



SYNTHESIS AND CHARACTERIZATION OF MCM-41 FROM COAL FLY ASH FOR TAPIOCA WASTEWATER TREATMENT

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ABSTRACT

The present study reports a green synthesis method for ordered MCM-41 materials from coal fly ash at room temperature during 24 h of reaction with Si/Al ratio 40, 50, and 60 using cetyltrimethylammonium bromide (CTAB) as template. The surfactant was removed by calcination at 550°C for 4 hours with heating rate 1°C/minute. The material properties of calcined MCM-41 was characterized by XRD, SEM, and BET. The MCM-41 material was applied as an adsorbent in the tapioca wastewater treatment. The XRD analysis results showed that the Si/Al ratio influence the crystallinity of product. The crystallinity of MCM-41 was increased by increasing Si/Al mole ratio. The obtained MCM-41 adsorption capacity for tapioca wastewater treatment was 15.92 mg/g.

Keywords: adsorption, fly ash, MCM-41, tapioca, wastewater.

INTRODUCTION

Lampung is the biggest producer of cassava in Indonesia about 8,329,201 ton of cassava per year [1], [2]. According to data based of service industry Lampung province about 70 tapioca factory in 2014 produce 20 m³/ton wastewater containing COD 18,000-25,000 mg/l. COD is causing odors and reducing the oxygen content in the wastewater. This research was studying about the synthesis of MCM-41 from coal fly ash to reduce the content of COD in tapioca wastewater [3], [4].

Coal fly ash is the solid waste from power plants which contained minerals such as quartz, mullite, subordinately hematite and magnetite, carbon, and a prevalent phase amorphous aluminasilicate [5]-[9].#

The power plant located in Tarahan produce 200Mw electricity from 80 tons coal/hour. The coal combustion generated about 5% (76.8 tons/day) of solid pollutants (i.e. fly ash and bottom ash). This research investigated the preparation of MCM-41 from solid waste coal fly ash for tapioca wastewater treatment.

According to International Union of Pure and Applied Chemistry (IUPAC), mesoporous materials are solids that contain pores with diameter of 20-500 Å. MCM-41 (Mobil Composition of Mater No. 41) is the mesoporous materials, which possesses the uniform pore size, very high specific surface area (ca. 1200 m²/g) and large pore volume (ca. 1cc/g)[10]. MCM-41 material could be synthesized using tetraethylortosilicate (TEOS) or other silica source such as rice husk ash, fly ash, etc. However, MCM-41 containing pure silica material has a low acidity which only has a weak Lewis acid side and do not have Bronsted acid side. It caused the problem when implemented directly as a catalyst and adsorbent. The Presence of metal ions on the MCM-41 structure will increase the acidity of this material, wherein the metal ion is going to be a Lewis acid side and play an active role in the process of the catalyst, further the addition of these ions could change the properties of the hydrophilic

material and thermal stability. Metals which could be used such as Co, Al, Cu, Zr and other transition metals [11].

This research was studied the synthesis of MCM-41 molecular sieve using coal fly ash as the source of Si and Al with molar ratio parameters 40, 50, and 60 to obtain the best crystalline order of MCM-41 materials. The reaction of MCM-41 was carried out at room temperature, it is agree with the approach of Green Chemistry. According K. S. Hui, et al. (2006) at room temperature synthesis method can be said to apply green chemistry because due to energy efficiency, design synthesis harmless and minimizing the potential for accidents [12].#

The application of obtained MCM-41 molecular sieve was conducted by the adsorption process to reduce COD content of tapioca liquid waste. Adsorption processes occurred on the surface of the solid adsorbent due to the interaction electrostatic, ion exchange, ion-dipole interactions, surface cation coordination, hydrogen bonding and hydrophobic interactions [13]. The COD value indicates the content of organic matter in the wastewater such as carbohydrates in the form of starch, fat, and protein.

MATERIALS AND METHODS

Materials

Fly ash used in this study was obtained from a power plant waste in Tarahan, Lampung. The fly ash was treated at 120 °C for 30 to remove water and other volatile impurities such as CO₂, CO, SO₂, etc.

Si and Al extraction

Si and Al extraction was conducted by mixing 50 grams of coal fly ash with 500 ml of 2M NaOH solution with the weight ratio NaOH and coal fly ash was 1: 1,2. The solution was treated in an oil bath at 100 °C for 4,5 h, stirred at 300 rpm. Then the solution was separated from the mixture using a filtration process. The obtained



solutions were analyzed using gravimetric methods to determine the concentration of Si, Al, and Na.

Preparation of CTAB solution

CTAB solution was prepared by dissolving CTAB in H₂O and stirred at 300 rpm. The composition of CTAB for each parameter was shown in Table-1.

Table-1. Composition of CTAB in CTAB solution.

Si/Al	CTAB (gram)	H ₂ O (ml)
40	4	34.71
50	4	53.66
60	4	66.30

The preparation of MCM-41 mother solutions

MCM-41 mother solutions was prepared by the following procedures:

- Run 1. Si / Al: 40
95.34 ml of fly ash filtrate solution, 1.64 ml Si solution was mixed with CTAB solutions at 300 rpm for 5 min.
- Run 2. Si / Al: 50
76.27 ml of fly ash filtrate solution, 1.76 ml Si solution was mixed with CTAB solutions at 300 rpm for 5 min.
- Run 3. Si / Al: 60
63.56 ml of fly ash filtrate solution, 1.83 ml Si solution was mixed with CTAB solutions at 300 rpm for 5 min.

Synthesis of MCM-41

The preparation of MCM-41 materials was conducted as follows:

- Adjust the pH of the solution became 11 by the addition of H₂SO₄ 5,25N with slowly stirring (50 rpm).
- Then the solution was allowed to stand at room temperature for 24 hours.
- The synthesized MCM-41 materials was washed with deionized water and dried at 100 °C for 2 hours.
- The calcination was conducted at 550 °C for 4 hours with heating rate of 1 °C / min.
- The obtained MCM-41 material was characterized by SEM-EDX, XRD, BET.

Application of MCM-41

Study the application of MCM-41 as adsorbent in tapioca liquid waste treatment was carried out in a batch reactor at 25° C, stirred at 600 rpm. 1 gram MCM-41 adsorbent was mixed with 100 ml tapioca wastewater for 100 min. Then filtered using filter paper with pore size 0.45 μm, and acidified by addition of 2% HNO₃ to decrease the pH below 3. Then measure the content of COD waste after adsorption process.

METHODS

X-Ray Diffraction (XRD)

The MCM-41 structure was identified by X-rays Diffraction. XRD could analyzed crystallinity of samples.

Scanning Electron Microscopy (SEM)

The morphology of surface material and micro structure of MCM-41 was observed by Scanning Electron Microscope.

Adsorption - Desorption isothermal analysis

The adsorption and desorption characteristic of sample was analysed using nitrogen at 44 K. The vapor pressure or nitrogen was varied from 0 to 1 with the increment 0.001. This method was also widely used to determine the specific BET (Brunnauer-Emmett-Teller) surface area, and pore size distribution.

Chemical Oxygen Demand Analysis (COD)

COD Analysis of tapioca liquid waste was carried out using titration method.

RESULTS AND DISCUSSIONS

Synthesis of MCM-41 in this study conducted by using a sold-gel conversion at room temperature for 24 hours. NaOH was changing the Si and Al into sodium silica and sodium alumina which more reactive than the silica and alumina as quartz and mullite in fly ash[14]. The results of XRD analysis was shown in Figure-1.

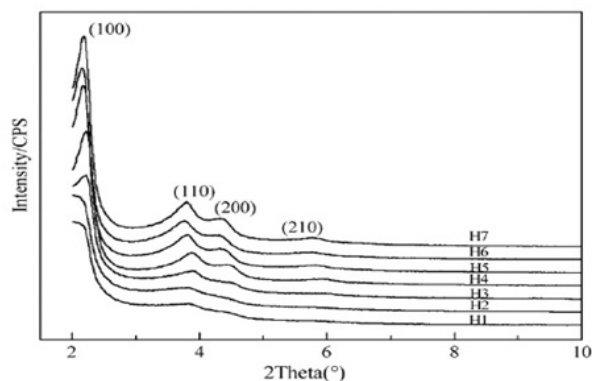


Figure-1. XRD pattern of MCM-41 standard at room temperature.

Based on the XRD pattern of MCM-41 standard shows a major peak at 2 theta 2° - 3°, and other peak at 3° - 4°, 4° - 5°, 5° - 6°. Peak formed on the sample analysis result is 2 theta 2° - 3°, and other peak at 3° - 4°, 4° - 5°, 5° - 6°. The main peak was also seen in samples of synthesized MCM-41. The MCM-41 structure was found in all samples. The sample with Si/Al ratio of 60 has the best crystallinity. CTAB surfactant was used as organic template in arrangement of hexagonal MCM-41 structure occurs through the ion exchange between the cationic surfactant Br silica in aqueous solution [15]. This synthesis begins with the dissolution of the CTAB



surfactant in distilled water, then forming micell. The surfactant comprises of a hydrophilic head will go beyond the direct contact with water, and the hydrophobic tails will stay away from the water solvent to form surfactant micelle. Once formed, the surfactant micelle will form micellar rod, and continue to a hexagonal array as initial formation hexagonal structure of MCM-41.

When CTAB solution was mixed with sodium silica and alumina, they will coat the sodium hexagonal structure which has been formed previously. The pH of solutions could give influence to the thickness of product. These phenomena indicating the nucleation has just begun. Gel early clot separately turned into a milky white gel homogeneous after pH 11. After 24 hours, the reaction of crystallization was finished. The calcination process aims to eliminate organic compounds such as surfactants.

X-ray Diffraction (XRD)

The as-synthesized MCM-41 was characterized by the method of X-ray Diffraction (XRD) to determine the structure. The XRD analysis results for each run is shown Figure-1 to 4.

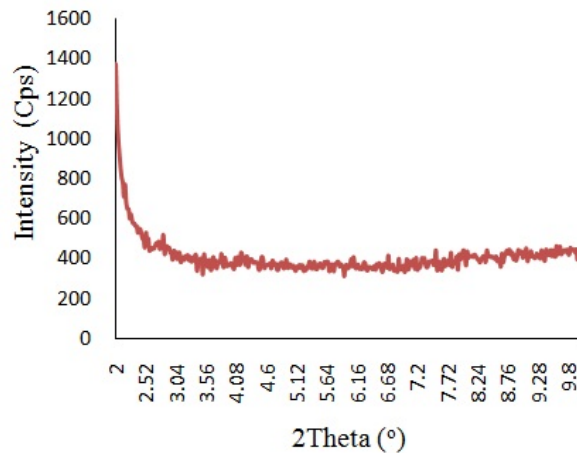


Figure-2. XRD pattern of Si/Al 40.

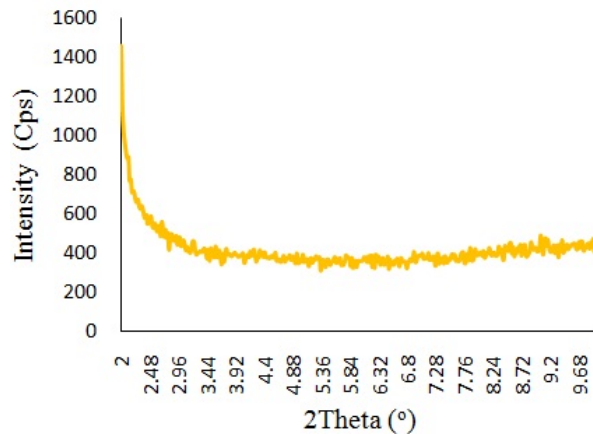


Figure-3. XRD pattern of Si/Al 50.

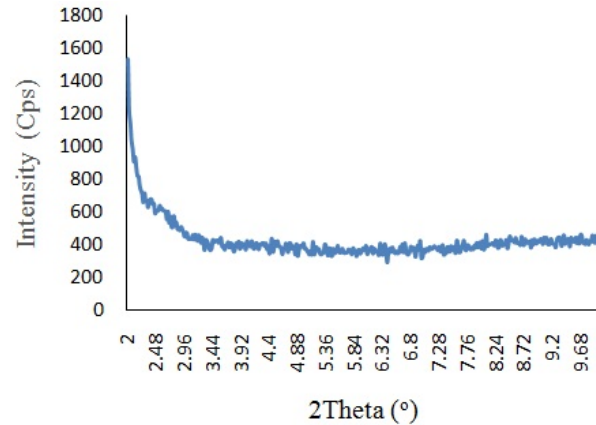


Figure-4. XRD pattern of Si/Al 60.

Scanning Electron Microscopy (SEM)

SEM analysis was carried out to observe the microstructure morphology of synthesized MCM-41. The results is shown in Figure-5 to 7.

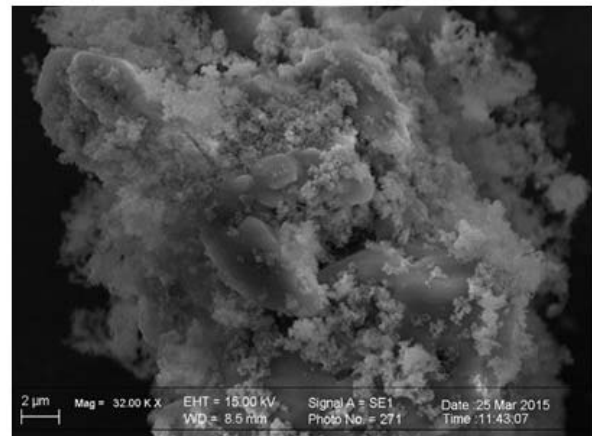


Figure-5. SEM of Si/Al 40.

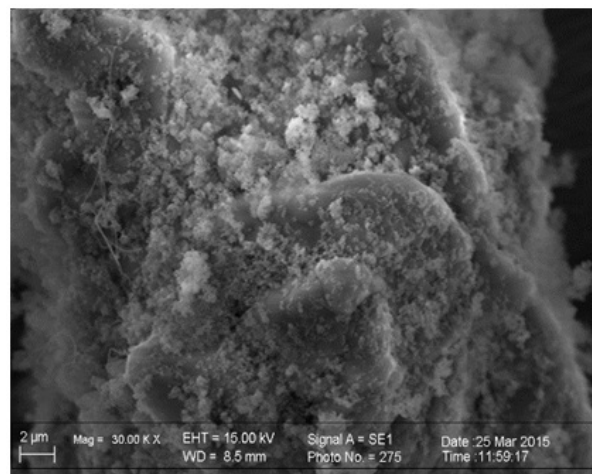


Figure-6. SEM of Si/Al 50.

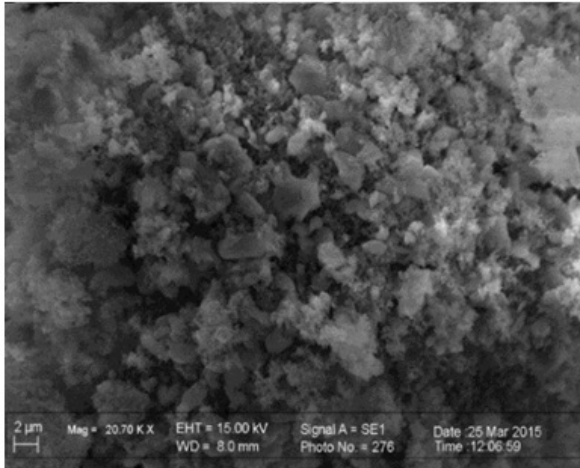


Figure-7. SEM of Si/Al 60.

Based on the picture in Figure-5 to 7, shows the crystal structure in the sample of as synthesized MCM-41. The amount of crystals in run 1 and run 2 was still few and many amorphous form. While on the run 3 the crystals was increased although the amorphous structure still exist. The crystals in the run 3 was not hexagonal, may be the metal binding framework Al into MCM-41 led to a reduction in the form of hexagonal symmetry of MCM-41. The formation of amorphous on this sample due to incomplete reaction silica.

Adsorption - Desorption isothermal analysis

The results of the adsorption-desorption analysis is shown in Figure-8. The BET specific surface area was 114.32 m²/g, pore diameter 88.38 Å, with a total pore volume of 0.253 cc/g.

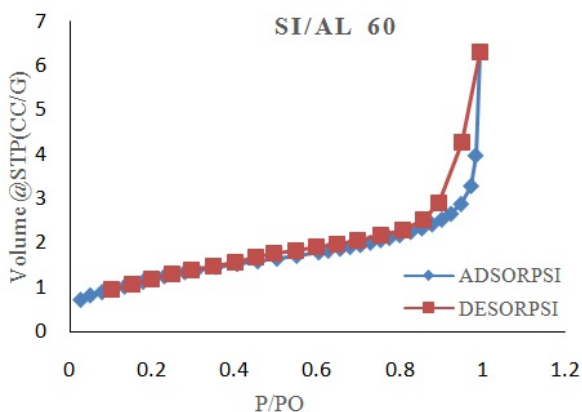


Figure-8. Adsorption and desorption of Nitrogen.

The adsorption volume of gas at P/Po = 0 was very small and the monolayer area has not been full then the pressure is increased more than 0.1 started happening gas adsorption that meet the monolayer. Although the change is not significant gas so happens branching point or loop hysterical when the pressure is lower. The amount of adsorbed gas is not equal to the amount of desorbed gas,

this hysterical loop occurs at a pressure P/Po 0.49. The hysteresis loop was caused by the phenomenon of capillary. The pore size inside the materials was larger than outside one.

Chemical Oxygen Demand Analysis (COD)

COD analysis was analyzed by using the titration method[16][17]. The tapioca liquid waste was mixed with the MCM-41 for 120 minutes, with sampling every 30 minutes. The results is shown in Table-2.

Table-2. Result of COD analysis.

No.	Sampel	Time (min.)	COD _{initial} (mg/l)	COD _{final} (mg/l)
1.	Run 1	30	729,6	601,4
2.		60	729,6	598,4
3.		90	729,6	582,4
4.		120	729,6	582,4
1.	Run 2	30	729,6	572,8
2.		60	729,6	566,4
3.		90	729,6	553,4
4.		120	729,6	553,4
1.	Run 3	30	729,6	537,6
2.		60	729,6	531,2
3.		90	729,6	521,6
4.		120	729,6	521,6

Based on the Table-2. The COD concentration in wastewater of tapioca was reduced after the adsorption process between tapioca liquid waste with MCM-41. The highest reduction of COD concentration was occurred in the sample run 3 with a contact time of 90 minutes. However, the concentration of COD at 120 minutes was rose so that it can be concluded that the optimum conditions for adsorption of COD by MCM-41 at the contact time of 90 minutes with Si/Al ratio of 60, using 1% wt. of adsorbent per liquid waste volume. This shows that lower concentration of COD indicated more number of organic substances that was absorbed by the MCM-41 with Si/Al ratio of 60. The higher of Si/Al ratio, the hydrophobic properties of MCM-41 was getting higher and therefore the case for hydrophobic interaction between MCM-41 material with organic materials that are non-polar. This results was supported by XRD and SEM analysis, showed that better and uniform MCM-41 structure was obtained at the higher ratio of Si/Al.

Isotherm adsorption

Isotherm adsorption was carried out for waste liquid tapioca with Si/Al 60 adsorbent. The observed parameter was variation of initial coccentration, and 100 minutes time adsorption with sampling every 10 minute. In this study are selected two isotherm adsorption, which are Langmuir isotherm[18] and Freundlich isotherm[19]. So it is given equilibrium concentration (C_e) and q_e. The results is shown in Table-3.

**Table-3.** Result of COD analysis variation C_0 .

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)	$\frac{C_e}{q_e}$	$\ln C_e$	$\ln q_e$
416	288	12,8	22,5	5,66	2,54
480	352	12,8	27,5	5,86	2,54
512	384	12,8	30	5,95	2,54
576	448	12,8	35	6,10	2,54
608	480	12,8	37,5	6,27	2,54
784	640	14,4	44,5	6,46	2,66

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (1)$$

Where

C_0 = initial concentration (mg/l)

C_e = equilibrium concentration (mg/l)

V = volume (l)

W = weight of adsorbate (1 g)

q_e = the amount of solute adsorbed from the solution in equilibrium (mg/g)

$$\text{Langmuir isotherm } \frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

$$\text{Freundlich isotherm } \ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (3)$$

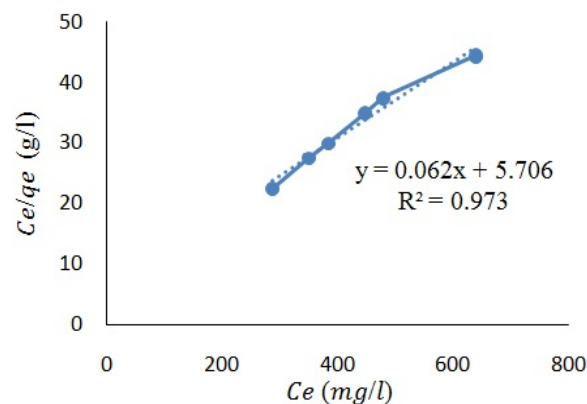
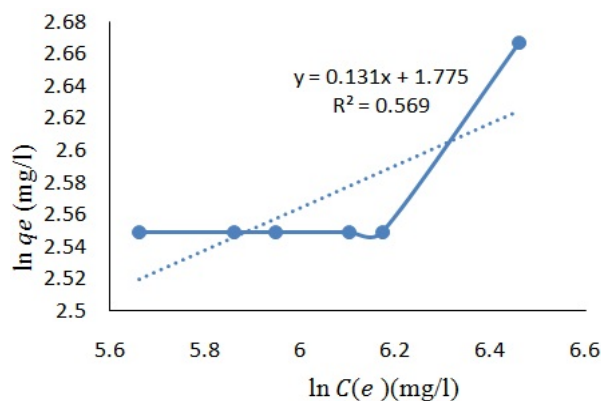
**Figure-9.** Langmuir isotherm of Si/Al 60.**Figure-10.** Freundlich isotherm of Si/Al 60.

Figure-9 and 10 show the regression results for the adsorption of organic material on MCM-41 at different initial concentration by langmuir isotherm and Freundlich isotherm respectively. The value of correlation coefficient (R^2) were found to be higher for Langmuir isotherm than Freundlich isotherm indicating that the equilibrium data fitting well the Langmuir model. The values of qm from the figure and were found to be 15.92 mg/g.

CONCLUSIONS

Based on the experimental study, it was concluded that pure (free of coal fly ash) and ordered MCM-41 materials could be successfully synthesized from coal fly ash at room temperature during 24 h of reaction. However, MCM-41 material produced has large pore, small pore volume, and small BET specific surface area. The MCM-41 materials was able to absorb organic material in tapioca liquid waste effectively with value of correlation coefficient (R^2) were found to be higher for Langmuir isotherm than Freundlich isotherm indicating that the equilibrium data fitting well the Langmuir model. The values of qm from the figure and were found to be 15.92 mg/g.

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