

Synthesis and Characterization of Zeolite Materials from Power Plant Fly Ash

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The natural zeolite has been successfully synthesized from Sungai Ringin power plant fly ash. The material was then used to reduce total organic carbon (TOC) of crude palm oil (CPO) industrial waste. Results show that the synthesis process using a 2.5 M of NaOH as mineralizer produces zeolite type of analcime and cancrinite (namely Zeo 2.5); a 5.0 M generates type of cancrinite (namely Zeo 5.0) and a concentration of 7.5 M produces type of cancrinite and losod (namely Zeo 7.5) with surface area, pore volume and pore size as much as 41.405 m²/g, 0.146 cc/g and 19.198 Å; 43.499 m²/g, 0.222 cc/g and 21.554 Å; and 42.605 m²/g, 0.152 cc/g and 19.271 Å, respectively. In application, Zeo 2.5, Zeo 5.0 and Zeo 7.5 can reduce total organic carbon by 60, 72.26 and 62.60 %, respectively, of the initial concentration of 2,329 mg/L.

Keywords: Synthesis, Zeolite, Fly ash, Reduction, Total organic carbon, Crude palm oil.

INTRODUCTION

Sungai Ringin power plant located in Kedabang Village, Sintang District of Indonesia, uses coal as its main source of energy. Chemically, coal combustion products are volatile materials, such as CO₂, SO₂, NO₂ and H₂O and non-volatile materials in the form of coal ash known as bottom ash and fly ash. During the process of coal combustion, a portion of the mineral fuses into fly ash particles, which can form crystalline phases like quartz and mullites, though the glass phase covers the aluminosilicate surface. This potentially creates detrimental impact on the environment [1]. Therefore, the problem of coal fly ash should be solved by utilizing wasted materials in order to avoid their accumulation in large amounts.

Fly ash contains metal oxides with main components of SiO₂ and Al₂O₃ with several crystal forms, such as quartz (SiO₂), mullite (2SiO₂·3Al₂O₃), hematite (α-Fe₂O₃) and magnetite (Fe₃O₄) [1]. The fly ash containing more than 85 % of SiO₂ and Al₂O₃ can be used as a raw material of sodium silicate and synthetic aluminate [2]. A new approach widely developed for the utilization of fly ash is converting it into value-added products as zeolites [2-4]. The X-ray fluorescence (XRF) analysis shows that Sungai Ringin's fly ash contains minerals of SiO₂ (about 53.26 %) and Al₂O₃ (about 28.13 %). So, it is reasonable to utilize it for synthesizing zeolite materials.

The components of SiO₂ and Al₂O₃ are the active side of fly ash and bottom ash, which can be used as zeolite base for removing heavy metals, phenol wastes and dye waste in waters.

Several studies have investigated synthesis parameters include Vucinic *et al.* [5] who studied the effect of the ratio of SiO₂/Al₂O₃ to the characteristics of the product zeolite and Kumar *et al.* [6] studied the pore properties of the resulting zeolite material. Itanawita *et al.* [7] reported the synthesis of zeolite 4A type for successful remediation of electroplating liquid waste containing Cu and Cr metals, while Septiani *et al.* [8] synthesized zeolite X and sodalite minerals using alkaline sea water by the hydrothermal process. The later study reported that temperature influenced the crystallization of synthesized zeolite significantly. Ojha *et al.* [9] synthesized zeolite A with a hydrothermal process at 100 °C and crystallization was carried out at 75 to 85 °C for 2 to 3 weeks. The longer crystal growth time and the lower temperature produced the larger crystal size. The type of zeolite produced depends on the starting material used and the higher composition number of Si/Al will produce a mixture of zeolite A and zeolite X. According to Whang *et al.* [10] the process of zeolite A formation can be done at optimum temperature of 100 °C in relatively short time and low base concentration and low molar ratio of Si/Al is in the range of 1 to 1.4.

The synthesis of zeolite can be carried out by a hydrothermal process at the glass phase dissolution stage using an alkaline solution. Glass phase is important in the formation of zeolites because it has a very high solubility in an alkaline solution [11]. The synthesis of zeolite from fly ash has been done through several methods and produces different types of zeolites. Of the various methods, melting using alkali

compounds (generally NaOH) is an important step because at that stage almost all the fly ash particles are converted to sodium silicate and sodium aluminate as synthesized precursors. The hydrothermal reaction resulted from fusion of NaOH will produce higher quantity and crystallinity of zeolite than without fusion [12].

Zeolite is widely used to reduce various types of liquid waste pollutants, especially heavy metals. This relates to the nature of the pores possessed, the active functional groups and the interchangeable cation balancer. The utilizations of zeolite from fly ash are for removing of radioactive cesium ions [13], as lead adsorbents [14] and for fixation of heavy metals such as Cu, Cd, Cr and Pb in waters [11]. One of the relatively underdeveloped zeolite utilizations is the material of crude palm oil (CPO) industrial waste processing. Palm oil, palm oil waste or palm oil mill effluent (POME) is abundant organic compound; if disposed directly into the environment, it will potentially cause pollutions. The most common technique used in the wastewater treatment plant installation of the palm oil industry is utilization of treatment pond system, reactor system or the combination of pool and reactor system. Based on the background mentioned before, this study employs synthesis and characterization of zeolite using the base material of fly ash from Sungai Ringin power plant. The utilization of fly ash from Sungai Ringin power plant as a basic material in zeolite synthesis has never been done. The parameters studied were the effect of NaOH concentration on the type and characteristics of zeolite produced. The next zeolite is used to decrease the liquid waste content of the CPO industry. The characterization of synthesized zeolite was done by Fourier transform-infrared (FTIR) spectrophotometry, X-ray diffractometry (XRD) and scanning electron microscopy with X-ray energy distribution (SEM-EDX). The determination of surface area, volume and pore size is done using surface area analyzer (SAA).

EXPERIMENTAL

The materials used are p.a, *i.e.*, HCl (Merck), NaOH (Merck). The samples of coal fly ash are taken from solid waste reservoir pools of Sungai Ringin Power Plant, Kedabang Village, Sintang District, West Kalimantan, Indonesia.

The apparatus used in this research are a set of glassware, 200 mesh sieve, hydrothermal reactor, autoclave, desiccator, analytical balance, oven, pH meter and furnace. The instruments used are SEM-EDX JEOL JED 2300 Analysis Station, FTIR Spectroscopy Shimadzu Series 96772, XRD Philip Xpert MPD and PANalytical Epsilon 3.

General procedure: Fly ash is filtered in sizes of ≤ 200 mesh and then dried for 3 h at 120 °C. Characterization of mineral types and elemental composition is done by XRD and XRF methods.

Decomposition, dealumination and calcination of fly ash are conducted in reference to Sutarno *et al.* [15]. Fly ash (5 g) is refluxed with 100 mL of 5 M HCl solution at 90 °C for 5 h. Then, the result of reflux is washed with distilled water until the pH of neutral wash filtrate and dried in an oven at 120 °C for 4 h. The resulting solids were then mashed and calcined at 800 °C for 4 h. The result of calcination is grinded and sieved for the synthesis process of zeolite.

The synthesis of zeolite is referred to Jumaeri *et al.* [11]. Firstly, the NaOH solution (5 M) was mixed with calcinated fly ash with the ratio of NaOH solution:fly ash = 10:1 and distilled for 24 h. The mixture is poured into Teflon tube in a stainless-steel autoclave. The hydrothermal reactor is then heated at 160 °C for 72 h. The reaction product is filtered and washed with distilled water to pH 9 to 10 and then dried in an oven at 105 °C for 2 h. The obtained solids were characterized using SEM-EDX, FTIR spectrophotometry, XRD, XRF and SAA methods.

Collection and preparation of CPO liquid waste: Oil palm liquid waste was taken and prepared based on the method in Indonesian National Standard (SNI) No. 6989.59: 2008. The waste samples were taken using a stem scoop, which did not react with the samples and had been washed by using samples, then accommodated in a brown glass bottle with a capacity of 2.5 L and finally sealed tightly. Samples were taken from several points in the pool of wastewater palm oil at PT. Sintang Agro Mandiri, in Sintang regency of West Kalimantan Province. The container bottles had also been washed by samples previously. Firstly, samples were filtered for separation of the suspensions and clumps from the wastewater, then put in container bottles and preserved at a temperature of $\pm 2-4$ °C in a special sampling box to keep the sample in unchanged condition during the trip. Furthermore, total organic carbon (TOC) measurements were performed to determine the initial concentration.

Determination of zeolite effectivity in CPO waste processing: The resulted zeolite was interacted with the sample of palm oil waste by ratio of weight (g) of zeolite to volume (mL) of liquid palm waste as much as 1:10. The mixture was stirred for 4 h and then it was filtered for separation of the adsorbent from the test solution. The tested samples were then analyzed by its TOC value. The TOC analysis was done using the SNI 06-6989.28-2005 method [16].

RESULTS AND DISCUSSION

The Sungai Ringin fly ash has the characteristic of solids in the form of blackish-coloured powder. To know the chemical composition of the elements of the fly ash compositors and the types of minerals contained therein, XRF and XRD characterizations were performed. The results are presented in Table-1 and Fig. 1.

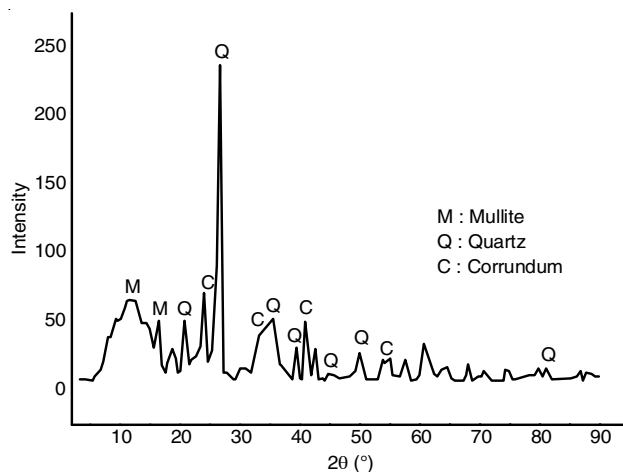


Fig. 1. Diffractogram of Sungai Ringin fly ash

TABLE-1
RELATIVE MASS PERCENTAGE OF THE ELEMENTS
AND OXIDE COMPOUNDS OF FLY ASH

Elements	Mass (%)	Oxide compounds	Mass (%)
Si	46.464	SiO ₂	53.261
Al	24.005	Al ₂ O ₃	28.136
Mg	0.963	MgO	1.071
P	0.989	P ₂ O ₅	1.064
S	0.857	SO ₃	0.994
K	1.901	K ₂ O	1.034
Ca	7.359	CaO	0.104
Ti	1.922	TiO ₂	1.332
Fe	14.349	Fe ₂ O ₃	8.023

Based on the results of XRF, the fly ash of Sungai Ringin power plant contains silica and alumina in highly enough concentration. The relative weight ratio of Si/Al on fly ash is 1.94; thus, dealumination was done to increase the Si/Al ratio. Pata *et al.* [17] reported that when the ratio of Si ions to Al increases, the cation density and electrostatic field decrease, so the affinity of the synthesized zeolite surface to non-polar adsorbates increases and consequently, it tends to choose non-polar molecules such as organic compound waste for adsorption.

The XRD results show that the fly ash samples contain minerals of mullite, quartz and corundum. Based on the JCPDS card standard 01-075-8322, the quartz mineral is shown by the characteristic peak at 2θ of 20.85°, 26.67°, 36.68°, 39.44°, 45.74°, 50.02° and 81.19° with d spacing value 4.25 Å, 3.34 Å, 2.45 Å, 2.28 Å, 1.98 Å, 1.82 Å and 1.18 Å; aluminium oxide (Al₂O₃) in the corundum mineral form is characterized by 2θ of 25.44°, 26.20°, 33.26°, 35.56°, 42.64° and 54.16° with d spacing of 25.44 Å, 26.20 Å, 33.26 Å, 35.56 Å, 42.64 Å and 54.16 Å, while the mineral mullite (3Al₂O₃·SiO₂) is characterized by 2θ of 12.64° and 16.49°. The minerals contained in the fly ash are similar to those of Sutarno *et al.* [15] and Jumaeri *et al.* [11] which stated that the fly ash of coal-based power plant contains minerals of quartz and mullite or aluminosilicates. Through the process of calcination, the minerals of silica and alumina in the fly ash are converted into a reactive amorphous silica and alumina form [18]. The reaction of silica and amorphous alumina with NaOH (zeolitization process) would be more effective; consequently, it hopefully increases zeolite crystals produced.

Characteristics of synthesized zeolites on various concentration of NaOH: Each concentration of NaOH used in the synthesis of zeolites, *i.e.*, 2.5 M, 5.0 M and 7.5 M, obtained zeolites as the symbols of Zeo 2.5, Zeo 5.0 and Zeo 7.5 respectively. The synthesized zeolites were then characterized using XRD and compared to the standard of the collection of simulated X-ray powder diffraction patterns for zeolite to determine the type of structure (Fig. 2).

Diffraction in Fig. 2 shows that the zeolites formed on the variation of NaOH concentration have different structural types. In Zeo 2.5, it is found a mixture of two types of zeolites, *i.e.*, analcime [Na₁₆(H₂O)₁₆(Si₃₂Al₁₆O₉₆)] and cancrinite [Na₇Ca_{0.9}(CO₃)_{1.4}(H₂O)_{2.1}(Si₆Al₆O₂₄)]. The analcime zeolite is characterized by 2θ of 15.77°, 18.22°, 24.15°, 25.87°, 30.43°, 33.17°, 35.69° and 47.61° with the value of d spacing of 5.61 Å, 4.87 Å, 3.68 Å, 3.44 Å, 2.93 Å, 2.69 Å, 2.51 Å and 1.91 Å,

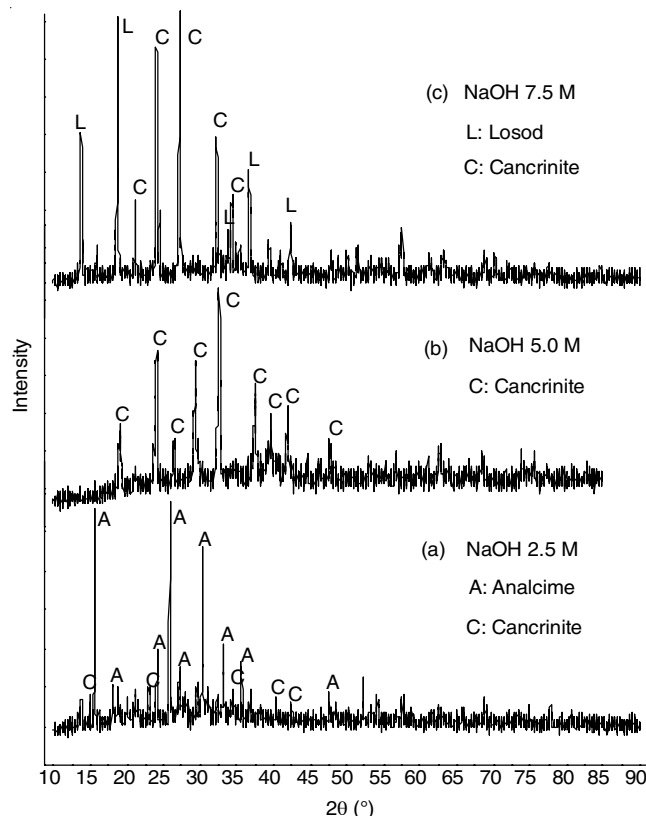


Fig. 2. Diffraction of synthesized zeolites: (a) Zeo 2.5; (b) Zeo 5.0 and (c) Zeo 7.5

whereas the presence of cancrinite zeolite is characterized by 2θ of 14.98°, 24.15°, 27.99°, 35.69°, 40.35° and 42.61° with the value of d spacing of 5.91 Å, 3.68 Å, 3.19 Å, 2.51 Å, 2.23 Å and 2.13 Å.

The use of 5 M NaOH (Zeo 5.0) produces zeolite type of cancrinite by characteristics 2θ of 14.12°, 19.07°, 21.46°, 24.36°, 27.58°, 32.57°, 34.68°, 42.66° and 48.17° with d spacing value of 6.26 Å, 4.65 Å, 4.14 Å, 3.65 Å, 3.23 Å, 2.75 Å, 2.58 Å, 2.12 Å and 1.88 Å. This result is in line with the study of Kriaa *et al.* [19]. They stated that the 2θ of 14°, 24° and 27° is characteristic for cancrinite type. In Zeo 7.5, the formed zeolite is a mixture of cancrinite and losod types [Na₁₂(H₂O)₁₈(Si₁₂Al₁₂O₄₈)]. The characteristics 2θ and d spacing for the losod are indicated by 2θ of 13.86°, 18.81°, 33.84°, 36.71° and 42.38° with d spacing value of 6.39 Å, 4.72 Å, 2.65 Å, 2.45 Å and 2.13 Å.

In addition to XRD, the characterization of the synthesized zeolite is done by FTIR spectrophotometry to confirm functional groups. The results are presented in Fig. 3.

The FTIR spectra of (Zeo 2.5), (Zeo 5.0) and (Zeo 7.5), show adsorption characteristics at wave numbers of 3487.53 cm⁻¹, 3478.65 cm⁻¹ and 3462.75 cm⁻¹, respectively, which correspond to the stretching vibration of -OH groups of silanol (Si-OH). Absorptions at 1640.41 cm⁻¹, 1641.30 cm⁻¹ and 1656.59 cm⁻¹ indicate the bending vibration of -OH groups of H₂O molecules trapped in the zeolite structure. Absorptions at 996.75 cm⁻¹, 998.75 cm⁻¹ and 982.27 cm⁻¹ indicate the asymmetric absorptions of vibration of Si-O/Al-O. Each absorptions at 456.49 cm⁻¹, 459.57 cm⁻¹ and 462.84 cm⁻¹ are bending vibration characteristics for Si-O/Al-O, while absorptions at wave

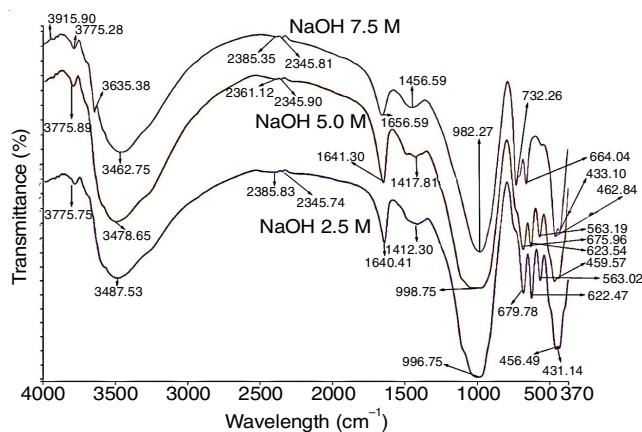


Fig. 3. FTIR spectrum of synthesized zeolites (a) Zeo 2.5; (b) Zeo 5.0 and (c) Zeo 7.5

numbers of 1412.30 cm^{-1} , 1417.81 cm^{-1} and 1456.59 cm^{-1} are characteristic absorptions of the presence of carbonate minerals that are characteristics of cancrinite zeolite [19,20]. To see the morphology of the synthesized zeolite surface, the SEM profile is presented in Fig. 4. The relative mass composition of each zeolite element is analyzed using EDX and the results are presented in Table-2.

TABLE-2
RELATIVE MASS (%) OF ELEMENTS
OF SYNTHESIZED ZEOLITES

Element	Zeo 2.5	Zeo 5.0	Zeo 7.5
C	28.80	29.27	52.60
O	32.08	31.41	20.88
Na	12.52	13.54	9.28
Al	10.75	10.70	7.96
Si	15.90	15.07	9.28

SEM profiles of three synthesized zeolites have a similar resemblance in which each zeolite contains the cancrinite-type zeolite crystals. The synthesized zeolite crystals have longitudinal-shaped crystals that overlap each another and there are small crystalline particles which are irregularly arranged on top of them. The shape and pattern of these synthesized crystals are similar to those of the cancrinite zeolite in the studies conducted by Kriaa *et al.* [19] and Deng *et al.* [21]. In Zeo 2.5 (Fig. 4a), an oval-shaped structure is found, which is

characteristic of analcime [22], whereas in Zeo 7.5 (Fig. 4c), a sheet structure is found in the form of clod, which is characteristic of losod. These results are in line with XRD data by which the cancrinite structure is found in the three types of zeolites produced.

The EDX analysis showed that the three synthesized zeolites contain Na, Al, Si, C and O minerals. These elements are the main minerals of composers of the cancrinite zeolite framework, analcime and losod. The ratios of Si/Al in the synthesized zeolites are varied. The higher the NaOH concentration used, the smaller the Si/Al ratio will be. The presence of element C on the EDX results is consistent with the data of FTIR and XRD results, wherein the cancrinite structure contains carbonate mineral composition.

Determination of the specific surface area in each synthesized zeolite was done with surface area analyzer using the adsorption method of BJH isotherm model. The results of the analysis are presented in Table-3.

TABLE-3
PORE CHARACTERISTICS OF SYNTHESIZED ZEOLITES

Pore parameters	Zeo 2.5	Zeo 5.0	Zeo 7.5
Specific surface area (m^2/g)	41.405	43.499	42.605
Pore volume (cc/g)	0.146	0.222	0.152
Pore size (\AA)	19.198	21.554	19.271

Surface area analysis results show that the specific surface area parameters, pore volume and size of Zeo 5.0 are greater than those of the other synthesized zeolites. This is probably due to the higher cancrinite purity levels in Zeo 5.0. This result is also in line with the SEM profile obtained, in which the morphology of Zeo 5.0 shows higher porosity as compared to that of Zeo 2.5 and Zeo 7.5. Based on the size of the pores, the synthesized zeolite is classified as mesoporous materials.

Application of synthesized zeolites to reduce TOC level of CPO industrial waste: The liquid waste of the CPO industry is generally a type of organic waste derived from residuals of the palm oil processing. The content of these organic compounds might generate bad colour and stinky odour. If directly disposed into the environment exceeding the limits of tolerance, it will cause water, soil and air pollution; this is due to large amounts of organic materials relatively take a long time to decompose naturally into H_2O and CO_2 .

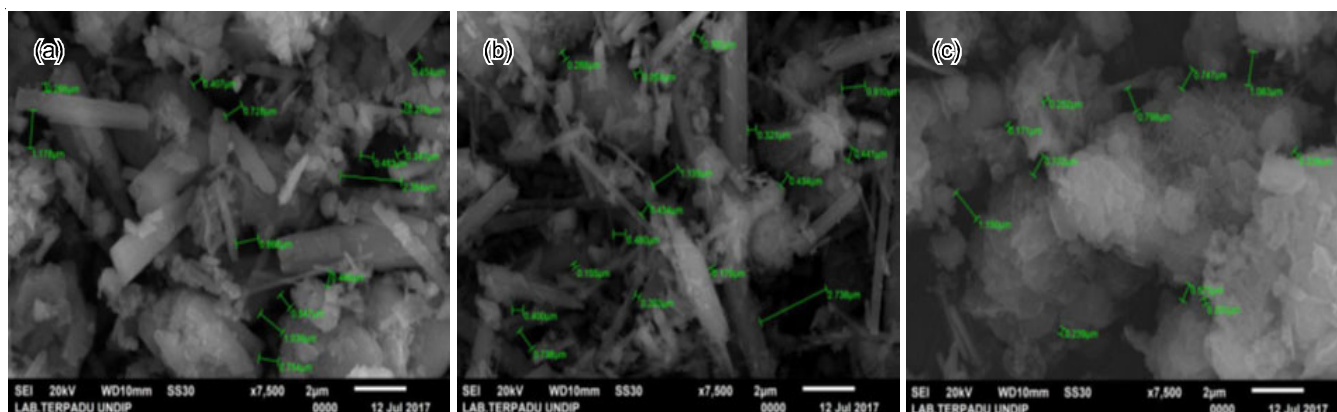


Fig. 4. SEM of synthesized zeolites: (a) Zeo 2.5; (b) Zeo 5.0 and (c) Zeo 7.5

The analysis result of CPO liquid waste sample used in this study has TOC level of 2,329 mg/L. The TOC concentration is so high that it should not be directly disposed into the environment. The reducing process of the TOC level is conducted by contacting the sample with the synthesized zeolites through the batch adsorption method for 4 h. The results are presented in Fig. 5.

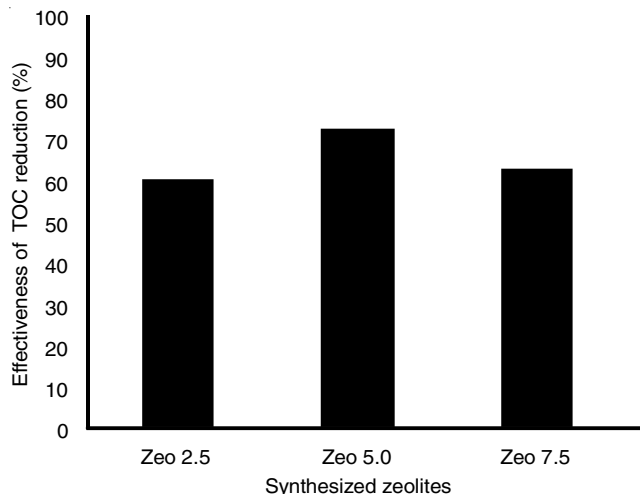


Fig. 5. Effectiveness percentage of TOC reduction by synthesized zeolites

The synthesized zeolites viz., Zeo 2.5, Zeo 5.0 and Zeo 7.5, can decrease TOC levels by 930 mg/L, 648 mg/L and 872.5 mg/L, respectively. The highest of TOC reduction is shown by Zeo 5.0. The absorption ability of an absorbent material is determined by many factors, such as the characteristics of surface area, volume and pore size. At Zeo 5.0, these three parameters have larger values than the other two of synthesized zeolites. Large areas and large pore volumes of suitable size allow more impurities to be absorbed, so that their capacity to TOC increases. The XRD results also show that Zeo 5.0 produced in higher purity cancrinite allows the TOC adsorption process to be more effective.

Conclusion

The types of zeolite produced based on Sungai Ringin fly ash are affected by the NaOH concentration used as mineralizer. The use of NaOH concentration of 2.5 M, produces zeolite mixture of cancrinite–analcime compound; at 5.0 M, it generates zeolite type of cancrinite; and at 7.5 M, it produces zeolite mixture of cancrinite–losod compound. The synthesized zeolite using 5.0 M NaOH (Zeo 5.0) has the highest crystalline purity and surface area with a pore diameter size of 21.5 Å.

The application of synthesized zeolite in reducing of the TOC level of the liquid waste in the CPO industry shows that Zeo 5.0 has the highest effectiveness in terms of a percentage value decrease of 72.6 % from TOC initial concentration of 2,329 mg/L. Synthesized zeolite has good prospect to be

applied as an alternative of the liquid waste processing technology in the CPO industry.

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