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***Research paper***

# Synthesis of Zeolite-A and Zeolite-Y Using Silica Gel Waste as Silica Source and Modifying with Fe

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## Abstract

The purpose of this research was to synthesize zeolite-A (Ze-A) and zeolite-Y (Ze-Y) using silica sources from silica gel waste, and also improving adsorption capacity with Fe which was trapped in the synthesized zeolites: Ze-Fe-A and Ze-Fe-Y. All synthesized zeolites were tested with lead solution of 40 mg/L at pH 5. For BET specific surface area, the parent Ze-A and Ze-Y presented surface area of 27.02 and 211.42 m2/g, respectively, whereas Ze-Fe-A and Ze-Fe-Y presented a lower surface area of 10.90 and 28.22 m2/g, respectively. SEM and TEM image demonstrated the cubic and polygon shapes for Ze-A and Ze-Y, respectively, while their modification with Fe presented more round shape. Additionally, both modified zeolites with Fe presented higher adsorption efficiency than their parents. Although the modified zeolites gave lower surface area, the efficiency removal of lead showed higher capacity than zeolite without Fe. It could be concluded that the adsorption mechanism of modified zeolites did not only rely on physical adsorption, but also on chemical adsorption.

***Keywords***: *Zeolite-A, Zeolite-Y, Silica gel waste, Adsorption*

## 1. Introduction

Zeolite is microporous aluminosilicate crystalline, the subunits of which consist of one silicon atom (or aluminium atom) and four oxygen atoms (SiO44- or AlO45-). Each subunit shares an oxygen atom, and its molecules are connected together in an orderly three-dimensional structure. Moreover, Zeolites – especially synthetic zeolites – are widely used in many industries because of its uniform composition, exact structure and high purity. Zeolite can be used as environmental treatment materials such as ion exchange, adsorbent and catalyst, etc. The type of zeolite can be defined by molar ratio of SiO2/Al2O3. Zeolite-A (Ze-A) presents SiO2/Al2O3 molar ratio of 2 whereas Zeolite-Y (Ze-Y) is 15 of SiO2/Al2O3 molar ratio [1]. The synthesis of Ze-A and Ze-Y is usually achieved by hydrothermal method. The hydrothermal method is a physical or chemical process under a closed system of precursor solutions at high temperatures and pressures [2]. There are many sources of silica used as a precursor in the synthesis of zeolites, such as sodium silicate and silica from waste, i.e., rice husk [3], fly ash [4]. The promising waste that can be used as silica source is silica gel waste, which has a high composition of silica or silicon dioxide at approximately 99.71% [5]. In the chemical laboratory, silica gel is used as desiccant when its color turns out from dark blue to be light blue or pink that means it is deteriorated. The deteriorated silica gel can be regenerated by removing moisture in an oven until its color turns to be dark blue as it is. On the other hand, the deteriorated silica which cannot be regenerated, call silica gel waste. This waste will be collected in container and waited for sending to dispose in secure landfill. The other technique to dispose the silica gel waste is recycling which is mixed with cement paste [6] or modified to be used as adsorbent [7].

The aim of this research is to synthesis Ze-A and Ze-Y using silica gel waste as silica source and also modified synthesised zeolites with Fe, i.e. Ze-Fe-A and Ze-Fe-Y, for enhancing adsorption capacity which were tested with lead solution.

## 2. Materials and Methods

### 2.1. Chemicals and silica gel waste

The chemicals used in zeolite synthesis were sodium aluminate (Al2O3 53.5%, Na2O 45%, Sigma-Aldrich), sodium hydroxide (99% NaOH, Merck), iron (III) chloride hexahydrate (98% FeCl3.6H2O, Sigma-Aldrich) and distilled water. The stock standard of lead solution was prepared from lead (II) nitrate (99% Pb(NO3)2, Sigma-Aldrich) in distilled water and stored at 4oC until use. In adsorption experiment, the pH of the lead solutions was adjusted to the desired value using either NaOH or HCl solutions. All reagents were analytical grade and used without further purification. Silica source was silica gel waste (2-5 mm in diameter), which was used as desiccant in laboratory. Silica gel waste was collected from the chemical laboratory of Department of Environmental Engineering, Khon Kaen University. Before using, the spent silica gel was dried in an oven at 100oC to remove moisture remaining in the saturated desiccant.

### 2.2. Analytical methods

The concentrations of lead were measured by means of Atomic Absorption Spectroscope (AAnalyst 800, PerkinElmer). The synthesized zeolites were characterized by X-ray Diffraction Analysis (XRD), Bruker D8 Advance, with Cu Kα radiation at 40 kV and 40 mA. The specific surface areas were attained by the Brunauer, Emmet and Teller (BET) method in an Autosorb 1 MP, Quantachrome. The microstructures were evaluated by Scanning Electron Microscopy (SEM), Hitachi S-3000N and Transmission Electron Microscope (TEM), JEOL, JEM-1010. EDX (HORIBA

EMAX x-act) was used for analyzing the elements in synthesized zeolites.

### 2.3. Synthesis of Zeolite-A (Ze-A)

The synthesized Zeolite-A (Ze-A) was prepared from the molar ratio of reactants which were 6Na2O : Al2O3 : SiO2 : 150H2O. Sodium hydroxide 12.27 g was dissolved in 90 ml distilled water then divided equally. The first part of the solution was mixed with 6.3552 g of sodium aluminate. The second part of solution was stirred with 2 g of silica gel waste at 90oC for 3 hours. Both solutions were mixed together and then transferred into the Teflon vessel which was sealed in the hydrothermal reactor and heated at 80oC for 2.5 hours. After cooling, the white precipitate (or synthesized Ze-A) was washed with distilled water until the pH of the runoff was lower than 9 and then the Ze-A was dried overnight at 100oC.

### 2.4 Synthesis of Zeolite Y (Ze-Y)

The synthesized Zeolite-Y (Ze-Y) was prepared from the molar ratio of reactants which were 4.62Na2O : Al2O3 : 3SiO2 : 180H2O. First, 14.13 g of sodium hydroxide was dissolved in 100 ml of distilled water and stirred until a clear solution was obtained. 27 g of silica gel waste was gradually added in the solution and the mixed solution was continuously stirred until the silica gel was completely dissolved and the solution turned to be a homogeneous mixture of sodium silicate solution. In the preparation of seed gel, 2.04 g of sodium hydroxide and 1.045 g of sodium aluminate were dissolved in 10 ml of distilled water. Then 11.36 g of sodium silicate solution was added slowly and the homogeneous solution was left in room temperature for aging for 24 hours. In preparing feed stock gel, 0.07 g of sodium hydroxide and 6.545 g of sodium aluminate were dissolved in 65.5 ml of distilled water, and then 71.215 g of sodium silicate solution was added slowly. Subsequently, the 8.25 g of seed gel solution was slowly mixed with feed stock gel which had been prepared in the prior step. The homogeneous solution was then transferred into the Teflon vessel which was sealed in the hydrothermal reactor and heated at 100oC for 24 hours. After cooling, the white precipitate (or synthesized Ze-Y) was washed with distilled water until the pH of the runoff was lower than 9 and then the Ze-Y was dried overnight at 100oC.

2.5 Synthesis of Zeolite-Fe-A (Ze-Fe-Y) and Zeolite-Fe-Y (Ze-Fe-Y)

For Ze-Fe-A or Ze-Fe-Y preparation, the Ze-A or Ze-Y at 40 g was stirred in 0.005 M of iron chloride solution for 30 minutes and then 1 M of sodium hydroxide was added in the mixing solution which was continuously stirred for 30 minutes. The white solid was separated and dried overnight at 100oC then burned at 550 oC for 4 hours. Finally, the white solid of Ze-A or Ze-Y would turn to brown solids of Ze-Fe-A or Ze-Fe-Y. The synthesized zeolites were finally stored in a closed container for further use.

2.6 Adsorption experiments

The adsorption experiments were carried out using a batch method in 1000 ml glass reactor. The 0.1 g of synthetic zeolites was used as an adsorbent in each experiment. Lead solution at 40 mg/l was adjusted to pH 5 before testing. The mixtures of lead solution and adsorbent were stirred at 150 rpm for 480 minutes at room temperature. Water samples were taken at certain times and the solids were then separated by centrifugation. The solutions were analyzed using a flame atomic absorption spectrometer to determine the lead concentration.

## 3. Results and Discussion

### 3.1 Synthesis of zeolites

The silica source to synthesize zeolite was blue silica gel with the size of □2-5 mm and having silica as the main element at the 99.71%. The sodium silicate solution prepared from dissolving blue silica gel waste in sodium hydroxide solution appeared a blue solution. When the blue solution was mixed with sodium aluminate, the final mixed solution became white opaque solution of aluminosilicate compound. This compound would turn into a crystalline after it was treated by hydrothermal process in various conditions. In this research, the synthesized zeolites (Ze-A and Ze-Y) were white powder (Figure 1 (a) and (b)) and the modified synthesized zeolites with Fe (Ze-Fe-A and Ze-Fe-Y) were brown powder resulting from iron oxide embedded in their structures (Figure 1 (c) and (d)).

### 3.2 Characterization of synthesized zeolites

#### 3.2.1 X-ray diffraction analysis

The synthesized zeolites: Ze-A, Ze-Fe-A, Ze-Y, and Ze-Fe-Y, which were synthesized using silica gel waste as silica source and modified by Fe were analyzed by XRD technique. The results are presented in Figure 2 and 3. XRD result shows a good crystallinity for Ze-A, while the XRD pattern of synthesized Ze-Y is mixed between peaks of Ze-A and Ze-Y. After modified, the synthesized products with Fe, both Ze-Fe-A and Ze-Fe-Y patterns did not show any peak of iron oxide. This confirmed that the modification with Fe had no effect on the crystallinity of parent zeolites.

**Figure 1.** Synthesized zeolites (a) Ze-A, (b) Ze-Y, (c) Ze-Fe-A, and (d) Ze-Fe-Y.

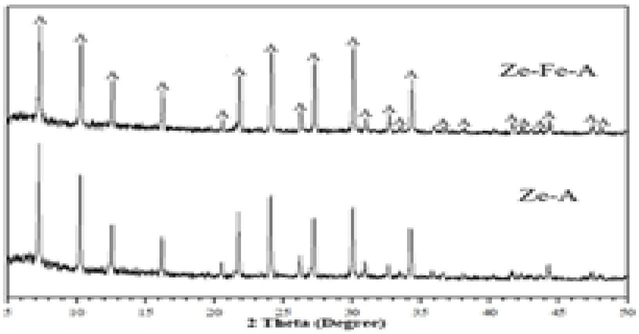

**Figure 2.** XRD pattern of Ze-A and Ze-Fe-A

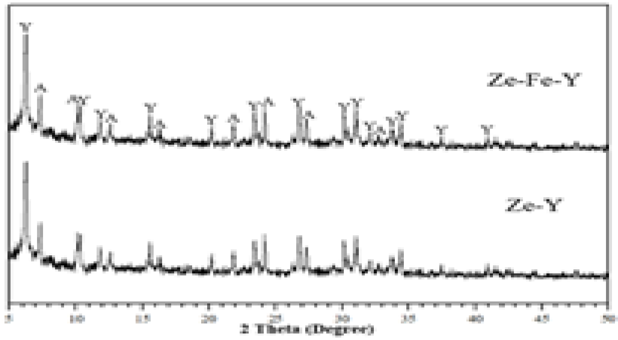

**Figure 3.** XRD pattern of Ze-Y and Ze-Fe-Y

### 3.2.2 Surface area and pore volume

As shown in Table 1, surface areas of Ze-A and Ze-Y are 27.02 and 211.42 m2/g, respectively. In addition, pore volume of Ze-A and Ze-Y are 0.0658 and 0.1784 cm3/g, respectively. For modified zeolites with Fe, the results show that both Ze-Fe-A and Ze-Fe-Y present lower surface areas, i.e., 10.90 and 28.22 m2/g, respectively. It is noticed that Ze-Fe-Y's surface area approximately decreases 10 times, whereas the surface area of Ze-Fe-A decreases 2 times from their parents. This may result from the fact that Fe was trapped inside the zeolites. However, pore volume of both Ze-Fe-A and Ze-Fe-Y slightly decrease, i.e, 0.0461 and 0.1046 cm3/g, respectively.

**Table 1.** Results of BET specific area and pore volume

| Synthesized zeolites | BET specific area, ($m^2/g$) | Pore volume, ($cm^3/g$) |
|---|---|---|
| Ze-A | 27.02 | 0.0658 |
| Ze-Fe-A | 10.90 | 0.0461 |
| Ze-Y | 211.42 | 0.1784 |
| Ze-Fe-Y | 28.22 | 0.1046 |

### 3.2.3 Scanning Electron Microscopic and Energy Dispersive X-ray analysis

Morphology of synthesized zeolites examined under an electron microscope is illustrated in Figure 4. Ze-A presents a cube shape which corresponds to the molecular structure of the zeolite A [8], whereas Ze-Fe-A is nearly a cube shape and sphere shape, which might be due to iron oxide inside its crystalline (Figure 4 (a) and (b)). Ze-Y presents a morphology as a polygon geometry which corresponds to zeolite Y which was synthesized from husk ash according to the previous study of Wittayakun et al. (2008) [9], even though some researchers found crystalline of Ze-Y was octahedral morphology [10][11] and mostly cubic [12]. The modified zeolite Y with iron, Ze-Fe-Y, presents its morphology in a rounder shape than the parent zeolite due to the fact that the iron oxide was trapped inside its structure (Figure 4 (c) and (d)).

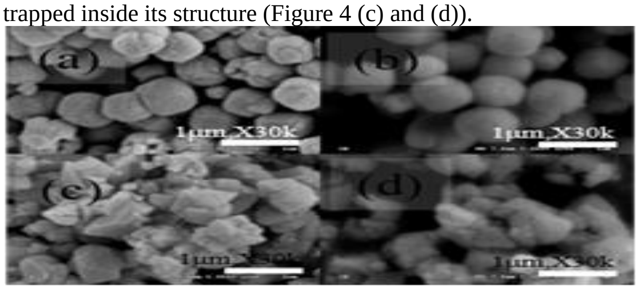

**Figure 4.** Morphology of synthesized zeolites (a) Ze-A, (b) Ze-Fe-A, (c) Ze-Y and (d) Ze-Fe-Y

EDX analysis is shown in Table 2. The results approve that Fe was trapped inside the modified zeolites: both Ze-Fe-A and Ze-Fe-Y at 0.61% and 0.50%, respectively. This confirms the success of synthesized Ze-A and Ze-Y and also confirms the modification of zeolite by trapping Fe inside their structures.

**Table 2.** Energy Dispersive X-ray (EDX) analysis

| Elements | Ze-A | Ze-Fe-A | Ze-Y | Ze-Fe-Y |
|---|---|---|---|---|
| Si (%) | 15.27 | 15.10 | 16.31 | 16.26 |
| Al (%) | 15.65 | 15.18 | 14.10 | 13.87 |
| Na (%) | 13.38 | 14.32 | 13.94 | 14.56 |
| O (%) | 55.70 | 54.80 | 55.66 | 54.81 |
| Fe (%) | - | 0.61 | - | 0.50 |

### 3.2.4 Transmission Electron Microscope

The morphology of synthesized zeolites was characterized for more images using Transmission Electron Microscope (TEM), as shown in Figure 5. Ze-A shows agglomeration of particles with cubic shape and more spherical morphology when Ze-A was modified with Fe (Figure 5. (a) and (b)). The images also show closely packed particles with small pores inside. For Ze-Y, as shown in Figure 5 (c), its image shows an irregular shape according to its SEM images. The modified Ze-Fe-Y shows more compacted particle due to its Fe-trapped structure (Figure 5. (d)). These results agree with XRD, BET, and SEM analysis as mentioned above.

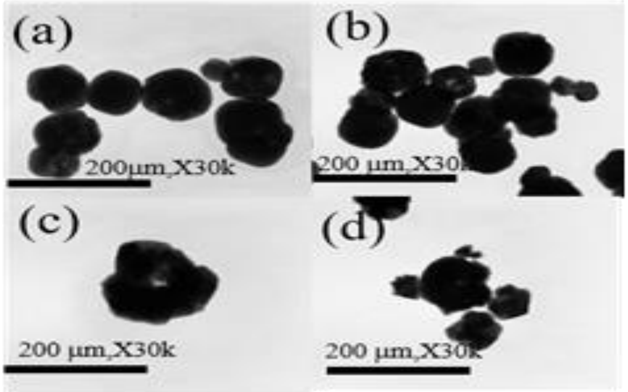

**Figure 5.** TEM image of (a) Ze-A, (b) Ze-Fe-A, (c) Ze-Y, and (d) Ze-Fe-Y

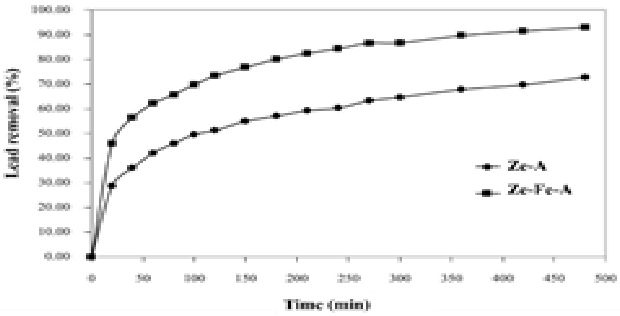

**Figure 6.** Efficiency of lead removal of Ze-A and Ze-Fe-A

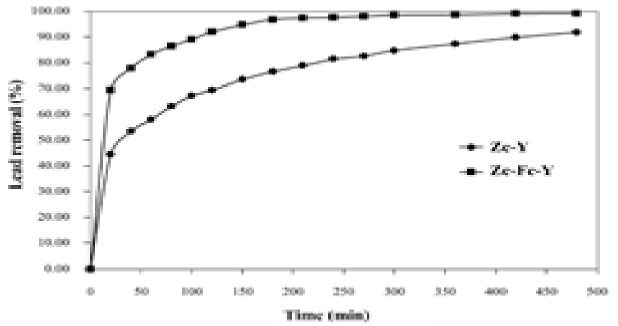

**Figure 7.** Efficiency of lead removal of Ze-Y and Ze-Fe-Y

## 3.3 Adsorption of synthesized zeolites

The 0.1 g each of synthetic zeolites i.e., Ze-A, Ze-Fe-A, Ze-Y, and Ze-Fe-Y, was tested with lead solution of 40 mg/L at pH 5 for 480 minutes. In Ze-A and Ze-Fe-A adsorption, the equilibrium time was 360 minutes after which the lead adsorption uptake was slight. At the end of the experiment, lead removal efficiencies are 72.85 and 93.02% for Ze-A and Ze-Fe-A, respectively (Figure 6.). The modified zeolite, Ze-Fe-A, shows higher efficiency than its parent. The adsorption of Ze-Y and Ze-Fe-Y shows the shorter equilibrium time of 180 minutes and lead removal efficiencies were 91.86 and 99.20% for Ze-Y and Ze-Fe-Y, respectively, as shown in Figure 7. It can be seen that modified zeolites with Fe improved lead adsorption on Ze-Fe-A and Ze-Fe-Y. Although the modified zeolites gave lower surface area, the efficiency removal of lead was higher than zeolite without Fe. It may be concluded that the adsorption mechanism of modified zeolite does not only rely on physical adsorption, but also on chemical adsorption.

## 4. Conclusion

Ze-A and Ze-Y were successfully prepared from silica gel waste which was used as silica source. Moreover, from modification of the synthesized zeolites with Fe; Ze-Fe-A and Ze-Fe-Y, were obtained for improvement of their adsorption efficiency. The parents Ze-A and Ze-Y presented surface areas of 27.02 and 211.42 m2/g, respectively, whereas the modified zeolites with Fe, Ze-Fe-A and Ze-Fe-Y, presented lower surface areas of 10.90 and 28.22 m2/g, respectively. SEM and TEM images illustrated the cubic and polygon shapes for Ze-A and Ze-Y, respectively, while the modification with Fe presented rounder shape for both Ze-Fe-A and Ze-Fe-Y because Fe was trapped inside their structure. However, the adsorption efficiencies of both modified zeolites increased even though the surface areas decreased. This might be due to adsorption mechanism which is not only physical adsorption, but also chemical adsorption. Further studies should be focused on the adsorption mechanism of modified zeolites, both Ze-Fe-A and Ze-Fe-Y, and their optimum adsorption condition as well.

ACKNOWLEDGEMENT
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