Zeolite Coating with Phenantroline for Adsorption of Ion Fe (III)

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ABSTRACT

Natural zeolite contains impurities such as Na, K, Ca, Mg and Fe and has poor crystallinity. The presence of these impurities can reduce the activity of zeolites. To improve the character of natural zeolite, activation and modification are carried out first. In addition to removing impurities contained in natural zeolites, zeolite activation processes are also used to modify the properties of zeolites, such as surface area and acidity. One of the advantages of zeolites is that they have a surface area. and readily modifiable acidity when used as an adsorbent. This research aims to; find out the natural zeolite coating process using phenantrolin; find out the pH of the solution against the adsorption process of iron (III) metal ions using phenanthrolin coated zeolites; find out the effect of other metals on the adsorption process of iron (III) metal using phenanthrolin with coated zeolite. The stages carried out in the study began with the preparation process of 250 mesh zeolite which was activated using 1 M HCl solution. Then the zeolite coating process was carried out by mixed it with 10 ml distirer for 1 hour, the residue was dried, and then it would be ready for the adsorption process. After that, it was followed by the characterization of the adsorbent with FTIR at a wavenumber of 3400-250cm-1 and repeated for the adsorbent that had adsorbed iron (III) ions. The final step is to carry out the adsorption of iron (III) ions, where the process is carried out with variations in pH 2,6,8 and variations in contact time, that were 5, 10, 15, 30, 45, 60 (minutes). The results showed that natural zeolite after the activation process with hydrochloric acid had increased crystallinity. The results of pH variations showed that for the natural zeolite the higher the pH, the higher the adsorbent's effectiveness, while for the activated zeolite, the higher the pH, the lower the adsorbent's effectiveness. the variation in contact time showed that the longer the contact time, the effectiveness of natural zeolites and activated zeolites will decrease. The results of the concentration variation showed that the greater the concentration, the lower the effectiveness of natural zeolites and activated zeolites. Adsorption of natural zeolite on Fe (III) metal ion follows the Freundlich isotherm pattern with an n value of 0.09. Activated zeolite adsorption on Fe (III) metal ions followed the Langmuir isotherm pattern with a maximum capacity (Qm) of 1.18 mg / g.

Keywords: *Fe (III) ion adsorption, Phenantroline, Zeolite.*

1. INTRODUCTION

Zeolite has high adsorption because it has many pores and has a high cation exchange capacity and can be applied over a wide temperature range so it is very suitable to be used as an. Zeolites are called molecular mesh because zeolites have molecular-sized pores that can separate or filter molecules of a certain size.

Zeolite contains many impurities such as Na, K, Ca, Mg and Fe and has poor crystallinity. The presence of these impurities can reduce the activity of zeolites. For the zeolite to be used as a catalyst, absorbent or other application, activation and modification can be carried out. The purpose of zeolite activation is to remove impurities found in natural zeolites, the zeolite activation process is also used to modify the properties of zeolites, such as surface area and acidity. One of the advantages of zeolite is that it has a surface area and acidity that is easily modified when used as an adsorbent.

Cu (II) is a heavy metal ion that is difficult to degrade. Heavy metal ions in wastewater pose a very big problem for organisms and the environment because they have a high level of toxicity. Sources of heavy metal ions in waste include mining and other industries [1]. The heavy metal content in metal coating waste includes Cu metal ions of 18.9 mg / L; Zn of 76.3 mg / L; Cd of 8.52 mg / L is at pH 7.89.

Several methods are used to remove heavy metal ions, such as neutralization, precipitation, ion exchange, biosorption, and adsorption. Adsorption is carried out to remove heavy metal ions by using various kinds of adsorbents, such as zeolite, allophane, chitin-chitosan, bio sorbents from algal species, fly ash, activated carbon, and cellulose. Among the methods already mentioned, the adsorption method is preferred and has been widely used in the process of separating heavy metal ions. The adsorption method plays a role in increasing the amount of metal or a high level of selectivity to certain metals is possible [2].

2. RESEARCH METHODS

This research was conducted from March to July 2020 at the Final Project Laboratory of the Faculty of Science and Technology, University of Jambi. The materials used in the research were natural zeolite powder, HCl, Aquades, and Fe (III) ion. The research method used in this research includes the following stages:

2.1 Zeolite Preparation

The zeolite mineral was crushed and then sieved with a size of 250 mesh and then activated with a 1 M HCl solution. The material was dried for 2 hours. Then stored in a desiccator.

2.2 Zeolite coating with

A total of 2 grams of material mixed with 10 ml of distirer for 1 hour. Then the mixture is filtered. The residue is dried for further adsorption.

2.3 Adsorbent Characterization by FTIR

A total of 3 mg of material were analyzed by FTIR. The wavenumber 3400-250cm-1 was selected. Repeat for the adsorbent which has adsorbed Fe (III) ion.

2.4 Adsorption of iron (III) ions

Variation in pH, as much as 4 water solutions containing a solution of Fe (III) ion 25 ppm, the pH is determined to be pH = 2. Then add 0.5 grams of the adsorbent. And stirred for 30 minutes. The mixture was filtered, the filtrate was measured by AAS. The experiment was repeated for pH 2, 6, and 8.

Variation in contact time, as many as 6 series of solutions containing a solution of Fe (III) ion of 25 ppm maximum pH. Then add 0.5 gram of adsorbent. And stirred for 30 minutes. The mixture was filtered, the filtrate was measured by AAS. The study was repeated for contact times of 5,10, 15, 30, 45, and 60 minutes.

3. RESULTS AND DISCUSSION

The natural zeolite resulted from the diffractogram showed a more amorphous form so that the crystallinity was lower and some peaks were not very visible, while the activated zeolite showed increased crystallinity and some peaks in intensity increased.

Figure 1. Adsorption mechanism

The types of natural zeolite minerals were identified by analyzing the types of peaks that appeared in the XRD analysis results and compared with the data (XRD Powder Patterns for Zeolite.

Table 1. Data of the diffraction peaks of natural zeolite and activated zeolite

No	Zeolit alam			Zeolit teraktifasi		
	Puncak 2θ	d(A)	Int (%)	Puncak 2θ	d(A)	Int (%)
1	9,7690	9,05419	68,32	9,7546	9,06749	60,56
2	22,2561	3,99444	73,31	22,2746	3,99116	49,11
3	25,6287	3,47594	100,00	25,6675	3,47077	100,00

Table 2. Interpretation data 2Θ

No	Zeolit Alam			Zeolit Teraktifasi		
	2θ	Treacy & Higgins	Interpretasi 2θ	2θ	Treacy & Higgins	Interpretasi 2θ
1	9,7690	9,77	Mordenit	9,77	9,7	Mordenit
2	22,2561	22,25	Afghanit	22,2746	22,25	Afghanit
3	25,6287	25,63	Mordenit	25,6675	25,63	Mordenit

Based on the data in Table 2, it is known that the types of natural zoelit minerals are mordenite and afghanite. The crystallinity of natural zeolite after activation is higher than that of natural zeolite before activation. This can be seen in the peaks that were initially still low after being activated, the intensity increased to become sharper. The activation process has removed impurities contained in the zeolite framework and made the zeolite framework more orderly so that its crystallinity increases. The increase in crystallinity makes activated zeolites more optimal in adsorbing metal ions, while natural zeolites usually give less than optimal results in the adsorption process because they still contain many impurities in their constituent framework. Variation in pH was carried out to determine its effect on the adsorption of Fe (III) metal ions using natural zeolites and activated zeolites. The adsorption results at the pH variation of the two adsorbents on Fe (III) metal ions are shown in Figure 2.

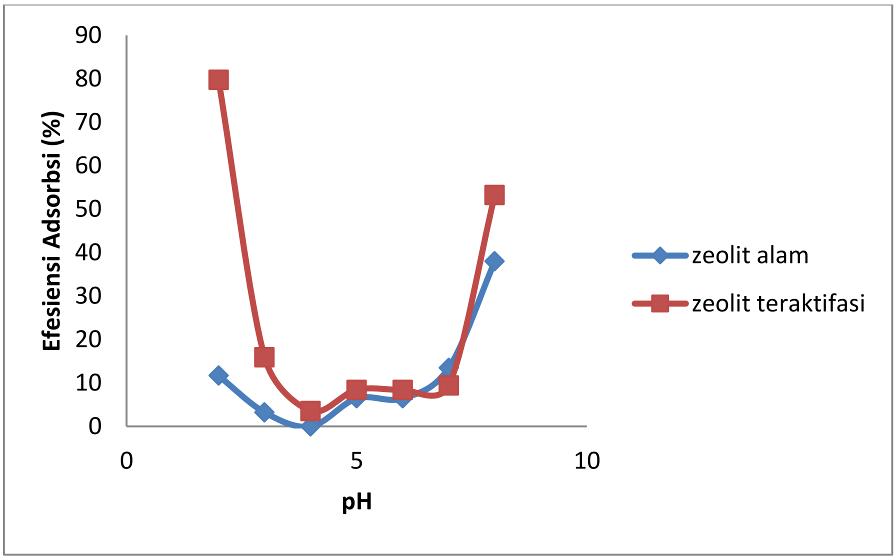

Figure 2. The curve of the influence of pH on the adsorption efficiency of Fe (III) ions

Speciation of Fe (III) metal ions in an acidic environment is in the form of Fe3 + ions, while in an alkaline atmosphere Fe (III) metal ions tend to precipitate to form Fe (OH) 3 compounds which result in Fe (III) ions unable to be adsorbed by adsorbents. Besides, due to the formation of Fe (OH) 3 deposits, the adsorbed levels of Fe (III) metal ions also decrease so that the levels will decrease a lot from the initial levels of the solution. Activated zeolites are more effective in adsorbing Fe (III) metal ions than natural zeolites. The higher the pH, the less Fe (III) metal ion adsorbed because in an alkaline atmosphere the Fe (III) metal ion tends to form a precipitate of Fe (OH) 3 which cannot be absorbed by the adsorbent. The variation of contact time was carried out to determine the effect on the adsorbent adsorption results.

When the optimum time is reached, the amount of metal ions adsorbed in the next minute decreases. This decrease is caused by the reduced ability of the adsorbent to absorb metal ions until a certain time because the adsorbent is saturated so that all the pores in the adsorbent have been filled by adsorbed Fe (III) metal ions. This causes the adsorbent to be unable to absorb the remaining Fe (III) metal ions in the next minute. The adsorption results at the variation in the contact time of the two adsorbents are shown in Figure 3.

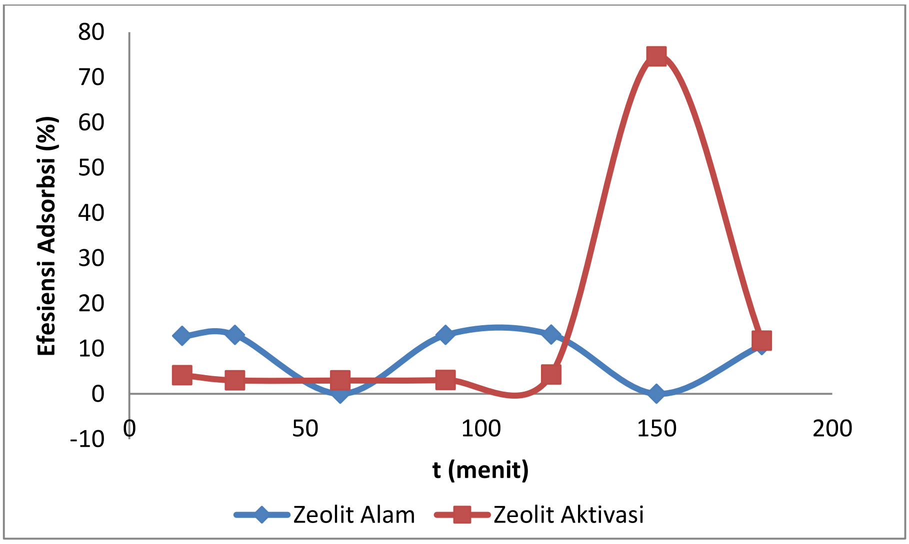

Figure 3.The curve of the effect of time on the adsorption efficiency of Fe (III) ions

It can be seen in Figure 3. After a certain time, there will be a decrease in adsorption. Activated zeolites are more effective in adsorbing Fe (III) metal ions than unactivated natural zeolites. This is because the activated zeolite impurities contained in the zeolite framework have been lost, while the unactivated natural zeolite still contains many impurities so that it reduces its effectiveness in adsorbing metal ions because it is disturbed by the presence of impurities. The optimum concentration variation was carried out to determine the concentration of the sample adsorbed by the adsorbent in the form of natural zeolite and activated natural zeolite.

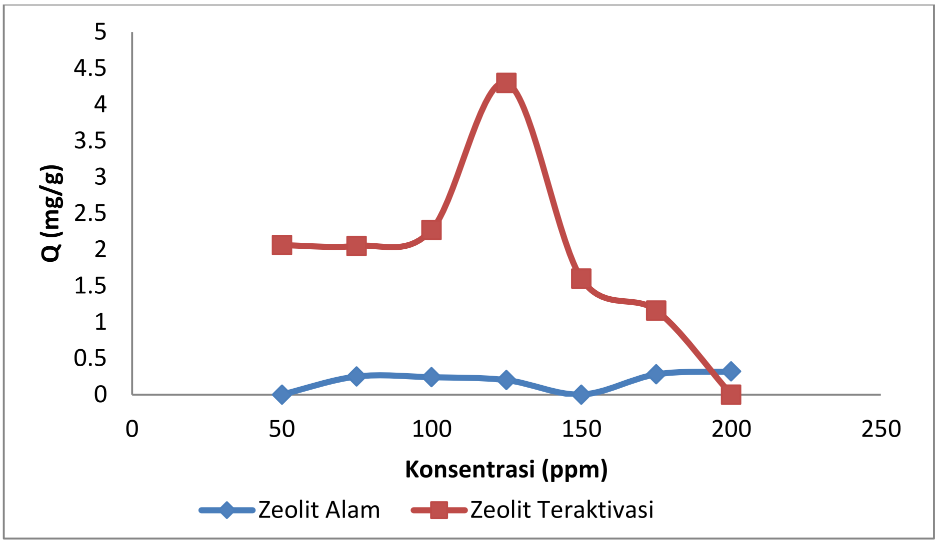

Figure 4. The curve of the effect of concentration on the adsorption efficiency of Fe (III) metal ions

The highest number of adsorbed Fe (III) metal ions for natural zeolite was obtained at a concentration of 200 ppm as much as 1.29 ppm while in activated natural zeolite at a concentration of 125 ppm as much as 17.35 ppm. In the adsorption of Fe (III) with natural zeolites, because the pH used is 8, this causes a precipitation process before the adsorption process. This precipitation causes the initial concentration of the solution to be smaller due to the presence of Fe (III) metal ions that have formed a precipitate so that when the adsorption and measurement are carried out, the results are relatively low. Based on Figure 4, it is known that activated natural zeolites are more effective in adsorbing Fe (III) and Cr (VI) metal ions compared to unactivated natural zeolites. This is because the unactivated natural zeolites still contain a lot of impurities so that they are less effective in adsorbing Fe (III) metal ions than activated natural zeolites. Determination of adsorption capacity was carried out to determine the ability of natural zeolite and activated zoellite adsorbents to adsorb Fe (III) metal ions. Based on the data obtained, the natural zeolite and activated zeolite adsorption isotherm graph were made. The adsorption isotherm patterns that are often used are the Langmuic and Freundlich isotherms.

Table 3. Natural zeolite adsorption parameters

Jenis ion Logam	Isotherm Langmuir			isotherm Freundlich		
	Q (mg/g)	b (L/g)	R^2	Kf (L/g)	n	R^2
Fe (III)	0,0628	110,3	0,677	2,8708 x10^{-10}	0,0878	0,7939

Table 4. Activated zeolite adsorption parameters

Jenis ion Logam	Isotherm Langmuir			isotherm Freundlich		
	Q (mg/g)	b (L/g)	R^2	Kf (L/g)	n	R^2
Fe (III)	1,1819	29,7	0,7261	4,5186	5,7339	0,0494

Based on the data in Table 3, the metal ion adsorption shows the Langmuir adsorption isotherm pattern, while the Fe (III) metal ion adsorption more closely follows the Freundlich isotherm pattern. Based on the data in Table 4, the adsorption of Cr (VI) metal ions shows the Freundlich adsorption isotherm pattern while the Fe (III) metal ions more closely follow the Langmuir isotherm pattern. Langmuir adsorption isotherm pattern states that the active sites on the adsorbent surface are homogeneous. The type of adsorption is chemisorption which means that the adsorption occurs chemically, which indicates the formation of a stronger bond between the adsorbate and the absorbent in the form of covalent bonds and hydrogen bonds. Freundlich's adsorption isotherm pattern occurs physically, meaning that the adsorption occurs physically on the surface of the adsorbent. In physical adsorption, the adsorbate is not strongly attached to the adsorbent surface so that the adsorbate can move from one part of the surface to another. Physical adsorption occurs because of the Van Der Waals bond, which is a weak attractive force between the adsorbate and the adsorbent surface. This isotherm describes the active sites on the heterogeneous adsorbent. Two-component adsorption in this study was carried out by mixing the two metal ions, namely Fe (III) and Cr (VI) metal ions. This adsorption is carried out to determine the effectiveness of the adsorption of an adsorbent in a solution containing more than one type of metal ion.

Table 5. Optimum conditions for two-component adsorbs with natural zeolite

Ion Logam	Konsentrasi awal (ppm)	pH	Waktu (menit)	Konsentrasi awal (mmol/L)	Konsentrasi akhir (mmol/L)	Efisiensi (%)
Fe(III)	87,80	8	120	1,5721	1.4998	4,60

Table 6. Optimum conditions for two-component adsorbs with activated zeolite

Ion Logam	Konsentrasi awal (ppm)	pH	Waktu (menit)	Konsentrasi awal (mmol/L)	Konsentrasi akhir (mmol/L)	Efisiensi (%)
Fe(III)	133,03	2	150	2,3820	1.5030	36,90

Based on the data in Tables 5 and 6, the results of the adsorption of this artificial waste mixture show the same results as the results of the variations that have been carried out. It can be seen that in natural zeolites the adsorption capacity is lower than that of activated zeolites, in the activated zeolites the capacity is more for the two metal ions. This shows that activated zeolite is better than natural zeolite because basically the characteristics of activated zeolite are better. Activated zeolite has gone through an activation process that aims to remove impurities that can interfere with the adsorption process. The removal of impurities causes the pores to become empty and can be filled with adsorbed metal ions while natural zeolites still have impurities in the adsorbent framework so they are not good for adsorbing a metal ion. According to research by Ngatijo, Basuki, R, Nuryono, and Rusdiarso, B. [3] Thermodynamic parameters with the Langmuir and Freundlich isotherm models of Au (III) absorption in 0.1 g sorbent in a series of 20 ml of Au (III) solution.

Table 7. Thermodynamic parameters with Langmuir and Freundlich isotherm models

Sorbent	Langmuir			Freundlich		
	B (mg/g)	$K(mole/L)^{-1}$	R^2	B (mg/g)	n	R^2
AMS	37.94	14491	0.993	55.34	2.68	0.984
QAMS	74.47	14809	0.997	466.02	1.84	0.959

This proves that the linear isotherm model of Langmuir is better than Freundlich because metal ions will occupy the active site which has the strongest interaction first, followed by the occupation of metal ions with the lower energy active side. Whereas the capacity (multilayer or multi-energy) indicates the absorption capacity of freundlich [N + (CH3) 3] and other active sites together. The interaction that occurs is thought to be the electrostatic force between the metal ions and the active QAMS site.

4. CONCLUSION

Based on the discussion, it can be concluded as follows:

a. Natural zeolite after activation process with hydrochloric acid has increased crystallinity.

b. The results of pH variations show that the higher the pH, the higher the adsorbent effectiveness, while the higher the pH of the activated zeolite, the lower the adsorbent effectiveness.

c. The results of the variation in contact time indicate that the longer the contact time, the lower the effectiveness of natural zeolites and activated zeolites. The results of the concentration variation showed that the greater the concentration, the lower the effectiveness of natural zeolites and activated zeolites.

d. Adsorption of natural zeolite on Fe (III) metal ion follows the Freundlich isotherm pattern with an n value of 0.09.

e. Adsorption of activated zeolite on Fe (III) metal ion follows the Langmuir isotherm pattern with a maximum capacity (Qm) of 1.18 mg / g.

REFERENCES

[1] A. Baraka, P.J. Hall, dan M.J. Heslop, Preparation and Characterization of Melamine-Formaldehyde-DTPA Chelating Resin and Its Use as An Adsorbent for Heavy Metal Removal from Wastewater. Reactive and Functional Polymers 67, 2007, 585-600.

[2] M.V. Dinu, dan E.S. Dragan, Evaluations of Cu^{2+}, Co^{2+}, Ni^{2+} Ion Removal From Aqueous Solution Using a Novel Chitosan/ Clinoptilolite Composite: Kinetics and Isotherms 160, 2010, 157-163.

[3] Ngatijo, R. Basuki, Nuryono dan B. Rusdiarso, Comparison of Au(III) sorption on amine-modified silica (AMS) dan quaternary amine-modified silica (QAMS): A Thermodynamic and Kinetics Study, *Indones, J.Chem.* Vol.19. No.2, 2019, P 337-346.