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Correspondence Address:
Research Journal of Chemistry and Environment
Sector AG/80, Scheme No. 54, **Indore** 452 010 (M.P.) **INDIA**
Phone and Fax: +91-731-4004000

Website: https://www.worldresearchersassociations.com E-mail: info@worldresearchersassociations.com

CONTENTS

Effect of Cetyltrimethylammonium Bromide (CTAB) Template on Synthesis of Zeolitic Material from Fly Ash and Application of Zeolitic Material obtained as an Adsorbent of Heavy Metals Cd and Cu

Upita Septiani*, Admi, Dedi Afriza and Yefrida
Department of Chemistry, Faculty of Mathematics and Natural Science, Andalas University, Padang, West Sumatera, INDONESIA
*upitas@yahoo.com

Abstract
Zeolitic materials were prepared from coal fly ash by hydrothermal synthesis method with and without Cetyltrimethylammonium Bromide (CTAB) template at pH 14, temperature 60°C and seawater as a solvent. The zeolitic material obtained was characterized by X-ray diffraction (XRD), Fourier transformed infrared (FT-IR) spectroscopy, Scanning electron microscopy (SEM) and has characteristics of zeolite hydroxysodalite. N_2 adsorption desorption results show that zeolitic materials prepared with and without CTAB template have a specific surface area 5.130 m^2g^{-1} and 4.889 m^2g^{-1}, average pore size 30.21 nm and 25.84 nm and total pore volume 0.078 cc g^{-1} and 0.064 cc g^{-1} respectively.

The zeolitic materials obtained were utilized as an adsorbent to heavy metal Cd and Cu. The maximum adsorption capacities of the zeolite materials that were prepared with and without CTAB template against heavy metal were 333.3 mg g^{-1} and 303.0 mg $g^{-1}$for Cd metal and 322.6 mg g^{-1} and 285.7 mg g^{-1} for Cu metal respectively. These results indicated that synthetic zeolite materials have potential as adsorbent of heavy metals Cd and Cu. The results also suggested that the adsorption capacity was affected by specific surface area, average pore size and total pore volume.

Keywords: Fly ash, zeolite, adsorption, heavy metal.

Introduction

Coal consumption in electric power plants is increasing significantly year by year in Indonesia. As a consequence, a lot of coal fly ash is generated in the electric power plants and its amount increases annually. As far as the diposal of fly ash is concerned, most of fly ash is disposed in landfill. Coal fly ash has the high content of amorphous aluminosilicates glass, it is as suitable source material in synthesis of zeolitic material as many researchers have widely reported.[1]

Zeolite is a porous crystalline aluminosilicates of SiO_4^{4-} and AlO_4^{5-} with a three dimensional open structure making them very useful for solving the mobility of toxic element in a number of environmental applications. Zeolite is widely used as ion exchanger, absorbent and catalyst due to their structural characteristic and valuable properties. Conversion of coal fly ash into zeolitic material becomes one important issue of waste management in the recent years.[3,8]

Toxic heavy metals are considered one of the most important pollutants that have direct effect on man and animals. The heavy metals are commnly released in the wastewater from various industries. Due to stringent regulations for heavy metals, the removal has become a serious environmetal problem. The common methods available to remove heavy metal from wastewater are coagulation, ion exchange, reverse osmosis, chemical precipitation and adsorption. Among these methods, the adsorption technique employing adsorbents is well established fo treating industrial wastewater cotaining heavy metal. Commercial adsorbent are those adsorbents which are produced commercially on a large scale such as activated carbon, silica gell, alumina, synthetic zeolite etc., however they are costly. Thus, there is a need to develop cheap and readily regenerative adsorbent for substituting the commercial adsorbents to perform metals purification function.[6]

In this study, we synthesized zeolitic material via hydrothermal synthesis method. The zeolitic materials were prepared from coal fly ash both with and without Cetyltrimethylammonium Bromide (CTAB) template at pH 14, temperature 60°C and seawater as a solvent. The effects of CTAB template on specific surface area, average pore size and total pore volume of the zeolitic materials obtained were investigated. The zeolitic materials were utilized as an adsorbent to heavy metal. Cadmium and cuprum metals were chosen as target heavy metal for the adsorption studies. Furthermore, the maximum adsorption capacities of zeolitic materials that were prepared with and without CTAB template against heavy metal Cd and Cu were studied.

Material and Methods

Materials: Coal fly ash was obtained from PLTU Ombilin electric power plant, Ombilin, Tanah Datar, West Sumatera, Indonesia. Seawater was obtained from Padang Bay in Padang West Sumatera. The sodium hydroxide (Merck), cetyltrimethylammonium bromide (CTAB), cadmium sulfat hydrat (Merck) and cuprum sulfat hydrat (Merck) were of analytical grade and used as received without further purification. Distilled water was used for washing of synthesized zeolite.

Zeolite preparation: 10 g of fly ash and 12 g of NaOH were ground in a mechanical mortal for a few minutes and then the powder, which was well mixed, was fused at 550°C for 1 h. The resultant fused mixture was cooled and milled in mortal again.[5] The powder thus obtained was mixed with 43 ml seawater which has been added by 3.14 g of CTAB template and kept in a strring condition for one night at room temperature before hydrothermal process. The solution was put into teflon-lined stainless steel autoclave and hydrothermally treated at temperature 60°C for 4 days. After heating, the solid products were filtered off, washed with distilled water and then dried at 80°C for 24 h in electric oven.

Characterizations of products obtained: The products were identified by X-ray diffraction (XRD)((Philips PW4030/60), Morphologies of the products were observed by Scanning electron microscopy (SEM) (JOEL JSM-6390LA), The specific surface area, average pore size and total pore volume of zeolitic particles were analyzed by the nitrogen adsorption-desorption technique. N_2 adsorption-desorption experiments were carried out on a Quantachrome NovaWin 4200e.

Adsorption experiments: Two heavy metal ion solutions (Cu^{2+} dan Cd^{2+}, 1000 mg/L for each) were prepared using $CuSO_4.5H_2O$ and $3CdSO_4.8H_2O$ of analytical reagent grade in distilled water respectively. The adsorption experiments of metal ions Cu^{2+} dan Cd^{2+} were carried out from 20 mL of the solution containing different concentration (50, 100, 150, 200 and 250 mg/L) with 0.015 g adsorbent in a stoppered conical flask. All adsorption process were carried out on a shaker at 150 rpm with various time 30, 60, 90, 120 dan 150 menutes. After adsorption, the solution was filtered. The metal ions Cu^{2+} dan Cd^{2+} concentration in solution were measure by an atomic adsotption spectromater (AAS) (Varian AA240).

After the preliminary experiment, the equilibrium time of all adsorption experment was set as 60 minutes. The adsorption capacity (Q) of the synthesized zeolitic materials that were prepared with and without CTAB template against heavy metal ions was calculated by equation :

$$Q = \frac{[C0]-[Ce]}{w} \text{ x V}$$

where C_0 and C_e are the initial and equlibrium heavy metal ion concentration of the solution respectively. V (L) is the test solution volume and W (g) is the amounts of adsorbent.

Results and Discussion

XRD result of products: XRD results of synthesized products from fly ash prepared by hydrothermal method both with and without CTAB template are shown in figure 1. The results suggested that synthesized product consisted of one major typy of compound : phase-pure zeolite hydroxysodalite (SOD). According to the powder patternt analysis of International Centre for Diffraction Data (ICSD) 72060, the intense peak of hydrothermal product both with and without CTAB template appeared at 2θ ; 14.04°, 24.44°, 32.16°, 34.90°, 37.84°, 43.06° and 14.05°, 24.70°, 32.17°, 37.84°, 43.03°, respectively. These intense peak may imply the presence of hydroxysodalite (14.11°, 24.71°, 31.82°, 35.02°, 38.05° and 43.03°) which belong to zeolite materials. Moreover, the zeolite crystal of synthetic product prepared by hydrothermal process with CTAB template was more crystalline than that by hydrothermal process without template.

Morphology of the synthesized zeolite materials: Scanning electron microscopy (SEM) images of synthesized zeolite from fly ash prepared by hydrothermal method both with and without CTAB template are shown in figure 2. SEM observations reveal the typical spherical crystal of zeolite hidroxysodalite and provide evidence of the crystalline growth of zeolite products prepared by hydrothermal process both with and without CTAB template. Moreover, the zeolite particle prepared by hydrothermal process with CTAB template have the smaller particle size, uniform particle, higher porosity and lower agglomeration of particle compared with the zeolite material particle prepared without CTAB template.

The zeolitic material particles prepared by hydrothermal method with and without CTAB template were analyzed by N_2 adsorption desorption technique, the textual data are presented in table 1.

From the table 1 we can see that the zeolitic material particles prepared with and without CTAB template have BET specific surface area 5.130 m^2g^{-1} and 4.889 m^2g^{-1}, average pore size 30.21 nm and 25.84 nm and total pore volume 0.078 cc g^{-1} and 0.064 cc g^{-1} respectively. The results show that the specific surface area, average pore size and total pore volume of zeolite prepared with CTAB template are higher than without CTAB template.

Adsorption capacity of the synthesized zeolite materials: Table 2 presents the maximun adsorption capacity of synthesized zeolite from fly ash prepared by hydrothermal process both with and without CTAB template.

Conclusion

We successeefully prepared the zeolite from fly ash by hydrothermal method with and wihout CTAB template at pH 14, temperature 60^0C and seawater as a solvent. The zeolite material obtained was characterized by XRD and SEM and has characteristic of zeolite hydroxysodalite (SOD). N_2 adsorption desorption results show that zeolites materials prepared by hydrothermal process with and without CTAB template have a specific surface area 5.130 m^2g^{-1} and 4.889 m^2g^{-1}, average pore size 30.21 nm and 25.84 nm and total pore volume 0.078 cc g^{-1} and 0.064 cc g^{-1} recpectively.

The application of zeolite materials is obtained as an adsorbent to heavy metal Cd and Cu. The maximum adsorption capacities of zeolites materials prepared with and without CTAB template against heavy metal ions were 333.3 mg g^{-1} and 303.0 mg $g^{-1}$for Cd^{2+} ion and 322.6 mg g^{-1} and 285.7 mg g^{-1} for Cu^{2+} ion respectively. These results indicated that synthetic zeolite material has potential as adsorbent of heavy metals Cd^{2+} and Cu^{2+}. The results also suggested that the adsorption capacity was affected by specific surface area, average pore size and total pore volume.

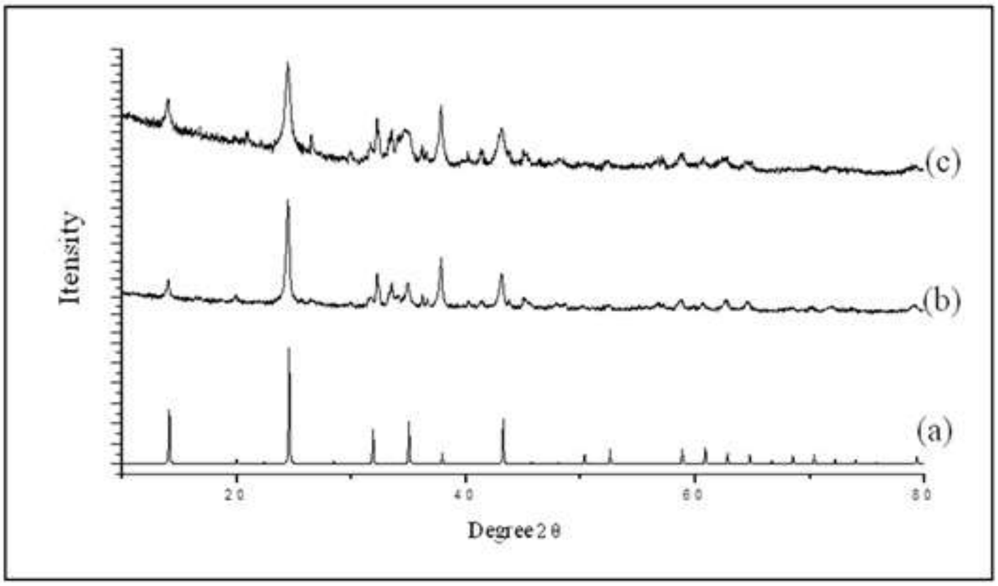

Fig. 1: The XRD patterns of synthesized products. (a) standard of zeolite hydroxysolalite (SOD) (International Centre for Diffraction Data (ICSD) 72060), (b) synthesized zeolite with CTAB template and (c) synthesized zeolite without CTAB template.

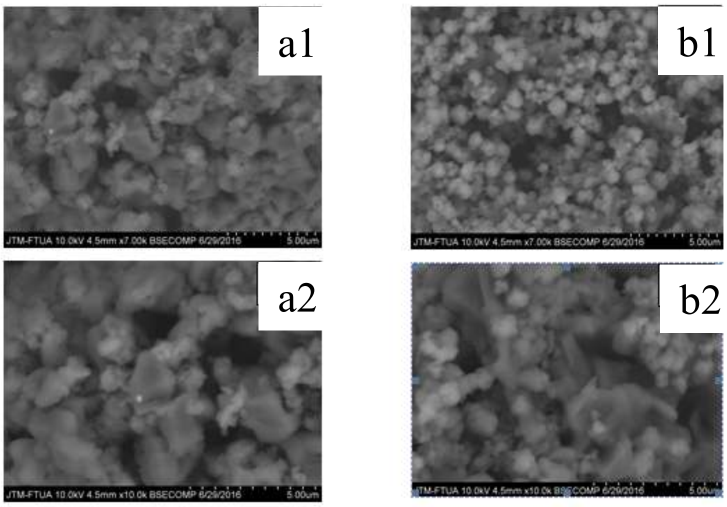

Fig. 2: SEM image of synthesized zeolite from fly ash prepared by hydrothermal process both without CTAB template (a1) magnification 7000x (a2) magnification 10000x and with CTAB template (b1) magnification 7000x (b2) magnification 10000x.

Table 1
N_2 adsorpsi-desorpsi results of zeolitic material particle prepared by hydrothermal prosess with and without CTAB template.

Zeolite material particle	specific surface area (S_{BET}) (m^2/g)	average pore size (nm)	total pore volume (V_{total}) (m^2/g)
Prepared with CTAB template	5.130	30.21	0.0775
Prepared without CTAB template	4.889	25.84	0.6371

Table 2
Langmuir parameters and Freundlich model for Cu (II) and Cd (II) adsorption on zeolite material prepared by hydrothermal process with and without CTAB template.

Zeolite material obtained	Ions	Langmuir			Freundlich		
		Q_{max} (mg/g)	K_L	R^2	K (mg/g)	n	R^2
Prepared with CTAB template	Cu^{2+}	322.6	6.199	0.999	214.6	4.413	0.568
	Cd^{2+}	333.3	50.251	0.715	280.5	19.801	0.871
Prepared without CTAB template	Cu^{2+}	285.7	3.003	0.998	183.2	6.579	0.881
	Cd^{2+}	303.0	110.010	1	277.3	35.714	0.998

Acknowledgement
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