

## PREPARATION OF ZEOLITE FROM COAL FLY ASH AND ITS ADSORPTION-DESORPTION BEHAVIOR ON AMMONIUM ION IN AQUEOUS SOLUTION

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### Abstract

Owing to the high content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , fly ash utilization as starting material for zeolite is becoming a great interest. In this research, fly ash was converted into zeolite using reflux method at  $138\text{ }^\circ\text{C}$  for 1 hour in NaOH 2M followed by heat treatment at  $90\text{ }^\circ\text{C}$  for 24 hours. The characterization of the resulting zeolite was carried out using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and BET surface area measurement. The study of its adsorption-desorption behaviors were also investigated using ammonium solution. Infrared spectra showed typical zeolite peaks for Si-O-Si or Al-O-Al stretching at  $985\text{ cm}^{-1}$ , Al-O-Si stretching at  $663\text{ cm}^{-1}$ , and Al-O or Si-O bending at  $455\text{ cm}^{-1}$ . XRD analysis confirmed the formation of sodium aluminium silicate hydrate, which is a sodalite zeolite. The surface areas of coal fly ash and zeolite were  $6.9\text{ m}^2/\text{g}$  to  $34.1\text{ m}^2/\text{g}$ , respectively. The ZFA was able to adsorb  $2.9\text{ mg/g}$  ammonium ions upon 135 minutes of adsorption time. During the desorption experiment, a slow release of only  $0.3\text{ mg}$  of  $\text{NH}_4^+$  was observed out of  $250\text{ mg}$  of  $\text{NH}_4^+$  adsorbed upon 24 hours of desorption time.

Keywords: Adsorption, Ammonium ion, Desorption, Fly ash, Zeolite.

## 1. Introduction

Nitrogen is the primary element of plant and animal proteins and is essential for all life forms [1]. In the water environment, nitrogen is generally present in the form of ammonium ions ( $\text{NH}_4^+$ ) [2]. Although ammonium is an important nutrient for plants, excess ammonium in the environment can cause serious pollution in the environment [3]. The high content of ammonium in water body strongly contributes to eutrophication, resulting in overgrowth phytoplankton and aquatic plants with consequent increase dissolved oxygen depletion and fish toxicity [4]. In addition, it also threatens the availability of safe drinking water and, thus, human health [5]. Therefore, the development of efficient technology for ammonium removal has become great attention in environmental issue [6]. Electricity-generating plants in a coal power plant or coal-based industries produce coal ash as combustion product such as fly ash and bottom ash. Globally, approximately 750 million tonnes of fly ash were produced, from which, only on average only of 25% is utilized and the rest is usually disposed of as waste [7]. Aldahri et al. [8] mentioned that efficient disposal of fly ash is a worldwide issue because of its massive production and its harmful effect on the environment.

Based on studies by Atun et al. [9], there is an active field of research directed towards developing alternate uses for fly ash, such as adsorbent for some water pollutants and as starting precursors for zeolitic materials. Fly ash consists of main oxides such as silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and calcium oxide ( $\text{CaO}$ ) [10]. Physically, fly ash is fine particles with an average size of  $<20 \mu\text{m}$  and has a moderate density ( $0.54 \sim 0.86 \text{ g/cm}^3$ ), with a high surface area ( $300 \sim 500 \text{ m}^2/\text{kg}$ ) and light texture (Fig. 1) [11]. All of these characteristics of fly ash make it a potential material for adsorbents [12].

Zeolite is a material composed of porous crystalline aluminosilicates (Fig. 2) that have a three-dimensional lattice building by primary units in the form of tetrahedral  $[\text{AlO}_4]$  and  $[\text{SiO}_4]$  [7]. The crystal structure contains numerous channels and chambers of different sizes giving them a range of unique ion-exchange, sorption, molecular-sieve, and catalytic properties [13].



Fig. 1. Fly ash (a) and (b) Zeolite from fly ash.

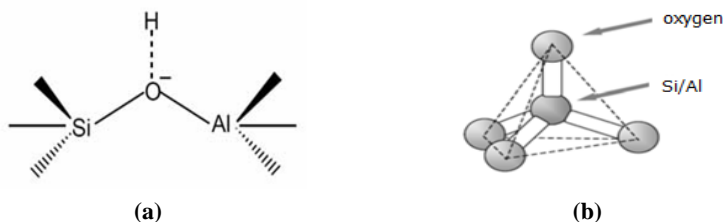


Fig. 2. (a) Zeolite structure and (b) Primary building block unit.

Zeolite prepared from fly ash commonly has considerable cation exchange capacity and has a huge potential to be applied as an adsorbent for the removal of ammonium from wastewater [14]. Ugurlu and Karaoglu [15] reported the utilization of fly ash as adsorbent and was reported to be able to remove ammonium from paper mill industry wastewater. Another researcher used zeolite from fly ash to remove ammonium and it was indicated that the zeolite exhibited a fast adsorption rate and high adsorption capacity for ammonium [16].

The most common method for zeolite synthesis involves a hydrothermal treatment using sodium hydroxide [17]. The hydrothermal method requires high temperature and high pressure utilizing expensive autoclave for zeolite synthesis, hence the energy consumption of this method is considered high and make it inefficient economically [18].

Therefore, in this study, the conversion of coal fly ash (CFA) into zeolite fly ash (ZFA) was carried out via direct low-temperature heating at 90 °C for 24 hours using NaOH alkali solution [19]. The synthesized zeolite was then applied as a sorbent for ammonium ions in aqueous solution. The desorption study of ammonium ions as also performed to investigate the possible regeneration of the used sorbent.

## 2. Materials and Method

### 2.1. Materials

CFA was collected from a local paper industry that utilized coal combustion processes. NaOH p.a. (95%), aquades, ethanol 95%, NH<sub>4</sub>Cl, phenol (C<sub>6</sub>H<sub>5</sub>OH), sodium nitroprusside (C<sub>5</sub>FeN<sub>6</sub>Na<sub>2</sub>O) 0.5%, alkaline citrate solution (C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>), and sodium hypochlorite (NaClO<sub>4</sub>) 5% were purchased from Merck.

### 2.2. Method

#### 2.2.1. Conversion of fly ash into zeolite

CFA sample was washed and dried at 30 °C overnight. The CFA was mixed with NaOH 2M and refluxed at 138 °C for 1 hour. The mixture was heated in an oven at 90°C for 24 hours. The ZFA was washed using ethanol and aquades until the pH was neutral and dried at 30 °C for 12 hours. The CFA and ZFA samples were then analysed using X-Rays Fluorescence Spectroscopy (XRF) Thermo Scientific ARL 9900FTIR-8400 Shimadzu, FTIR-8400 Shimadzu, XRD Rigaku Miniflex 600, SEM Jeol JSM-6360LA, and BET NOVA instrument.

#### 2.2.2. Adsorption study

The 1000 ppm stock solution of NH<sub>4</sub>Cl was made by diluting 3.819 g NH<sub>4</sub>Cl in 1000 mL of water in a volumetric flask. Then, the 0.2 g of ZFA were mixed with 50 mL of ammonium solution with different concentrations (50, 75, 100, 125, 150, and 175 ppm) in beaker glass.

The mixture was shaken at 200 rpm for 135 minutes. The ZFA was separated from the solution by centrifugation. The concentration of ammonium ions in the solution was measured using a Shimadzu UV-1700 Spectrophotometer with the phenate method (SNI 06-6989.30-2005).

### 2.2.3. Desorption study

The desorption of ammonium ion was carried out by column method (Fig. 3). The ZFA was placed in a column and the leaching process was began by draining aquades with a flow rate of 5 mL/min. The residual concentration of ammonium ions in the collected solution was measured using a Shimadzu UV-1700 Spectrophotometer.

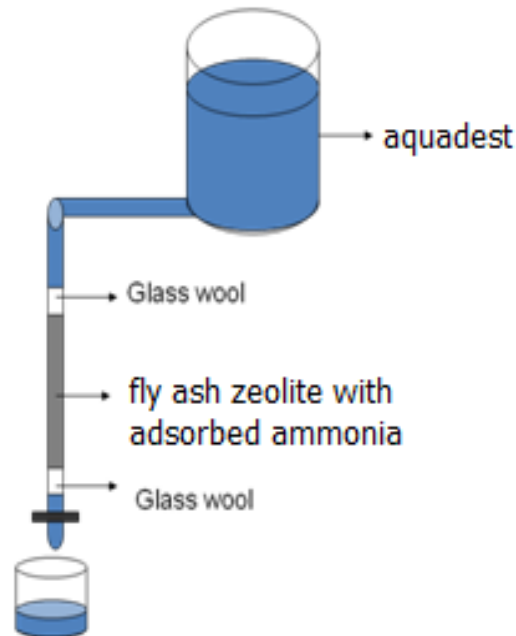


Fig. 3. Set up for desorption experiment.

## 3. Results and Discussion

### 3.1. Characteristic of CFA and ZFA

The XRF analysis of CFA and ZFA (Table 1) was conducted to determine the elemental composition of CFA and ZFA. The oxide composition of CFA and ZFA obtained from XRF analysis indicated that the major components of the CFA and ZFA were  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaO}$ .

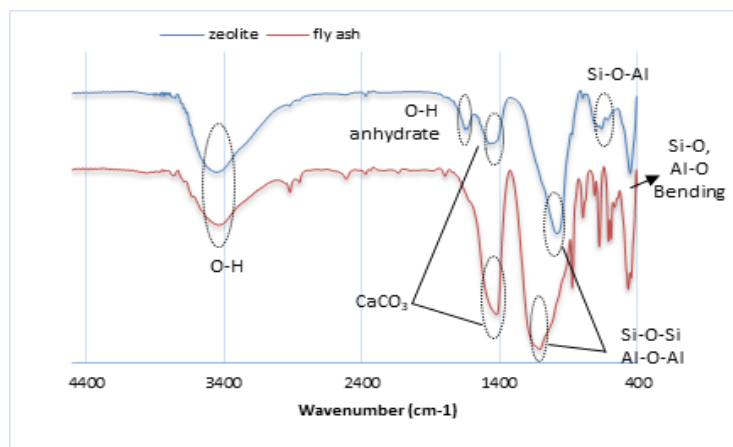
The functional groups on CFA and ZFA were characterized by FTIR (Fig. 4). The FTIR spectra showed the characteristic peaks for CFA and ZFA. The formation of a  $\text{SiO}_4$  or  $\text{AlO}_4$  tetrahedral skeleton in the zeolite framework [20] was signified by a shift at  $1112\text{ cm}^{-1}$  to  $985\text{ cm}^{-1}$ . The absorption peak at  $455\text{ cm}^{-1}$  was assigned from Al-O or Si-O bending vibrations.

Whereas, the stretching of Al-O-Si was indicated at  $663\text{ cm}^{-1}$ . The absorption peak at  $1659\text{ cm}^{-1}$  and  $3474\text{ cm}^{-1}$  in ZFA was due to the vibrations of O-H bending derived from water molecules (anhydrous in zeolites) and O-H stretching, respectively [21]. The decreasing intensity at  $1400\text{ cm}^{-1}$  indicated the reduction of  $\text{CaCO}_3$  content in ZFA upon conversion.

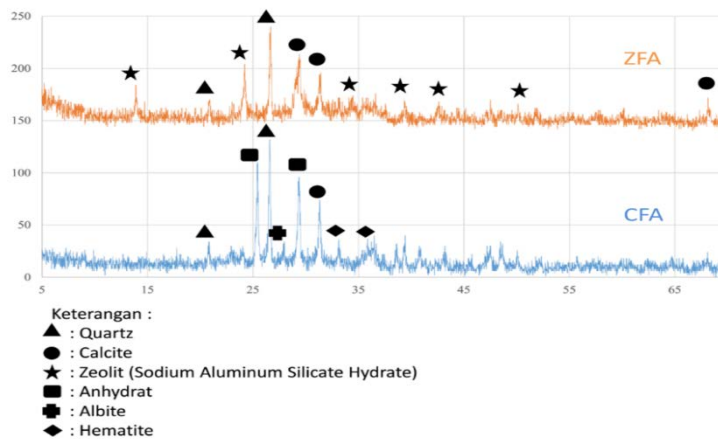
The XRD analysis of CFA and ZFA is provided in Fig. 5. Several new sharp peaks were detected at  $2\theta$  values of  $14^\circ$ ,  $24^\circ$ ,  $34^\circ$ ,  $42^\circ$ , and  $51^\circ$ . These new peaks were identified as sodium aluminium silicate hydrate that belongs to sodalite zeolite group according to the JCPDS no. 31-1271, with the formula of  $1.08\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1.68\text{SiO}_2 \cdot 1.8\text{H}_2\text{O}$ . This type of zeolite is different from the zeolite synthesized using a similar method [18].

**Table 1. The composition of CFA and ZFA.**

Oxide	Amount (%)		Oxide	Amount (%)	
	CFA	ZFA		CFA	ZFA
SiO <sub>2</sub>	33.18	29.98	ZnO	2.32	1.90
Al <sub>2</sub> O <sub>3</sub>	19.62	17.18	K <sub>2</sub> O	0.57	0.35
Fe <sub>2</sub> O <sub>3</sub>	7.01	6.17	SO <sub>3</sub>	4.76	0.14
MnO	0.095	0.086	Na <sub>2</sub> O	0.31	4.95
TiO <sub>2</sub>	1.32	1.19	P <sub>2</sub> O <sub>5</sub>	0.18	0.14
CaO	24.69	23.21	LOI	8.58	13.12
MgO	1.18	1.41	-	-	-



**Fig. 4. FTIR spectra of CFA and ZFA.**



**Fig. 5. XRD analysis of CFA and ZFA.**

The morphology of CFA and ZFA were analyzed using SEM instrument (Fig. 6). The SEM photos showed the changes in surface properties of coal fly ash upon conversion into zeolite. Figures 6(a) and (b) showed that CFA was mostly spherical with size between 10  $\mu\text{m}$ -50  $\mu\text{m}$ , while the ZFA was smaller with radius pore about 1.129  $\mu\text{m}$  (Figs. 6(c) and (d)).

The BET analysis result showed the surface area, pore radius, and pore volume of CFA and ZFA. The BET analysis provided in Table 2. Based on the BET analysis, the surface area and pore volume of zeolite were significantly higher than those of coal fly ash. The surface area was increased from 6.9  $\text{m}^2/\text{g}$  to 34.1  $\text{m}^2/\text{g}$  and the pore volume was markedly increased from 0.002  $\text{cm}^3/\text{g}$  to 0.289  $\text{cm}^3/\text{g}$ . On the contrary, the pore radius of ZFA was smaller than that of the coal fly ash indicating smaller pore sizes.

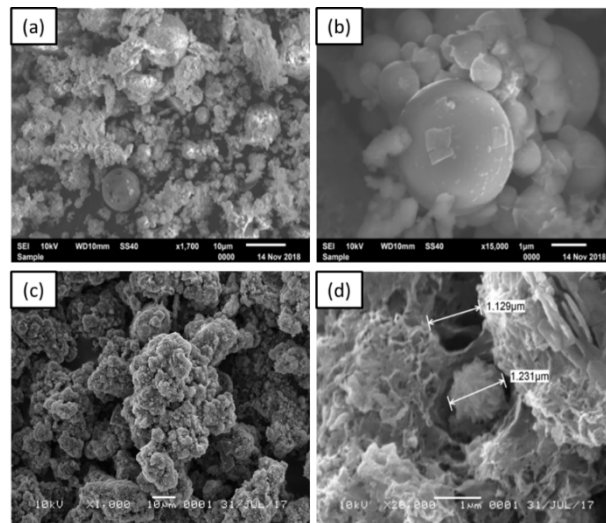


Fig. 6. (a) and (b) SEM analysis of CFA, (c) and (d) ZFA.

Table 2. BET analysis of CFA and ZFA.

Sample	Surface area ( $\text{m}^2/\text{g}$ )	Pore radius (nm)	Pore volume ( $\text{cm}^3/\text{g}$ )
Fly ash	6.9	2.09	0.002
ZFA	34.1	1.53	0.289

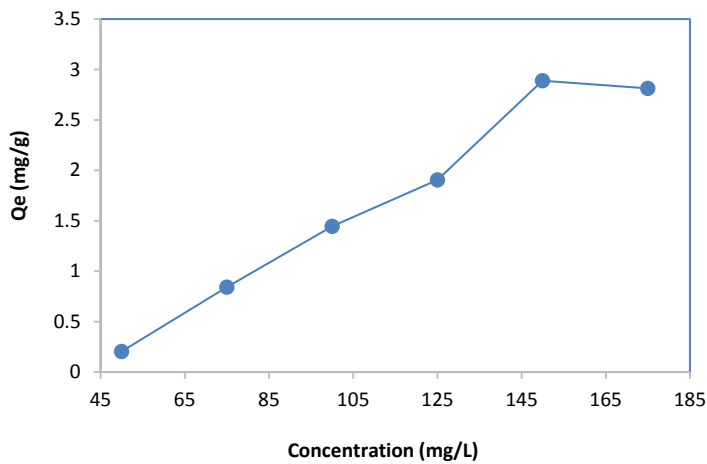
## 2.1. Adsorption and desorption study

The adsorption capacities of ZFA was investigated using a batch method (Fig. 7). The sorption experiment was conducted at different concentration of ammonium ions. It was found that the equilibrium concentration was achieved at 150  $\text{mg}/\text{L}$  and the adsorption capacity was calculated at about 2.9  $\text{mg}/\text{g}$ .

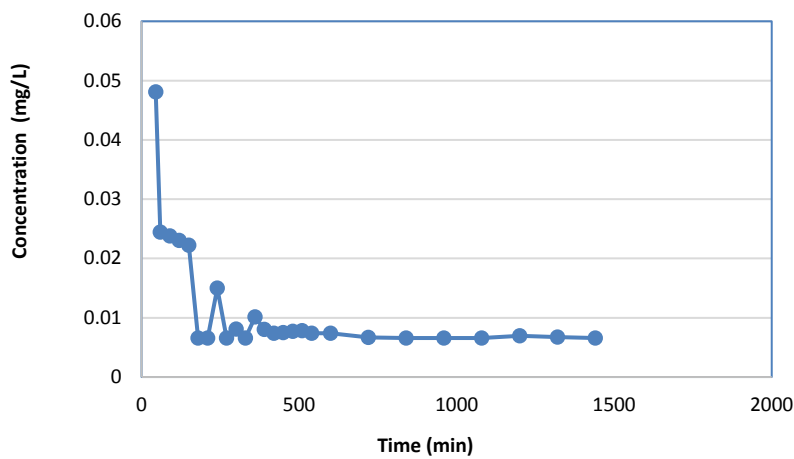
It is estimated that the active sites in the ZFA are filled first by the ammonium ion until the equilibrium was established (Fig 7). The sorption data were then plotted using Langmuir and Freundlich isotherm models [22, 23]. Based on the correlation factors, the adsorption data fitted the Freundlich isotherm model: Sample (ZFA), Freundlich  $1/n$  (3.3808),  $K_F$  ( $3.92 \times 10^{-7}$ ) and  $R^2$  (0.9908). Freundlich

isotherm assumes that the adsorption mechanism is heterogeneous with multilayer interaction. The amount of adsorbed particles increases with an increase in concentration [24].

Additionally, the desorption experiment of ammonium ion from ZFA was studied using column method (Fig. 8). The desorption process occurred slowly and only a small amount of ammonium ions leached. The ammonium leached was only about 0.3 mg from a total of 250 mg absorbed during 24 hours of the experiment. Based on these findings, it can be concluded that the ZFA has considerably high adsorption capacity for ammonium ion. However, the further application as ammonium carrier and slowly release the adsorbed ammonium still needs to be enhanced.



**Fig. 7. Adsorption capacities of ZFA on ammonium ion.**



**Fig. 8. Desorption process of ZFA on ammonium ion.**

#### 4. Conclusion

A zeolite coal fly ash-based has been synthesized using NaOH solution at 90°C for 24h. The synthetic zeolite has a formula of  $1.08\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1.68\text{SiO}_2 \cdot 1.8\text{H}_2\text{O}$  confirmed by XRD analysis. The BET analysis indicated the marked increase of fly ash surface area from 6.9 m<sup>2</sup>/g to 34.1 m<sup>2</sup>/g upon conversion to zeolite. When applied as an adsorbent for ammonium in aqueous solution, it was found that the adsorption capacity was about 2.9 mg/g. However, the desorption process of adsorbed ammonium occurred slowly, only about 0.3 mg out of the total of 250 mg absorbed during 24 hours of the experiment.

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