NANOCASTING OF ORDERED MESOPOROUS CARBON FROM POLYETHYLENE GLYCOL 400 AND ITS ADSORPTION POTENTIAL FOR PHARMACEUTICALS

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ABSTRACT

The feasibility of polyethylene glycol 400 (PEG-400) as a carbon precursor for the nanocasting of ordered mesoporous carbon is investigated in this work. The presence of ordered hexagonal meso structures in silica template and carbon replica have been confirmed through transmission electron microscopy and x-ray diffraction analysis. The total surface area of the synthesized carbon replica is 772 m^2/g. The average particle diameter measured at 1.5 µm is determined from scanning electron microscopy. A series of adsorption tests conducted at 30ºC with initial concentration of 200 mg/L on three different solutes (methylene blue, riboflavin, and chloramphenicol) has shown a promising potential of 80, 70, and 35% removal, respectively. A less hazardous, non-edible PEG-400 is therefore proposed as a promising alternative carbon precursor for ordered mesoporous carbon synthesis.

Keywords: nanocasting, ordered mesoporous carbon, adsorption.

1. INTRODUCTION

Producing mesoporous carbon with ordered structures through nanocasting remains a big challenge nowadays. The tailoring of intrinsic channel networks arrangement requires delicate chemistry approaches and in depth understanding on the mechanisms involved. A careful selection of parent template or mold to suit the desired final applications is very crucial in influencing the shape of the developed pore structures and networks. The template should have excellent pore orderness with sufficient surface area, high-temperature resistant for carbonization stage, and easy to remove from carbon replica. Among the common reported templates used for nanocasting of ordered mesoporous carbons include the Santa Barbara Amorphous (SBA) silica group (SBA-1, SBA-1 and SBA-16) and Mobil Composition of Matter silica group (MCM-41 and MCM-48) [1]. Often, an organic carbon precursor is mainly contacted to the solid template in a liquid state in order to maximize the carbon molecular occupation in the template volume. Currently, only limited substances have been successfully promoted as carbon precursors for the nanocasting process. For instance, glucose, sucrose, glycerol, resorcinol-formaldehyde have been tested earlier [1-4]. In order to encourage a greener and safer environment, it is believed that good carbon precursors should be inedible, low in toxicity, ease of handling and low cost. Therefore, an idea to manipulate a less toxic inedible PEG-400 has been brought forward and executed in this work. This work reports the findings related to materials characterizations and performance of ordered mesoporous carbon produced from PEG-400 to adsorb methylene blue, riboflavin, and chloramphenicol from aqueous solutions.

2. MATERIALS AND METHODS

2.1 Chemicals

The chemicals used include tetraethyl ortosilicate (TEOS), Si $(OC_2H_5)_4$ and a triblock copolymer, Pluronic 123, $(C_3H_6O.C_2H_4O)$ x. Sigma-Aldrich, Malaysia supplied all the reagent grade chemicals (purity ≥ 98%). Merck, Malaysia supplied a fuming 37 % hydrochloric acid. Polyethylene glycol 400 (PEG-400) was obtained from R&M Chemicals, United Kingdom. Fisher, Malaysia, supplied analytical grades of methylene blue (MB), riboflavin (Rb) and chloramphenicol (CPC).

2.1 Synthesis of hexagonal mesoporous silica and ordered mesoporous carbon

Synthesis of hexagonal mesoporous silica (HMS) was carried out by dissolving 12 g P-123 in 450 mL HCl solution (2.5 molar) until a clear mixture was obtained. A controlled thin flow TEOS (23 mL) was introduced to the mixture at 40ºC and stirred for 2 h or until a cloudy white solution was obtained. The mixture was left for aging in water bath shaker for 48 h at 40ºC with 100 rpm agitation speed. The white precipitation powder was recovered by vacuum filtration technique and left for drying. The dried white powder was then calcined in a muffle furnace at 550ºC with heating step of 1ºC/min and 4 h soaking time. The resultant white silica powder was kept in air-tight container for further use.

Ordered mesoporous carbon (OMC) was prepared through nanocasting method adding 1.0 g HMS to 5.0 g PEG-400 in a 100 mL ceramic crucible. A small amount of concentrated sulfuric acid was dropped into the mixture and mixed thoroughly at room temperature until the mixture changed into dark-brown color. The mixture was then placed in an oven at 100ºC for 24 h for partial carbonization and drying purposes. The mixture in powdery form was later undergone a thermal treatment at 800ºC (1ºC/min) with 2 h dwelling time using fabricated pyrolisis furnace. Nitrogen flow (50 cm^3/min) was kept

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constant throughout the process. The resultant carbon-silica composite was washed with 1.0 mol NaOH solution at elevated temperature to remove the silica template. Finally, the carbon sample obtained was filtered, washed and dried until further use.

2.3 Materials characterizations

Surface area properties of the silica and carbon particles were measured by using the surface area analyzer (Micromeritics ASAP 2010, USA). Nitrogen adsorption–desorption isotherm was obtained by admitting successive known volumes of nitrogen in and out of the sample and measuring the equilibrium pressure at -196ºC. Surface morphology was investigated by using scanning electron microscope (SEM Quanta FEG 450, USA). Textural images were captured through transmission electron microscopy (Philips TEM CM12, The Netherlands) technique. The X-ray powder diffraction (XRD) analysis was conducted in the 2θ range of 0.5-10° by using materials research diffract meter (PANalytical X'Pert PRO PW3040, The Netherlands).

2.4 Adsorption test

0.1 g of OMC was added into 200 mL conical flask filled with 200 mL MB, Rb and CPC solutions with initial concentration of 250 mg/L, respectively. The conical flasks was sealed and placed in a programmable water bath shaker at 30ºC for 24 h with shaking speed of 100 rpm. Changes in solutions concentrations were determined by using a UV-visible spectrophotometer (Shimadzu UV-1800, Japan). The amount of riboflavin adsorbed at a given period of time, q_t (mg.g^{-1}) and at equilibrium condition, q_e (mg.g^{-1}) were calculated according to the following equations (Equation 1):

$$q_t = \frac{V(C_0 - C_t)}{w} \tag{1}$$

Where C_0 is the initial solute concentrations (mg.L^{-1}). C_t is the solute concentration at a given time, t (mg.L^{-1}). V is the volume of solution (L) and w is the mass of adsorbent (g). A similar method has been described elsewhere [5].

3. RESULTS AND DISCUSSIONS

3.1 Physicochemical characteristics of materials

Figure-1 displays nitrogen adsorption-desorption isotherms of HMS and OMC, respectively. HMS demonstrates a H2 hysteresis loop (P/P$_o$ = 0.44 − 0.66), which is a common signature for materials with a complex pore structure, made up of interconnected networks consist of different pore sizes and shapes. While, OMC exhibits a capillary condensation, H4 hysteresis loop (P/P$_o$ = 0.55 − 0.99) attributed to slit-shaped pores of regular structure. The isotherm shape of type IV indicates OMC with a mesoporous type material. The total surface area of HMS and OMC is 596 and 772 m^2/g, respectively. Kruk et al. (2000) previously reported that a various selections of SBA-15 prepared at different conditions with surface area ranging from 400-870 m^2/g [6]. As for the carbon surface

area, the present observation is comparable to that of the previously reported synthesized ordered mesoporous carbon [7]. The total pore volume for HMS and OMC is 0.487 and 0.431 cm^3/g, respectively. Pore diameter measured from the nitrogen adsorption branch of Barrett-Joyner-Halenda (BJH) model is 36.53 and 49.88 Å for HMS and OMC, respectively. Figure-2 apparently shows narrow pore size distributions of both samples. TEM images on both silica template and its carbon replica revealed the presence of ordered macrostructures with the average pore opening size measured at 2.2 nm. Figure-3a (inset) displays a typical hexagonal pore shape of HMS in resemblance to the SBA-15 framework. TEM cross-sectional view of carbon replica displaying an array of short channel structures confirms an inverse replication of PEG-400 over HMS as a template (Figure-3b inset). A similar observation has also been reported by Tian and co-workers (2011) on the preparation of ordered mesoporous carbon using SBA-15 template and furfuryl alcohol/trimethylbenzene as the carbon source [8]. According to the report, the white points surrounded by dark lines were the projection of the tubular interiors of the silica template channels, which were not filled with the carbon.
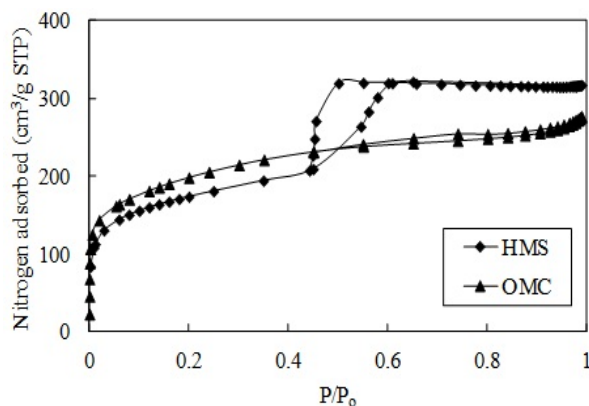

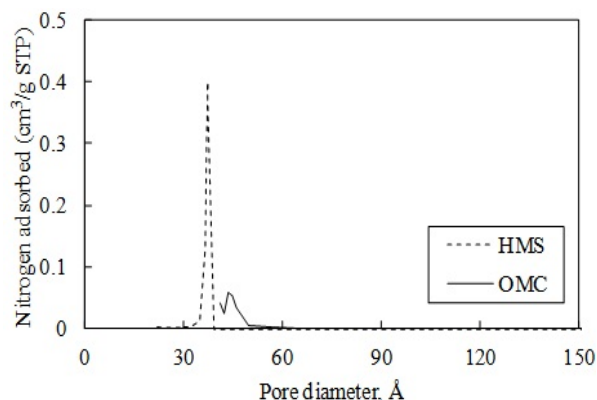**Figure-1.** Nitrogen adsorption-desorption isotherms of HMS and OMC.

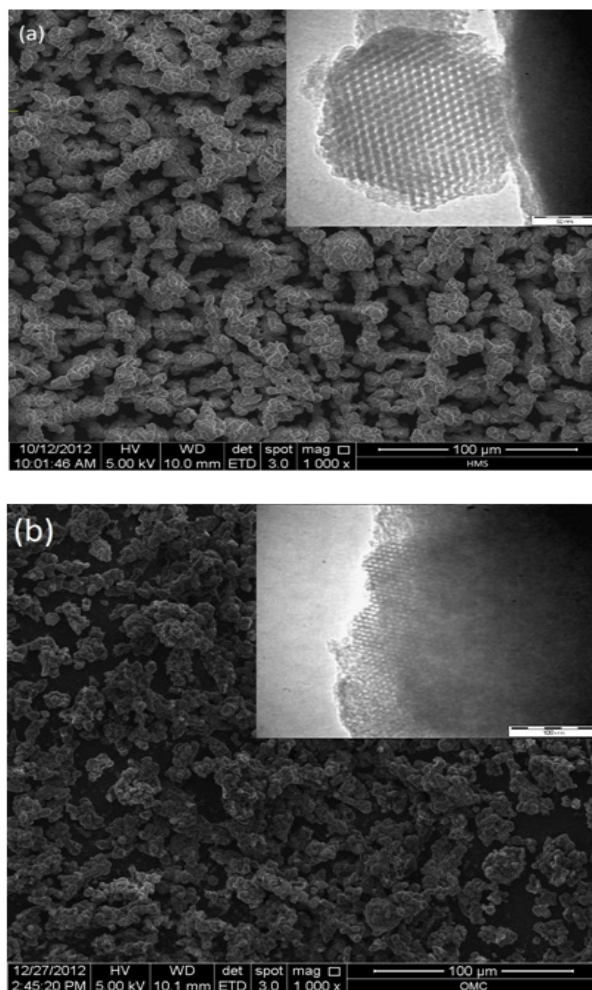**Figure-2.** Pore size distributions of HMS and OMC.

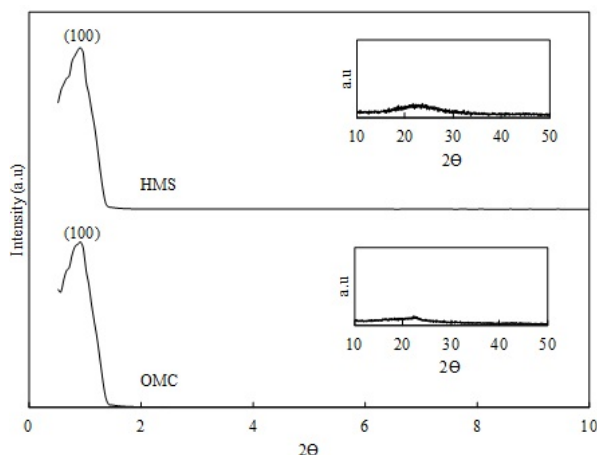**Figure-3.** SEM (1000x) and TEM (inset) of (a) HMS and (b) OMC.

Figure-4. XRD patterns of HMS and OMC.

Figure-4 shows the XRD pattern of HMS and OMC, respectively. The XRD shows an intense (100) reflection at 2θ = 0.9o attributed to periodically ordered channel macrostructures. A similar observation was reported on the preparation of ordered mesoporous carbon from organic-organic nanocomposite [9]. These two identical XRD patterns indicate a successful replication by the resulted carbon over HMS by holding up its original structure of the template and mesoporosity. The presence of amorphous phase in HMS and OMC is reflected by a weak broad peak around 2θ = 15-30o (inset). An interplanar distance in the (100) plane of HMS and S400-10 is 99.5 and 99.6 Å, respectively. The wall thickness, Wt was calculated by manipulating selected XRD and nitrogen adsorption data into the following equations (Eqs. 2-3):

$$W_t = a_o - D_p \tag{2}$$

$$a_0 = \frac{2d_{100}}{\sqrt{3}} \tag{3}$$

Where a_o (Å) represents the sum of pore diameter, D_p (Å) and the silica wall thickness (Å). Details of the theory and calculation techniques have been thoroughly discussed by Souza and co-workers (2006) on the synthesis hexagonal mesoporous silica of MCM-41 [10]. The calculated wall thickness for HMS and OMC is 78.36 and 65.13 Å, respectively. A similar wall thickness ranging from 45 to 68 Å has been reported for SBA-15, previously [11]. Summary of the physicochemical properties of the HMS and OMC is presented in Table-1.

Table-1. Surface area properties of HMS and OMC.

Samples	Characteristics					
	S_{BET}	d_{100}	D_p	V_p	V_m	W_t
HMS	596	99.5	36.53	0.487	0.09	78.36
OMC	772	99.6	49.88	0.431	0.136	65.13

S_{BET} - total surface area (m²/g), d_{100} - d (100) spacing value (Å), D_p - BJH pore diameter (Å), V_p - total pore volume (cm³/g), V_p - micropore volume (cm³/g), W_t - wall thickness (Å).

3.2 Adsorption performance

Figure-5 exhibits the adsorption profiles of the selected meso size solutes on the produced OMC, originating from PEG-400. The 'C' shape curves indicate a favorable adsorption process. During the experiment, OMC has removed up to 99, 88, and 43.5 % of MB, Rb and CPC, respectively, which is equivalent to the equilibrium adsorption capacity of 198, 175 and 87 mg/g corresponding to the given percentages. From the observation, a period of 150 min was approximated for MB and Rb to achieve the equilibrium. CPC demonstrates faster equilibrium time of 75 min compared to MB and Rb. A good removal of cationic MB and anionic Rb suggests OMC is a polarized adsorbent. However, further analysis on the carbon surface chemistry is needed in order to confirm the claim. Low removal of CPC is possibly due to the high competition between the cationic nitro group of

CPC and water molecules to form the H-bond with the active sites available on the OMC surface. Hence, water solubility increases with increasing polarity, thus decreases the adsorption potential of the solutes [12].
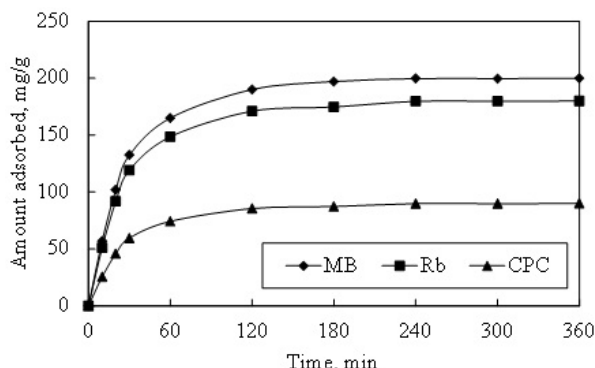

Figure-5. Adsorption profiles of MB, Rb and CPC on OMC at 30°C.

4. CONCLUSION

Non-edible PEG400 is a promising alternative carbon source for ordered mesoporous carbon synthesis. Utilization of PEG-400 offers a greener, safer and economical route for nanocasting of ordered mesoporous carbon due to low hazardous feature and relatively cheaper than the established carbon sources. The nanocasted ordered mesoporous carbon had shown a great potential for meso size bio molecules adsorption. This material is recommended for separation and purification of pharmaceutical products, drug delivery, biosensors and pharmaceuticals waste treatment.

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