SYNTHESIS OF MESOPOROUS CARBON MATERIAL BY HARD TEMPLATE METHOD: APPLICATION TO REMOVAL OF DYE FROM AQUEOUS SOLUTION

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ABSTRACT

Ordered mesoporous carbon (OMC) was successfully synthesized by using hard template method with SBA-15 silica samples as templates and sucrose as carbon sources. The structural and textural properties of the synthesized sample was characterized by XRD, TEM, and N_2 adsorption-desorption Brunauer-Emmett-Teller (BET). The results showed that OMC was successfully synthesized with ordered structure, high surface area (1,126 m^2/g) and average pore width 4.46 nm. The effects of temperature and adsorbent dosage on MB adsorption were also investigated. The equilibrium adsorption amount (Q_e) of methylene blue onto OMC slightly decreases with increasing temperature and increases with increasing adsorbent dosage. Moreover, OMC sample exhibited high methylene blue adsorption capacity with Q_m of 385mg/g. OMC material was synthesized approach toward removal of methylene blue, exhibiting high adsorption capacity, thus holding a great promise for treatment of methylene blue in wastewater.

Keywords: *Ordered mesoporous carbon materials, SBA-15 template, hard template method, methylene blue, dye adsorption*

INTRODUCTION

Recently, the treatment of the environment contains toxic organic substances are concerned. Methylene Blue (MB), a typical cationic dye with high toxicity and potential carcinogenic effect on human health, can be a model compound for adsorption studies of organic contaminants in aqueous solutions due to its stability to heat, oxidizing agents as well as biodegradation [1].

Therefore, the removal of MB from the wastewater stream becomes important to the environment. Of the many methods that have been studied to remove the toxic pigments in water, the adsorption method is often known to be one of the most effective methods for removing toxic substances in the environment.

OMC is an advanced class of ordered mesoporous materials, combining the high porosity properties of mesoporous materials with the physico-chemical characteristics of

carbons. So, OMC is widely used in many applications such as gas storage [2], gas separation [3], catalysis [4], electrochemical energy storage [5] or adsorbent [6,7]. OMC is synthesized by hard-templating and soft-templating methods.

In this study, OMC material was synthesized by hard method and studied MB adsorption capacity and effect of different parameters. MB adsorption of OMC was evaluated according to Frendlich, Langmuir isotherm models.

EXPERIMENTAL

Synthesis of ordered mesoporous carbon material

SBA-15 silica following synthesis procedure was reported by Nie et al. [8]. OMC was synthesized by SBA-15 silica sample as templates and sucrose as carbon sources with sulfuric acid [9]. Briefly, 1g of SBA-15 was added to a solution obtained by dissolving 1 g of sucrose and 0.14 g of H_2SO_4 in 5g of H_2O. The mixture was placed in a drying oven for 6h at 100°C, and subsequently the oven temperature was increased to 160°C and

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maintained for 6h. The sample turned dark brown or black during the treatment in the oven. The silica sample, containing partially polymerized and carbonized sucrose at the present step, was treated again at 100 ^{o}C and 160°C using the same drying oven after added 1 g of sucrose, 0.14 g of H$_2$SO$_4$ and 5g of H$_2$O. The carbonization was completed by pyrolysis with heating to typically 800°C under nitrogen flow. The carbon-silica composite obtained after pyrolysis was immerged in HF 40% solution and then washed with H$_2$O before being washed with mixture of 50 vol% ethanol + 50 vol% H$_2$O. Final product was dried at 100°C for 3h.

Characterization

The powder X-ray diffraction (XRD) patterns of the samples were collected in a range angles from 0.5^o to 5° with a Shimadzu XRD-6100 analyzer using Cu K$_\alpha$ radiation (λ = 1.5417 Å). Transmission electron microscopy (TEM) was recorded using JEOL1010 instrument operating at 80 kV with magnification of 25,000 – 100,000. Surface area of sample was determined on Quantachrome Instruments version 3.0 at 77K and using nitrogen adsorbent.

Adsorption experiments

The methylene blue (C$_{16}$H$_{18}$N$_3$SCl, 95% of purity) was purchased from Merck (Germany). The adsorption of aqueous MB to OMC was conducted using batch adsorption tests. In this approach, batch experiments were carried out in a set of 250mL Erlenmeyer lasks, in which a 100mL of MB solution with initial concentrations in the range of 100 – 300 ppm was added. Equal masses (m) of adsorbent were added to the MB solutions (V). Adsorption capacity (Q$_t$) of MB is defined as follows:

$$Q_t = \frac{(C_0 - C_t).V}{m} \qquad (1)$$

where Q$_t$ is adsorption capacity of MB; V is solution volume (V = 0.1L); m is masses of

OMC; C$_0$ and C$_t$ (ppm) are initial and time t MB concentration.

Determine the remaining MB concentration on UV-Vis spectrophotometer (DR/4000U) - Department of Surface Chemistry, Institute of Chemistry, Vietnam Academy of Science and Technology (VAST).

Adsorption isotherms

Two empirical equations, Langmuir and Freundlich isotherm models, were often used to analyze the experimental data [3].

The Langmuir equation is expressed as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m.K_L} + \left(\frac{1}{Q_m}\right).C_e \qquad (2)$$

The Freundlich equation is expressed as follows:

$$\log Q_e = \log K_F + \left(\frac{1}{n}\right).\log C_e \qquad (3)$$

Where Q$_m$ and K$_L$ in the Langmuir equation represent the maximum adsorption capacity of adsorbents (mg/g) and Langmuir adsorption constant related to the free energy of adsorption, respectively. K$_F$ and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

RESULTS AND DISCUSSION

Physical and structural characterization of the mesoporous materials.

X-Ray Diffraction (XRD)

XRD patterns of SBA-15 and OMC samples are showed in figure 1.

The XRD pattern of the resulting OMC shows ordered mesostructures with p6mm symmetry, the presence of (100), (110) and (200) reflections, indicating that it has retained the ordered structure of its parent silica template. Structural shrinkage also results in poor resolution of the (110) and (200) diffraction peaks of the ordered mesoporous carbons [3].
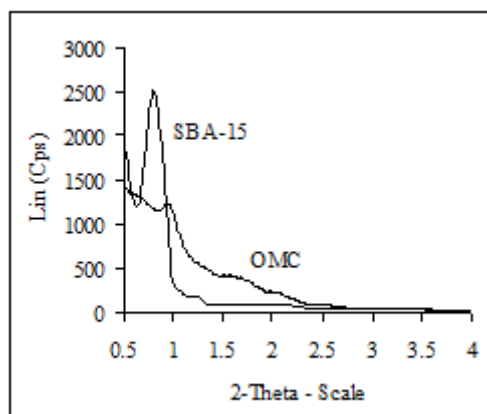
Fig.1. *XRD pattern of SBA-15 and OMC*

Transmission Electron Microscopy (TEM)

The morphology of the synthesized mesoporous sample was characterized by TEM and the result is presented in figure 2. The image confirms the results obtained from XRD. The ordered mesoporous carbon shows a ordered hexagonal structure.
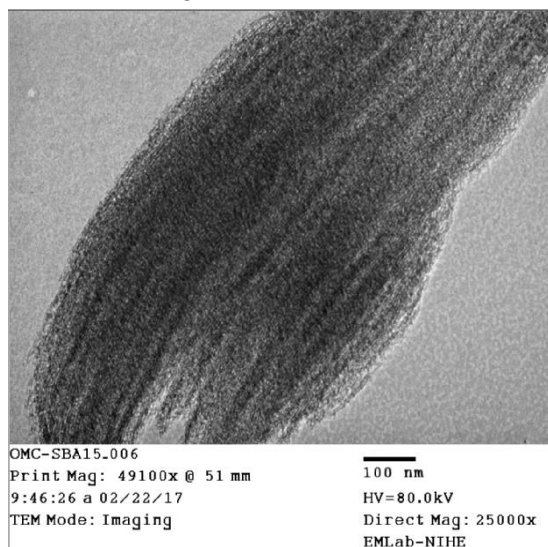

OMC-SBA15.006
Print Mag: 49100x @ 51 mm   100 nm
9:46:26 a 02/22/17   HV=80.0kV
TEM Mode: Imaging   Direct Mag: 25000x
                                 EMLab-NIHE

Fig.2. *TEM image of OMC*

N₂ Adsorption–Desorption Isotherm (BET)

N$_2$ adsorption–desorption isotherm and pore-sized distribution of OMC are presented in figure 3. As observed in figure 3, OMC showed the isotherm curves of type IV with the hysteresis loop, characteristic for capillary condensation which is typical for mesoporous material.
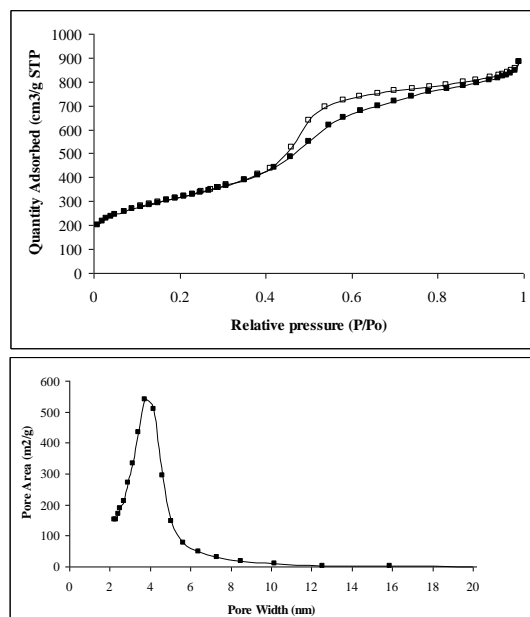

Fig.3. *N$_2$ adsorption–desorption isotherm and pore-size distribution of OMC*

Textural properties of samples are showed in table 1. As observed in table 1, OMC exhibited high surface area (1,126 m^2/g and pore width of OMC is narrow distributed with the average pore width of 4.46 nm.

Table 1. *Textural properties of samples*

Average pore width (nm)	Mesopore volume (cm^3/g)	Surface area (m^2/g)
4.46	1.255	1,126

Adsorption of MB onto the sorbents and effect of different parameters

The effect of temperature on the adsorption of MB onto OMC was investigated by adding 5 mg of the adsorbent into 100 mL of 100ppm MB and shaking the mixture for 6h at different temperatures of 23°C, 33°C and 43°C in a water bath. The results indicated that the equilibrium adsorption amount (Q_e) of MB onto OMC slightly decreases with increasing temperature (figure 4), indicating that the adsorption process is exothermic in nature. The value of Q_e slightly decreases from 236 to 215mgMB g^{-1} adsorbent by increasing temperature from 23°C to 43°C. The subsequent adsorption studies were performed at ambient temperature (25°C).

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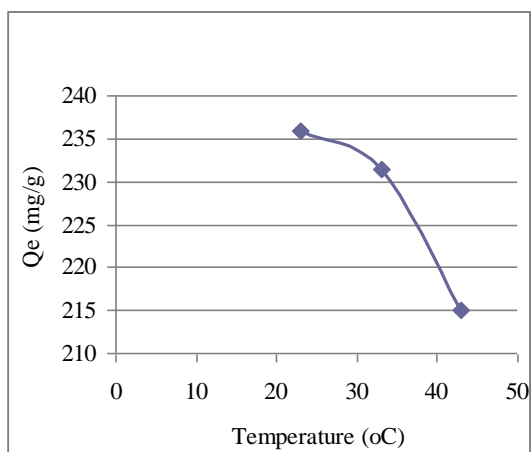
Fig.4. *Effect of temperature on the adsorption of MB by OMC in the range of 23 – 43°C (initial MB concentration - 100ppm; adsorbent dosage - 0.5 g/L; shakingtime - 6h)*
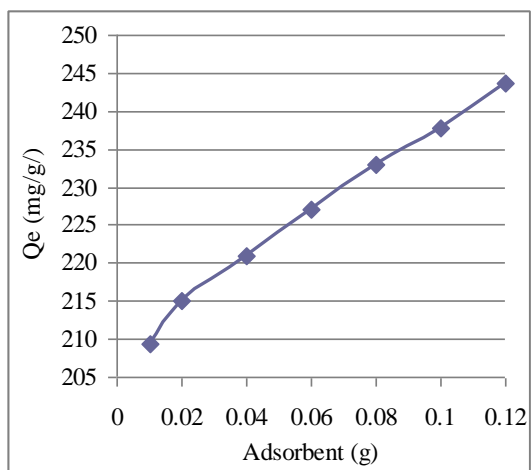

Fig.5. *Effect of the amount of adsorbent on MB adsorption capacity of OMC at 25°C (initial MB concentration - 100ppm; shaking time - 6h)*

The effect of adsorbent dosage (m) on the amount of MB adsorbed at equilibrium (Q_e, mg/g), was investigated by adding different weights of adsorbent (OMC) into 100 mL of 100ppm MB and shaking the mixture for 6h at ambient temperature. As can be seen in figure 5, Q_e increases by increasing m from 0.01 to 0.12g. The increase in the amount of Q_e can be attributed to the availability of greater surface area and more adsorption sites.

Adsorption Isotherms
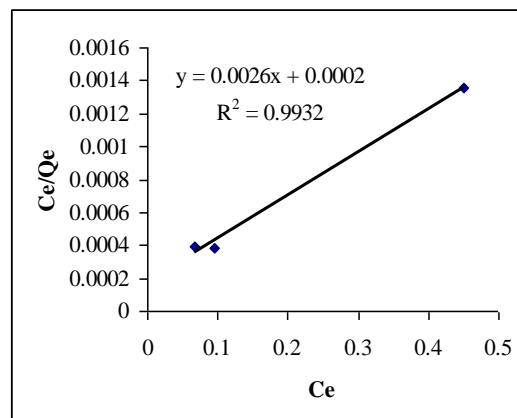
(a)
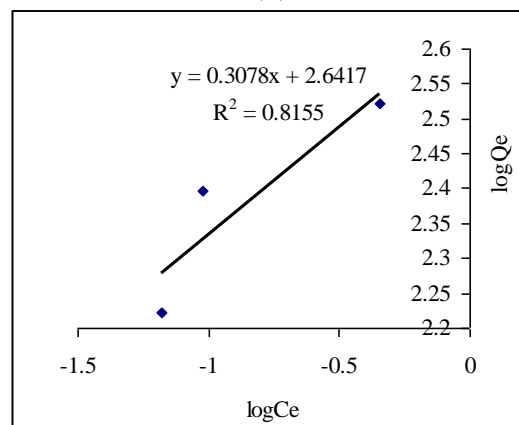
(b)

Fig.6. *Experimental adsorption data fitted to different isotherm models (a) Langmuir and (b) Freundlich (adsorbent dosage - 0.5 g/L; shaking time - 6h , temperature - 25°C)*

Figure 6a shows the Langmuir plot (C_e/Q_e versus C_e) for the adsorption data of MB onto OMC as well as the fitted results by linear regression analysis (solid line). The Langmuir isotherm shows a good fit to the adsorption data with regression coefficients (R^2) of 0.9932. The values of Q_m and K_L for the adsorbent, obtained from the slope and intercept of the linear plots, respectively, are presented in table 2. The maximum adsorption capacity (Q_m) was found to be 385mg/g at 25°C.

Figure 6b shows the Freundlich plots ($\log Q_e$ versus $\log C_e$) for the adsorption data and the fitting results.

Table 2. *Langmuir and Freundlich isotherm constants of OMC*

Langmuir isotherm		Freundlich isotherm	
Q_m (mg.g^{-1})	385	1/n	26
K_L (L.mg^{-1})	13	K_F [(mgg^{-1}) (mg^{-1})$^{1/n}$]	438
R^2	0.9932	R^2	0.8155

The parameters of the Langmuir and Freundlich models were calculated and given in table 2. As observed in table 2, the value of $R^2 = 0.9932$ for Langmuir model is higher than that of $R^2 = 0.8155$ for Freundlich model. This result was indicating that the Langmuir model fits much better than the Freundlich model for OMC material.

CONCLUSION

Ordered mesoporous carbons were successfully synthesized by using hard template method. From XRD, TEM and N$_2$ adsorption–desorption (BET) results, it revealed that the obtained OMCs showed high surface area (1,126 m^2/g) with uniform pores and large average pore width (4.46 nm). The equilibrium adsorption amount (Q_e) of MB onto OMC slightly decreases with increasing temperature and increases with increasing adsorbent dosage. OMC sample exhibited high MB adsorption capacity with Q_m of 385 mg/g. This result opens high application potential of OMC material as efficiency adsorbent in environmental treatment.

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TÓM TẮT
TỔNG HỢP VẬT LIỆU CACBON MAO QUẢN TRUNG BÌNH BẰNG PHƯƠNG PHÁP CỨNG: ỨNG DỤNG LOẠI BỎ CHẤT MÀU RA KHỎI DUNG DỊCH NƯỚC

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Cacbon mao quản trung bình trật tự (OMC) được tổng hợp thành công bằng phương pháp cứng với SBA-15 là chất tạo cấu trúc và đường saccarozơ là nguồn cacbon. Những đặc tính và cấu trúc của mẫu được đặc trưng bởi phương pháp XRD, TEM, BET. Kết quả cho thấy OMC được tổng hợp thành công với cấu trúc trật tự, diện tích bề mặt lớn (1.126 m^2/g) và độ rộng trung bình mao quản 4.46 nm. Ảnh hưởng của nhiệt độ và lượng chất hấp phụ đến khả năng hấp phụ xanh metylen cũng được nghiên cứu. Hơn nữa, vật liệu OMC thể hiện khả năng hấp phụ xanh metylen cao với Q_m bằng 385mg/g. Vật liệu OMC tổng hợp được hướng tới loại bỏ xanh metylen, thể hiện ở khả năng hấp phụ cao, hứa hẹn việc xử lý xanh metylen trong môi trường nước.
Từ khóa: *vật liệu cacbon mao quản trung bình, chất tạo cấu trúc SBA-15, phương pháp cứng, xanh metylen, hấp phụ chất màu.*

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