milling, the optimum contact time obtained is 30 minutes with adsorption ability of 4.16 mg/g while at activated zeolite is 15 minutes and 4,44 mg/g. After passing the optimum contact time point, the adsorption ability on activated zeolite milling appears having a decrease in adsorption ability. This is presumably because metal ions that have bonded to the active site in the zeolite have been released back into the solution. As the contact time between adsorbents and metal solutions increases, the metal ions that have been bonded can be released again[16]. This release process is often referred to as desorption [19]. This release process occurs because of the equilibrium between adsorbent and adsorbate [20].

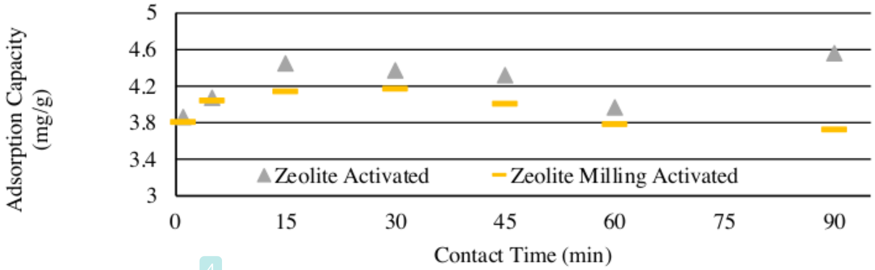

Figure 5. Adsorption capacity of Cd(II) metal ion

Based on the experimental results in Figure 6 shows the adsorption ability of activated zeolite and activated zeolite milling of Zn(II) metal ion. For activated zeolite, the optimum contact time was obtained at 45 minutes with adsorption ability, which is 4.96 mg/g.

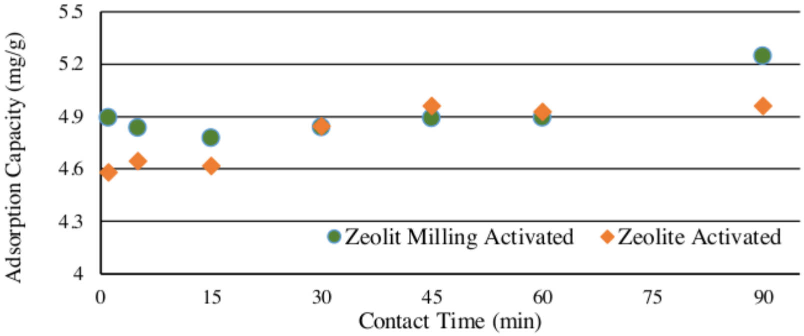

Figure 6. Adsorption capacity of Zn(II) metal ion

In activated zeolite milling, the optimum contact time is obtained at 1 minute with adsorption ability that is equal to 4.9 mg / g. Activated zeolite milling which has a larger surface area, is possible to adsorb more metal ions. The greater the surface area will provide greater space for the adsorbate to be absorbed into the adsorbent[21]. After passing the optimum point of the second data, the adsorbent showed that the adsorption ability tends to be constant. This happened because the active site of the adsorbent was filled with metal ions so that it was unable to bind to the remaining metal ions[17]. Zeolite milling activated work better compared to zeolite activated on Zn(II) adsorption than Cd(II). It suspected because of the differences of the ionic radius of the both metal ions. Zn(II) has smaller ionic radius than Cd(II) so that increase the intensive interaction to surface of zeolite milling which has larger surface area than zeolite activated. In general, the result shows that the adsorption ability of both zeolite to Zn(II) is a litte bigger than Cd(II). In this case, Zn(II) is borderline acid[16] which has probably stronger interaction with O atoms on zeolite structure than Cd(II) as a soft acid.

4. Conclusions

In summary, with HEM the surface area and pore volume of activated zeolite milling increasing otherwise the pore size is not. Activated zeolite and activated zeolite milling have the same highest concentration (800ppm) to adsorp Cd(II) and Zn(II) ions, nevertheless lower in adsorption ability to Cd(II) ions than Zn(II) ions. Activated zeolite milling is able to adsorp Zn(II) ions in shorter optimum contact time than activated zeolite however longer time in adsorption to Cd(II) ions. Zn(II) ions adsorption on both of the zeolites are relatively better in capacity than Cd(II) ions.

Acknowledgment

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