



# Influence of Alumina Incorporated on MCM 41 Surface for Mesoporous Characteristic and Methylene Blue Adsorption

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## Abstract

Al-MCM 41 is an important material for reducing methylene blue waste through adsorption technique. The MCM 41 adsorption was mostly influenced on the MCM 41 framework that was built. Hence, the alumina incorporated on the MCM 41 will change the MCM 41 frameworks to become negative charge so that it influences the adsorption process of methylene blue. In this study evaluated the effect of alumina on MCM 41 frameworks in the adsorption process of the methylene blue. The research resulted that Al-MCM 41 has been synthesized directly, it showed any different on MCM framework because alumina caused the isomorphic substitution with Si atom. This indication can be identified from the shift of FTIR wavenumbers at 795 cm<sup>-1</sup> that showed any different vibration of Si-O-Si and Si-O-Al, while the decreasing intensity of XRD indicated any different crystallinity formed. Al-MCM 41 has a good ability as an adsorbent for removing methylene and it is more effective than Si-MCM 41. Al-MCM 41 follows the adsorption model appropriate the Langmuir isotherm equation.

**Keywords:** Al -MCM 41, Si-MCM 41, Methylene blue, Langmuir isotherm, Adsorbent

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## Introduction

A framework of MCM 41 is an integral part that influences the adsorption process. MCM 41 can be applied as adsorbent because it contains porous with meso size. MCM 41 will interact and adsorb the dye waste using silanol group that has been formed on materials framework. Therefore, one way to maximize the adsorption of dye waste is change the MCM 41 frameworks to become negative charge. The alumina addition in the directly synthesis of MCM 41 is able to change its frameworks gained negative charge. Moreover, alumina is also building the new acid sites [1]. The negative framework of MCM 41 will influence the interaction between Al-MCM 41 with dye waste especially cationic dyes and will probably increase the adsorption ability. The negative framework of Al-MCM 41 can change the interaction between adsorbent and adsorbate because it related with the adsorption-desorption process. The physical

interaction tends the desorption process of adsorbate, because it had weak interaction with the framework of MCM 41. While the chemical interaction will tend to create a good interaction and the desorption process is not happened. Hence, The use of Al-MCM 41 can lead the chemical interaction because it has negative charge in the MCM 41 framework.

However, the negative sites of Al-MCM 41 framework attracts and causes electrostatic interactions. These interactions can adsorb the cationic dyes through chemical interaction with the adsorbent. Besides, the addition alumina will produce Brønsted acid sites on MCM 41 can be modified using AlCl<sub>3</sub> [2]. The acidic properties of MCM 41 were influenced by the Si/Al ratio [3]. The acidity sites increase due to the increase of aluminum content on MCM 41 pore walls [4]. Hui

and Chao [5] also concluded that the incorporation of Al metal on MCM 41 framework can increase the acidity sites which can be used in catalysis and adsorption process. The aluminum only gives the rising of acid sites as much as 10-15% [6]. Therefore, this research will determine the adsorption interaction of Si-MCM 41 and Al-MCM 41 approached using Langmuir and Freundlich isotherm models. The differences of MCM 41 framework may be able to cause any different in the adsorption process of methylene blue.

## Materials and Methods

### *Synthesis MCM 41 and Al-MCM 41*

Molar composition 1 SiO<sub>2</sub>: 0.25 CTAB: 0.29 Na<sub>2</sub>O: 50 H<sub>2</sub>O were a formulation to produce MCM 41. A total of 2.277 g CTAB dissolved in 18.882 g distilled water for 30 min at a temperature of 60°C and cooled. Then, 7.512 g Na<sub>2</sub>SiO<sub>3</sub> is added to CTAB solution by dropwise. This mixing process is heated at temperature of 60°C for 1 h and stirred until homogeneous and cooled again. Then the pH solution must be adjusted to pH 10 using 1 M acetic acid and stirred for 2 h. This mixture is placed on autoclave and heated at temperature of 100°C for 24 h. After that, the mixture is filtered and washed using distilled water becomes neutral and dried in the oven at temperature of 100°C overnight. After drying process, MCM 41 is calcined at temperature of 550°C for 5 h. That product is characterized by X-ray diffraction, infrared spectrometer and a surface area analyzer and test adsorption against methylene blue. So, the Al-MCM 41 was made with same process with the ratio Si/Al :23.

### *Determination of adsorption model of MCM 41 and Al MCM 41 to methylene blue*

0.0205 g of MCM-41 materials is placed on beaker glass which is containing 20 mL of methylene blue. The methylene blue concentration is varied between 10-90 ppm for the Si-MCM-41 and between 110-200 ppm of methylene blue for Al-MCM-41. The adsorption process is carried out at neutral pH and then stirred for 120 min. Then, the solid is separated from the solution by centrifugation at 7000 rpm for 10 min. After that, the solution of methylene blue is analyzed using

UV-visible spectrometer (Hitachi, U2010) at a wavelength of 664 nm.

## Results and Discussion

### *Characterization of XRD and FTIR*

The addition of aluminate in the direct synthesis of MCM 41 also caused deterioration in the crystallinity of MCM 41 which is marked by a slight decline its intensity in the field [100], while the hexagonal structure of MCM 41 was not significantly affected by aluminate. However, Al in the MCM 41 framework can decrease its crystallinity due to Al species causes the distorted hexagonal structure or amorphous pore of MCM 41[7]. The hexagonal structure was proven by other peaks that have appeared on the field [110] and [200] (Fig. 1). Araujo et al., [8] reported that MCM 41 without [110], [200], and [210] Bragg planes which describe poor ordering the pore structure. This similar research by Hernandez et al., [4] also reported that other signals which have risen from diffraction analysis using XRD including the small [110] plane indicated a more orderer porous on MCM 41 framework. The one of the peaks is observed at  $2\theta = 2.28^\circ$  as the plane [100] and other peaks between  $3.2 < 2\theta < 5.4^\circ$  as the planes [110], [200], and [210] [9]. Fig. 1 also showed that the smaller the Si/Al ratio cause MCM 41 intensity becomes lower. Boukoussa et al., [10] reported that the aluminum present is significantly affected by number of aluminum because it causes alteration between hexagonal porous shape without destroying its primary crystal. This phenomenon demonstrated that any different pore that was built using the condensation process. Besides that, the present study suggests that aluminate also cause changes in the unit cell on MCM 41. A unit cell of Al-MCM 41 decreased because of unstable Si-O-Al bond during calcination where occurs insistence inter-pores.

The aluminate loaded through direct synthesis cause the Al on MCM 41 framework. The isomorphic substitution of Si with Al become the thermal stability and hydrothermal properties increased. These materials can be applied as an alternative of heterogen catalyst. The Al atoms on MCM 41 framework will cause a change on MCM 41 structure that makes the different application

resulted. The substitution of Al in the MCM 41 framework can be detected in the molecular vibration (Fig. 2). This research showed a shift of wavenumber 1080  $\text{cm}^{-1}$  region as Si-O-Si vibration asymmetric. Then, it showed the vibration at wavenumber 795  $\text{cm}^{-1}$  as TOT vibration (T: Si or Al) and other vibration around 463  $\text{cm}^{-1}$  as vibration  $\text{TO}_4$ . Suyanta et al., [11] based on the research, there are a Si-O-T vibration asymmetric showed in the FTIR spectrum at wavenumber 1103  $\text{cm}^{-1}$  and shoulder around 1235  $\text{cm}^{-1}$ . The peak at 466  $\text{cm}^{-1}$  illustrated the O-Si-O vibration, the peak at 1092  $\text{cm}^{-1}$  described the Si-O-Si stretching vibration, and others at 964  $\text{cm}^{-1}$  and 1632  $\text{cm}^{-1}$  corresponded the Si-OH bending vibration [12].

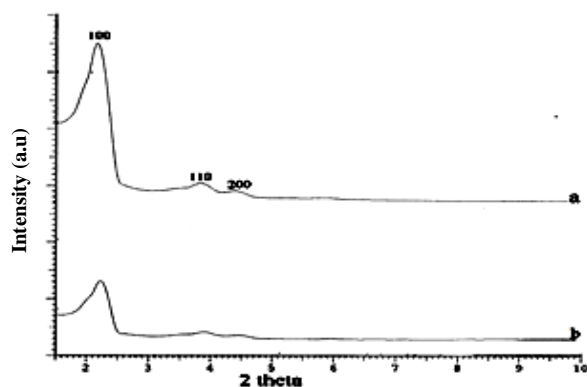


Figure 1. X-ray diffraction pattern of the MCM 41 : a) Si-MCM 41, b) Al-MCM 41 (Si/Al: 23)

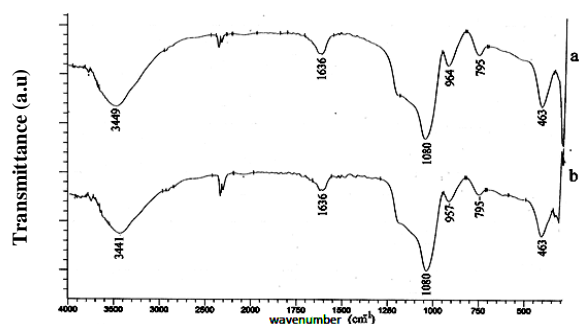


Figure 2. FTIR spectra : a) MCM 41 calcined , b ) Al-MCM 41 calcined

### Characterization of surface area MCM 41

This research showed that Al-MCM 41 produced a mesoporous material that has a larger diameter pore size of 20 Å. The  $\text{N}_2$  adsorption showed that the loaded aluminate leads the decreasing of the surface area, pore volume and

pore diameter on MCM 41 but there are not significant different. The directly synthesis of Al-MCM 41 caused the differences structure of MCM 41 seen from pore volume and surface area of MCM 41 decreased.

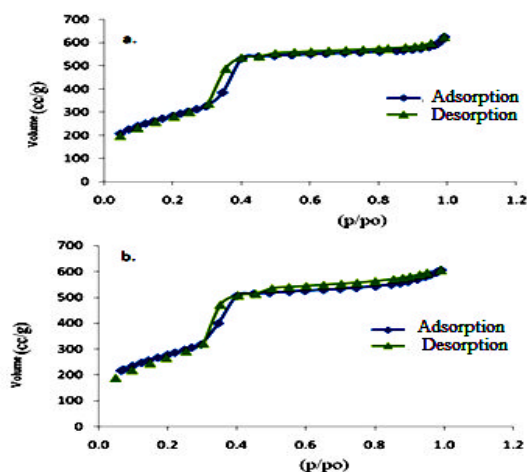


Figure 3. The results of  $\text{N}_2$  adsorption of MCM 41: a) Si-MCM 41 and b) Al-MCM 41

The adsorption and desorption isotherms of MCM 41 follows the classification type IV, which is mesoporous typical (Fig. 3). Both isotherms resulted the similar hysteresis shape where formed H1 type. H1 type indicates capillary cylinder pore form. It is attributed as the silica mesoporous characteristic [13]. However, Al-MCM 41 resulted the pore size diameter greater 2 nm than MCM 41. Hence, Al-MCM 41 has different pore size as evidence the Al replaced Si on MCM 41 framework. Based on the  $\text{N}_2$  adsorption was reported that MCM 41 and Al-MCM 41 have a porous volume of 0.717  $\text{cm}^3/\text{g}$  and 0.584  $\text{cm}^3/\text{g}$ , respectively while the porous diameter of 30.440 (Å) and 30.448 (Å), respectively. Besides, both materials also resulted the surface area of MCM 41 and Al-MCM 41 of 1019.13  $\text{m}^2/\text{g}$  and 995.51  $\text{m}^2/\text{g}$ , respectively. This evidence proven that all alumina are not incorporated on MCM 41 frameworks but some alumina go in MCM 41 pore walls.

### Adsorption models of Si-MCM 41 and Al-MCM 41 to absorb methylene blue

The adsorption isotherm models determine the adsorption process by adsorbent. Adsorption isotherm models consist Langmuir and Freundlich models. Langmuir adsorption isotherm model

establishes a single layer (monolayer) that shows same number of active sites between adsorbent and adsorbate. The model Freundlich adsorption isotherm describes a multilayer adsorption process causing the physisorption interaction. Determination the adsorption isotherm models of MCM 41 and Al-MCM 41 at equilibrium conditions which is approximately 120 min. The adsorption process was carried out at pH neutral to maximize the effectivity of negative charge in the Al-MCM 41 framework. This result was similar with Lewandowski et al., [14] reported that the most efficient in amount of dyes adsorbed was influenced by physicochemical interaction with the silica surface. The efficiency of MCM-41 for removing the organic waste was depended on adsorbate-adsorbent interactions based on hydrogen bonding and or electrostatic interactions [15].

This study indicates that adsorption process of methylene blue will occur as a monolayer on MCM 41 surface. This can be described with linearity of coefficient determination ( $R^2$ ) value while indicated MCM 41 follows Langmuir isotherm equation (Fig. 4). Adsorption isotherms model shows the ability of Al-MCM 41 was better than Si-MCM 41 to absorb methylene blue. The use of Al-MCM 41 as adsorbent is good adsorbent because methylene blue was more absorbed. The capacity of Al-MCM was greater fourfold than Si-MCM 41 while this phenomenon is due to the formation of acid sites on Al-MCM 41 frameworks. This case was reported by Brankovic et al., [16], the presence aluminum tends the four-coordinate on MCM 41 framework that resulted higher acidity. This is a potency of MCM 41 as adsorbent of dyes waste and for removing it from aqueous solution is very high [17] including methylene blue dye with adsorption capacity of  $316 \text{ mg.g}^{-1}$  [18].

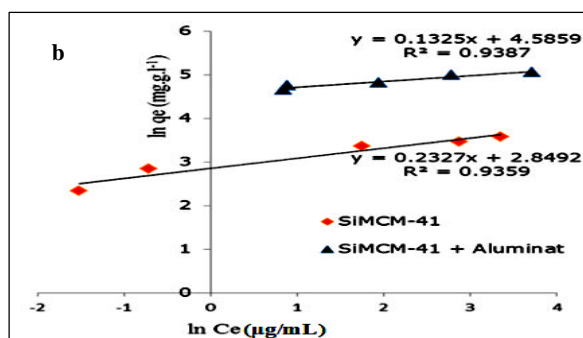
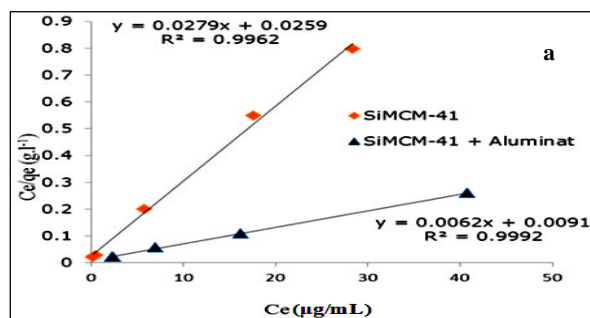


Figure 4. Adsorption models of Si-MCM 41 and Al-MCM 41 of methylene blue: Langmuir adsorption models (a) and Freundlich adsorption models (b)

### Conclusion

Al-MCM 41 has been successfully synthesized directly. The differences of MCM 41 framework were experienced and indicated by the shift at wavenumber  $795 \text{ cm}^{-1}$  as pull symmetric TOT (T: Si or Al) vibration. Beside that, intensity of XRD was also decreased as any different conformation on MCM 41 framework. The use of Al-MCM 41 as an adsorbent is better than Si-MCM 41 and the adsorption model of Al-MCM 41 against methylene blue follows the Langmuir isotherm equation.

### References

1. A. S. Diez, M. Alvarez and M. A. Volpe, *J. Braz. Chem. Soc.*, 26 (2015). <http://dx.doi.org/10.5935/0103-5053.20150122>.
2. M. Xu, A. Arnold, A. Buchholz, W. Wang and M. Hunger, *J. Phys. Chem. B*, 106 (2002) 12140. <http://dx.doi:10.1021/jp021308a>.
3. T. Shindo, M. Kato, S. Kitabayashi and S. Ozawa, *Int. J., Soc. Mater. Eng. Resour.*, 10 (2002) 165. <http://dx.doi:10.5188/ijsmr.10.165>.
4. A. Hernández, J. Escobar, J. G. Pacheco, J. A. de los Reyes and M. C. Barrera, *Rev. Soc. Quím. Méx.*, 48 (2004) 260. ISSN 0583-7693.
5. K. S. Hui, and C. Y. H. Chao, *J. Hazard. Mater.*, 137 (2006) 1135. <https://doi.org/10.1016/j.jhazmat.2006.03.050>
6. R. Locus, D. Verboekend, R. Zhong, K. Houthoofd, T. Jauman, S. Oswald, L.

- Geibeler, G. Baron and B. F. Sels, *Chem. Mater.*, 28 (2016) 7731.  
<https://doi.org/10.1021/acs.chemmater.6b02874>
7. N. La-Salvia, J. J. Lovón-Quintana, A. S. P. Lovón and G. P. Valença, *Mater. Res.*, 20 (2017) 1461.  
[doi:http://dx.doi.org/10.1590/1980-5373-MR-2016-1064](http://dx.doi.org/10.1590/1980-5373-MR-2016-1064).
8. R. S. Araujo, F. S. Costa, D. A. S. Maia, H. B. Sant'Ana and C. L. Cavalcante Jr, *Braz. J. Chem. Eng.*, 24 (2007) 135.  
<http://dx.doi.org/10.1590/S0104-66322007000100012>.
9. B. Nassima, B. Abdallah and D. Abdelkader, *Bio. Rxiv.*, (2017) 118182.  
[doi:https://doi.org/10.1101/118182](https://doi.org/10.1101/118182).
10. B. Boukoussa, R. Hamacha, A. Morsli and A. Bengueddach, *Arab. J. Chem.*, 10 (2017) 160.  
[doi:https://doi.org/10.1016/j.arabjc.2013.07.049](https://doi.org/10.1016/j.arabjc.2013.07.049).
11. N. Suyanta, E. T. Wahyuni and Triyono, *Indo. J. Chem.*, 10 (2010) 41.  
[doi: https://doi.org/10.22146/ijc.21478](https://doi.org/10.22146/ijc.21478).
12. P. Qin, Y. Yang, X. Zhang, J. Niu, H. Yang, S. Tian, J. Zhu and M. Lu, *Nanomater.*, 8 (2018) 1.  
[doi:10.3390/nano8010004](https://doi.org/10.3390/nano8010004).
13. H. Chen, S. Fu, L. Fu, H. Yang and D. Chen, *Minerals*, 9 (2019) 1.  
[doi:10.3390/min9050264](https://doi.org/10.3390/min9050264).
14. D. Lewandowski, A. Olejnik and G. Schroeder, *Cent. Eur. J. Chem.*, 12 (2014) 233.  
[doi: 10.2478/s11532-013-0361-x](https://doi.org/10.2478/s11532-013-0361-x).
15. L. Bai-Jun, M. Qing-Lei, W. Hui and M. Qing-Min, *Acta Phys. Chim. Sin.*, 26 (2010) 3257.  
[doi: 10.3866/PKU.WHXB20101140](https://doi.org/10.3866/PKU.WHXB20101140).
16. M. D. Branković, A. R. Zarubica, T. D. Andjelković and D. H. Andjelković, *Adv. Technol.*, 6 (2017) 50.  
[doi:http://dx.doi.org/10.5937/savteh1701050B](http://dx.doi.org/10.5937/savteh1701050B)
17. Z. Salahshoor and A. Shahbazi, *Eur. J. Environ. Sci.*, 4 (2014) 116.  
[doi:http://dx.doi.org/10.14712/23361964.2014.7](http://dx.doi.org/10.14712/23361964.2014.7)
18. E. C. Santos, L. S. Costa, E. S. Oliveira, R. A. Bessa, A. D. L. Freitas, C. P. Oliveira, R. F. Nascimento and A. R. Loiola, *J. Braz. Chem. Soc.*, 29 (2018) 2378.  
[doi:http://dx.doi.org/10.21577/0103-5053.20180115](http://dx.doi.org/10.21577/0103-5053.20180115)