

1 **Investigation of ordered mesoporous carbon potential as CO₂ adsorbent**

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6 **Abstract**

7 In this study, an investigation was carried out in order to determine the potential of ordered mesoporous
8 carbon including high ratio sucrose in its composition as a CO₂ adsorbent. Structural characterizations of
9 silica and carbon material were determined by using a scanning electron microscope (SEM), N₂
10 adsorption/desorption and X-ray diffraction (XRD) analysis. CO₂ adsorption capacities of developed
11 adsorbent at various temperatures (25°C, 35°C and 50°C) were determined by using a thermogravimetric
12 analyzer under CO₂ flow. The maximum adsorption capacity was obtained as approximately 2.27 mmol g
13 CO₂ g⁻¹ adsorbent which was remained almost the same in the desorption process. The first order reaction
14 kinetic model was well fitted with the experimental data. Arrhenius equation was used to calculate
15 activation energy which was obtained as -2.86 kJ mol⁻¹ indicating barrier-less type adsorption. Results
16 showed that ordered mesoporous carbon could be a potential source for an efficient and low-cost
17 adsorbent for CO₂ capture.

18
19 **Keywords:** Ordered mesoporous carbon; CO₂ adsorption/desorption; kinetics

20 1. Introduction

21 In recent years, greenhouse gases have become one of the most concern issues [1]. The main factors of
22 increasing greenhouse gas emission are economic and population growth. The environment has been
23 affected negatively by the gas emissions such as increased global temperatures (0.12°C per decade since
24 1951), ocean acidification (26% increase in acidity since 1750), and rising average sea levels (0.19 m
25 since 1901) [2]. At the same time, if it doesn't take precaution for this, it is estimated that the global
26 temperature will increase by 1-5°C in 2050 [3, 4]. One of the main components of greenhouse gases is
27 CO₂ and it is significantly produced from anthropogenic sources and fossil fuel combustion [5, 6]. Also, it
28 is reported that CO₂ contributes 60% of the total global warming caused by all greenhouse gases [7]. For
29 all these reasons, researchers pay attention to CO₂ capture. Solvent absorption, pressure and temperature
30 swing adsorption, membrane separation and cryogenic distillation have also been used to capture CO₂ [8-
31 10]. Nevertheless, some CO₂ capture processes have serious problems, such as energy penalties [11],
32 economic and environmental drawbacks [12, 13] and amine waste during operation [14]. To overcome
33 such problems, the development of solid adsorbents to CO₂ capture has come to the prominence [15]. A
34 large variety of adsorbents may be used for CO₂ captures, such as zeolites, microporous silicates,
35 aluminum phosphates, carbons, other porous oxides, metal-organic frameworks (MOFs), amine-grafted or
36 impregnated silica [2, 16].

37 Solid adsorbents are very suitable for adsorption of CO₂ owing to high adsorption capacity, fast
38 adsorption rate, and good stability [17]. One of the solid adsorbents is porous carbon materials have been
39 attracting lots of awareness as potential large-scale adsorbents because of the many advantages such as
40 well-ordered structure, high surface area, large tunable and uniform mesoporous size, high mechanical
41 strength and good hydrothermal stability at extensive temperature ranges [18-21]. Carbons must have
42 open pores to be accessible for the CO₂ molecules. Ryoo and co-workers [22] prepared a new family of
43 mesoporous carbons to represent as the CMK series. These carbon materials have a well-ordered pore
44 structure with the larger surface area [23]. All of this properties made CMK series excellent applicant for
45 hydrogen storage, gas separation, electrochemistry, catalysis, and adsorption [24-26]. *Li and et al.* (2017)
46 studied on CO₂ sorption over activated mesoporous carbon (AMC) and metal oxides (CeO₂, CuO, Mn₃O₄
47 and NiO) modified AMC with different pressure. The best result of CO₂ adsorption was 4.66 mmol/g at
48 273 K and 1 bar by using pure AMC as an adsorbent [27]. *Chomiak and et al.* (2017) investigated that

49 CO₂ adsorption on microporous granular activated carbons (GACs) that has been prepared by KOH
50 activation of walnut shell-based carbons. Carbons showed very high CO₂ adsorption, at 273 K up to 7.2
51 and 18.2 mmol/g under 1 and 30 bar, respectively[28]. *Ma et al.* (2018) studied CO₂ capture with
52 nanoporous carbons materials which was prepared by using a metal-organic framework (MOF-5) as a
53 template. The highest CO₂ adsorption capacity was obtained by nanoporous carbon that carbonized at
54 900°C (3.70 mmol/g at 0°C (1 atm)) [16]. In the study of *Pham et al.* (2016) nano-zeolite was evaluated
55 for its potential use in CO₂ capture via temperature swing adsorption. As a result of the experiments, the
56 best adsorption capacity of CO₂ by nano-zeolite was 4.81 mmol/g at a temperature of 20 °C and at a
57 pressure of 1 atm[8]. *Lashaki et al.* (2018) examined the impact of the support pore structure on the CO₂
58 adsorption performance of triamine-tethered SBA-15 silica. Large-pore supports exhibited the highest
59 surface density of amine groups (up to 35 μmol/m²) and highest CO₂ uptakes (up to 1.88 mmol CO₂/g)
60 [2].

61 In most of the previous studies, adsorption isotherms of CO₂ adsorbents have been investigated and their
62 adsorption capacities have been examined by various characterizing technics. However, there are few
63 studies on CO₂ adsorption kinetics of such adsorbents. It is critical to examine adsorption kinetics, to
64 better understand the events that occur during the adsorbent-goal material reaction, and also to estimate
65 the time required to complete the adsorption process. Also, information on adsorbent characteristics and
66 reaction kinetics is important for proper adsorbent selection, reactor sizing and process optimization.
67 Thus, in this work we have carried out a comprehensive study both on CO₂ adsorption on to CMK-3
68 including characterization and kinetics.

69 In this study, it was carried out for the potential of the ordered mesoporous carbon to be used in carbon
70 dioxide removal. SBA-15 was used as a template to synthesize ordered mesoporous carbon material,
71 CMK-3, for CO₂ capture. Characterization of the adsorbent was carried out with different analytical
72 instruments such as BET (Brunauer–Emmett–Teller), SEM (Scanning Electron Microscope), XRD (X-ray
73 powder diffraction) and TGA (Thermogravimetric Analyzer). In addition, the mechanism of adsorption
74 reaction was investigated and related kinetic parameters were calculated.

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78 2. Materials and Methods

79 2.1. Materials

80 Sucrose (C₁₂H₂₂O₁₁), pluronic 123 (P123), sulfuric acid (H₂SO₄) and hydrochloric acid (HCl) was
81 supplied by Sigma-Aldrich. Tetraethylorthosilicate (TEOS) was purchased from Sigma-Aldrich with 97%
82 purity. Hydrofluoric acid (HF) was supplied by Merck. The purity of hydrofluoric acid is 40%.

83 2.2. Synthesis of adsorbent

84 SBA-15 was synthesized according to Zhao et al. (1998) [29]. For the synthesis of CMK-3, sucrose
85 (C₁₂H₂₂O₁₁), sulfuric acid and deionized water were used as a carbon source, acid solution, and solvent,
86 respectively. CMK-3 was synthesized according to Jun et al. (2000)[30]. In briefly, 1.25 g sucrose, 5 g of
87 deionized water and 0.14 g H₂SO₄ were stirred until a homogeneous solution was formed. 1 g of SBA-15
88 was added to this solution and continued to stir. The mixture was placed aged in a furnace at 100°C for 6
89 hours and the furnace temperature was increased to 160°C and maintained for 6 hours. 0.8 g sucrose, 0.08
90 g H₂SO₄ and 5 g of deionized water were added to this solution and were treated again for the same
91 process (step 2). The resulting material was milled and carbonized in an inert atmosphere at 900°C for 3
92 hours at 7°C/min as a heating rate. After carbonization, the material was washed with HF and ionized
93 water and dried overnight.

94 2.3. Characterization of adsorbent

95 The surface area, pore size, pore size distribution and pore volume values of synthesis samples were
96 determined by using nitrogen adsorption/desorption isotherms. Nitrogen adsorption/desorption isotherms
97 were studied by using Quantachrome Corporation, Autosorb.

98 Silica and carbon structures were investigated to use STOE IPDS II Model X-ray diffraction device. X-
99 ray diffraction pattern of the synthesized sample, the step in the range of 0.02 and 0.025 (2θ/s) CuKα
100 beam having a wavelength of 0.15406 nm were obtained. The characteristic peaks of silica and carbon
101 were determined at 2θ between 1°-10°. Unit cell parameter (a₀), d100 spacing values (d₁₀₀) and pore wall
102 thickness (δ) for SBA-15 and CMK-3 were calculated by using equation (1), equation (2) and equation
103 (3), respectively. In equation (3), dp is pore diameter which is calculated by using the BJH method.

$$104 \quad d_{100} = \frac{n\lambda}{2\sin\theta} \quad (1)$$

105 $a_0 = \frac{2d_{100}}{\sqrt{3}}$ (2)

106 $\delta = a - 0,95 \times dp$ (3)

107 The morphologies of all the materials were observed using a scanning electron microscopy (SEM). The
108 surfaces of silica structures were plated with a thin layer of gold-palladium before inspection under SEM.
109 The SEM analysis was conducted with JEOL JSM-7001FTTSL LV SEM machine.

110 2.4. *CO₂ adsorption experiments*

111 CO₂ adsorption capacity was determined by DTA-TG Analysis unit (Shimadzu, Japan) (Creamer et al.,
112 2016). A sample weight of carbon approximately 20 mg was placed into an alumina sample pan. The
113 placed sample was dried at 393 K for 1 h in a nitrogen atmosphere to potential volatile components out of
114 the sample and then cooled down to room temperature. Nitrogen gas flow rate was 50 mL/min for both
115 heating and cooling. When the system was at equilibrium, the CO₂ gas stream was switched on at a rate of
116 50 mL/min for 3 h. The adsorption capacity in percent was computed from the weight change of the
117 sample in the TG adsorption process.

118 2.5. *Kinetic studies*

119 The CO₂ adsorption kinetics onto carbon adsorbent can be described using various kinetic model such as
120 pseudo-first order (Eq. 4) and pseudo-second order (Eq. 5) model [31].

121 $\frac{dq_t}{dt} = k_1 \times (q_e - q_t)$ (4)

122 $\frac{dq_t}{dt} = k_2 \times (q_e - q_t)^2$ (5)

123 Where q_t (mg g⁻¹) and q_e (mg g⁻¹) are the concentrations of CO₂ adsorption at time t and at equilibrium,
124 respectively, k_1 and k_2 (g mg⁻¹ s⁻¹) is the first and second-order adsorption rate constants.

125 The activation energy must be minimum value in order to facilitate the adsorption process. The activation
126 energy can be calculated using the Arrhenius equation shown in Equation (6) [32].

127 $\ln k = \ln A - \frac{E_a}{RT}$ (6)

128 According to Equation (6), k_l is the rate constant, A is the temperature impact factor, E_a is the activation
129 energy for adsorption (J/mol), R is the gas constant (8.314 J/mol K) and T is the adsorption temperature in
130 K.

131 3. Result and Discussion

132 3.1. Characterizations of carbon materials

133 The ordered pore structure, surface area and morphological structure of the synthesized adsorbent were
134 determined by XRD, nitrogen adsorption/desorption isotherm and SEM, respectively.

135

136 3.1.1. N_2 adsorption/desorption

137 The textural parameters of SBA-15 and CMK-3 samples are investigated using N_2 adsorption/desorption
138 technique. The textural parameters of these samples including the specific surface area, specific pore
139 volume, and average pore size are summarized in Table 1. The specific surface area and total pore volume
140 of the CMK-3 are 1360 m²/g and 1.167 cm³/g, respectively. These results are consistent with the literature
141 [1, 33].

142 Figure 1 shows the N_2 adsorption/desorption isotherms and pore distributions of samples. The synthesized
143 SBA-15 and CMK-3 have been shown to exhibit Type IV isotherm behavior in the BDDT (Brunauer-
144 Deming-Deming-Teller) classification as in the literature [34, 35]. According to Figure 1.a, SBA-15 and
145 CMK-3 samples prove to have a mesopore structure. It also shows that in addition to mesoporosity, the
146 structures also have microporosity. From the adsorption/desorption isotherms, the hysteresis loop for the
147 SBA-15 and CMK-3 samples are observed at partial pressure values in the range of 0.65-0.80 and 0.45-
148 0.6 for P/P₀, respectively. This type of hysteresis (H1 hysteresis) shows that the structure has a cylindrical
149 structure [36]. The sharp increase and decrease in the hysteresis region is indicative of the narrow pore
150 size distribution in accordance with the pore size distribution shown in Figure 1b. The pore size
151 distributions shown in Figure 1.b are performed by the BJH method for mesopore and SF method for
152 micropore. The average pore size of CMK-3 is 2.03 nm.

153 3.1.2 Small Angle X-Ray Diffraction

154 Figure 2 shows the small angle powder XRD patterns of SBA-15 and CMK-3 samples. The SAXS
155 patterns of SBA-15 show the dominant signal peak corresponding to the (100) plane and two small

156 diffraction peaks at higher angles (110) and (200) plane, characteristic of a well-defined hexagonal 2D
157 structures of P6mm symmetry [37, 38]. CMK-3 was obtained from pore filling of SBA-15 and uniform
158 hexagonal carbon rods were formed. The CMK-3 sample provides a diffractogram with a dominant peak
159 corresponding to the (100) plane, characteristic of these kinds of ordered mesoporous carbons [39]. This
160 shows that CMK-3 successfully replicate SBA-15 templates. The patterns for both SBA-15 and CMK-3
161 indicate that they are ordered mesoporous materials with well-defined pore geometry.

162 Unit cell parameter (a_0), d100 spacing values (d100) and pore wall thickness (δ) of all materials are given
163 in Table 2. The wall thickness of the SBA-15 and CMK-3 sample was calculated at 8.91 nm and 10.38
164 nm, respectively. It was found to be consistent with the wall thickness (3-9 nm) specified in the literature
165 [29, 40].

166 3.1.3. SEM images

167 The morphology of SBA-15 and CMK-3 are illustrated in Figure 3. SBA-15 structures are formed
168 homogeneously. SEM images have proven that CMK-3 is synthesized without change of the surface
169 morphology of SBA-15. SBA-15 and CMK-3 structures have rod-type morphology. The obtained SEM
170 images of SBA-15 and CMK-3 are good agreement with literature [41, 42]. EDX analysis of these
171 materials shows that the template has only silica for SBA-15 and the CMK-3 sample has only carbon,
172 confirming the success of the synthesis.

173 3.2. Kinetic studies of CO₂ adsorption on the carbon material

174 The TGA data on the CO₂ adsorption capacity of CMK-3 at 25 °C, 35 °C and 50 °C are shown in Figure 4.
175 It has been found that different CO₂ adsorption capacities at various temperatures. Because of CO₂
176 adsorption is an exothermic reaction, lower temperature is most suitable for CO₂ adsorption, The highest
177 adsorption capacity is obtained at 25 °C as approximately 2.27 mmol CO₂/g adsorbent. This indicates that
178 the higher driving force at 25 °C. As seen from Table 3, the adsorption capacity of the produced adsorbent
179 is within the range of previously reported ones. Thus it can be said that this type of adsorbent have a
180 potential for CO₂ capture processes.

181 CO₂ adsorption kinetics is determined by using different adsorption kinetic models such as pseudo-first-
182 order and pseudo-second-order. The pseudo-second-order model poorly fits into the kinetic data in which
183 low R^2 values were obtained. For this reason, the pseudo-first-order model can describe the adsorption

184 process of CO₂ on carbon adsorbent. Kinetic parameters at various temperatures are given in Figure 5a.
185 Pseudo-first order fits the CO₂ adsorption at all temperatures with high regression coefficient values
186 (>0.90). With the increase in temperature, decrease in rate constant which indicates an exothermic
187 process. The rate constant at 25°C, 35°C and 50°C are 0.0030103 s⁻¹, 0.0028958 s⁻¹ and 0.0027798 s⁻¹,
188 respectively.

189 The *lnk* has been plotted versus the inverse of temperature (1/T) to determining the activation energy at
190 Figure 5b. The value of activation energy is found -2.86 kJ/mol. The activation energy is negative
191 because the reaction rate decreases as the temperature increases. CO₂ adsorption with negative activation
192 energy is categorized as barrier-less adsorption. This adsorption process depends on the capture of CO₂
193 molecules in a potential well.

219 In this case, the probability of collision of CO₂ molecules decreases as the temperature increases [43].
220 The activation energy value of different adsorbents is given in Table 4. The activation energy of CMK-3
221 for CO₂ adsorption showed similarity with literature.

222

223 3.3. CO₂ Desorption on the carbon material

224 Reusability is one of the most important parameters for adsorbents. For this reason, the reusability of
225 CMK-3 for CO₂ adsorption is also studied at 25°C. Desorption process carried out an inert atmosphere
226 (N₂ flow) after CO₂ adsorption. This adsorption/desorption cycle was repeated two times and
227 distinguished variety are not observed in the CO₂ desorption or adsorption. As seen in Figure 6, similar
228 curves for both fresh and regenerated adsorbents and this indicates that the CO₂ adsorption capacity is the
229 almost the same. Therefore, CMK-3 can be reported as fast, easily, and completely regenerated over
230 multiple cycles without noticeable loss of adsorption capacity.

231 4. Conclusion

232 In this study, CMK-3 has been synthesized and characterized in order to evaluate the potential of ordered
233 mesoporous carbon as a CO₂ adsorbent. According to the characterization, CMK-3 was successfully
234 synthesis from pore filling of SBA-15. The adsorption capacity reduced with increase in temperature. The
235 highest adsorption capacity is obtained at 25°C as approximately 2.27 mmol CO₂/g adsorbent. Kinetic
236 parameters were evaluated with pseudo-first order kinetics where a negative value of activation energy
237 obtained indicating barrier-less type CO₂ capture process. The desorption performance of the adsorbent

238 was almost same the adsorption capacity. Results showed that ordered mesoporous carbon, CMK-3, has
239 a potential in efficient CO₂ adsorbent.

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373 **Table List**

374 **Table 1** Textural properties of SBA-15 and CMK-3

375 **Table 2** Unit cell parameter (a_0), d100 spacing values (d100) and pore wall thickness (δ)

376 **Table 3** Comparison of adsorption capacities

377 **Table 4** Activation energy of CO₂ adsorption for various adsorbent

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378 **Table 1** Textural property of SBA-15 and CMK-3

Adsorbents	BET Surface Area (m²/g)	Total Pore Volume (cm³/g)	BJH Method Average Pore Size (nm)	SF Method Average Pore Size (nm)
SBA-15	753	1.285	3.9	0.47
CMK-3	1360	1.167	2.03	0.46

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Table 2. Unit cell parameter (a_0), d100 spacing values (d100) and pore wall thickness(δ)

Adsorbents	d (nm)	a (nm)	δ (nm)
SBA-15	10.63	12.61	8.91
CMK-3	10.64	12.28	10.38

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382 **Table 3.** Comparison of adsorption capacities with literature

Material	Condition	Capacity (mmol/g)	Reference
Activated carbon	273 K and 1 bar	4.66	[27]
PEHA-loaded SBA-16	343 K and 1 atm	2.1	[44]
KOH activated walnut shell-based carbons	273 K and 1 bar	7.2	[28]
Metal-organic framework	273 K and 1 atm	3.70	[16]
Nano zeolite	293 K and 1 atm	4.81	[8]
Nano structured carbon	303 K and 1 atm	1.5	[45]
Amine activated kenaf		2.086	[46]
Palm activated char	303 K and 1 bar	1.66	[47]
Al salt activated cottonwood	298 K and 1 bar	1.61	[5]
CMK-3	298 K and 1 atm	2.27	<i>This study</i>

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385 **Table 4** Activation energy of CO₂ adsorption for various adsorbent

Adsorbent	Activation Energy (kJ/mol)	References
Activated Carbon	-2.28	[48]
Thermally treated graphene nanosheets	-7.21	[49]
Amine functionalized KIT-6*	-6.56	[50]
CMK-3	-2.86	In this study

386 * CO₂ concentration (vol %60)

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387 **Figure List**

388 **Figure 1 (a)** N₂ adsorption/desorption isotherms **(b)** Pore distributions of SBA-15 and CMK3

389 **Figure 2** XRD Patterns of SBA-15 and CMK-3

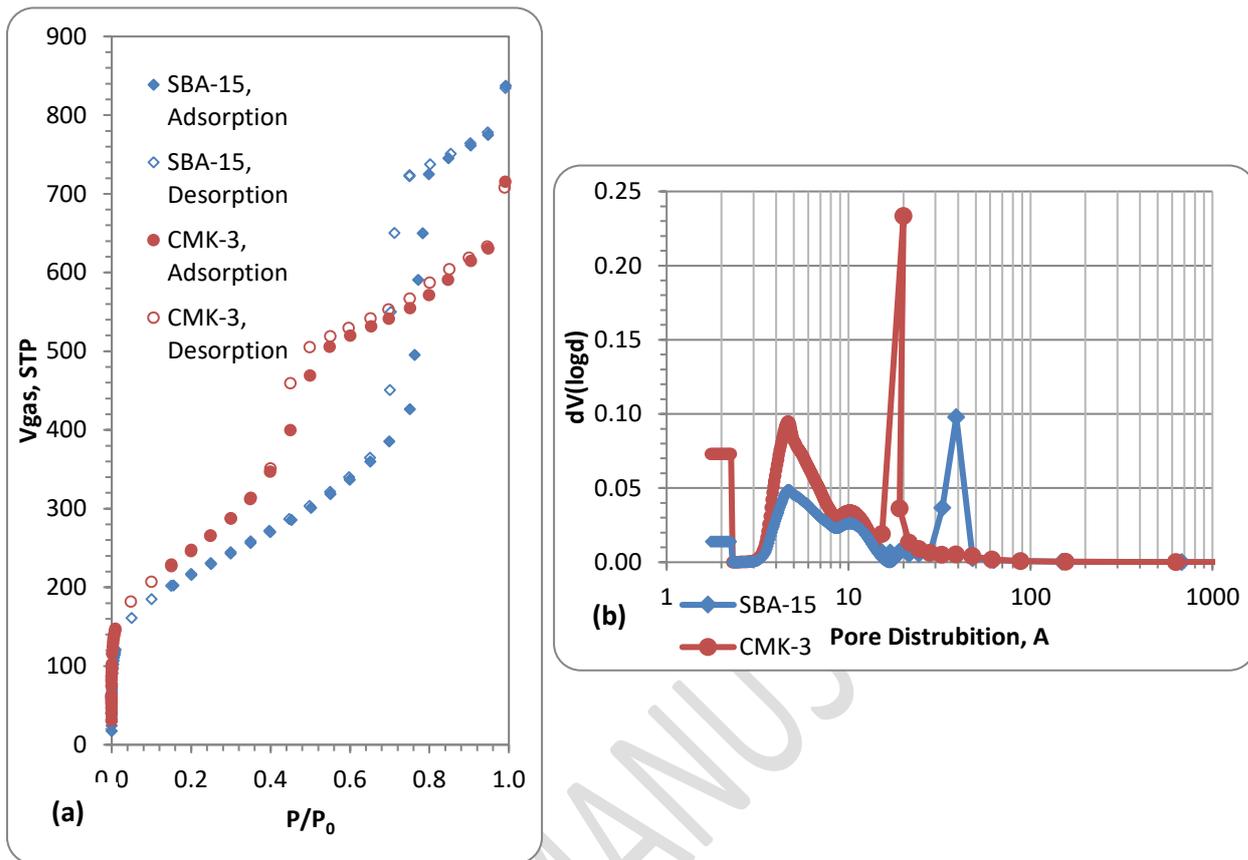
390 **Figure 3** SEM images of (a) SBA-15 and (b) CMK-3

391 **Figure 4** CO₂ adsorption capacity of CMK-3 at various temperatures

392 **Figure 5 a)** Kinetic plot of pseudo first order model with various temperatures **b)** Arrhenius plot for
393 activation energy calculation

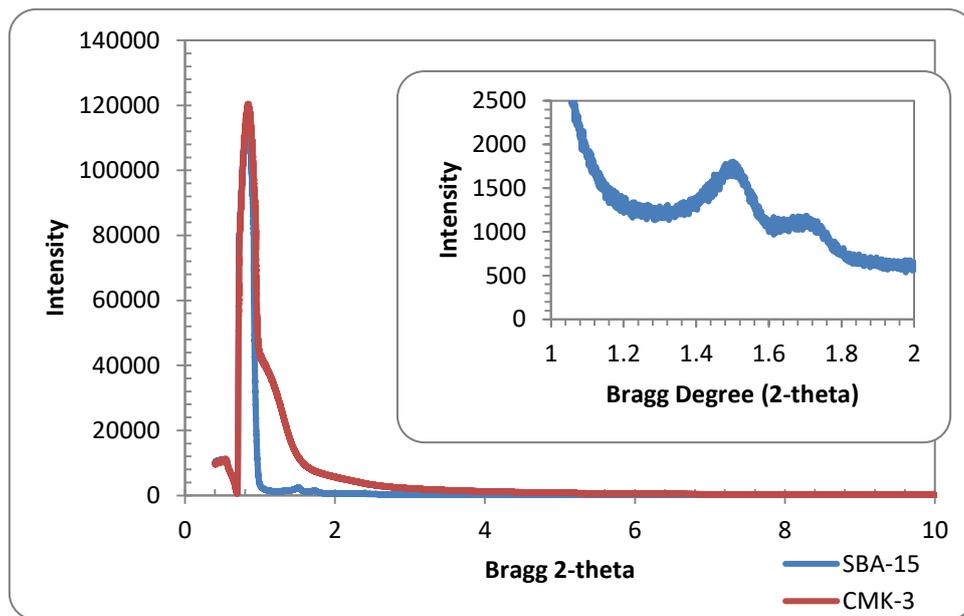
394 **Figure 6** CO₂ adsorption and desorption capacity of CMK-3

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Figure 1 (a) N_2 adsorption/desorption isotherms (b) Pore distributions of SBA-15 and CMK-3

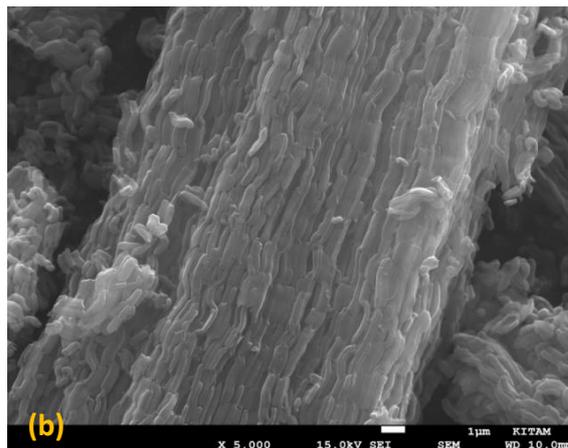
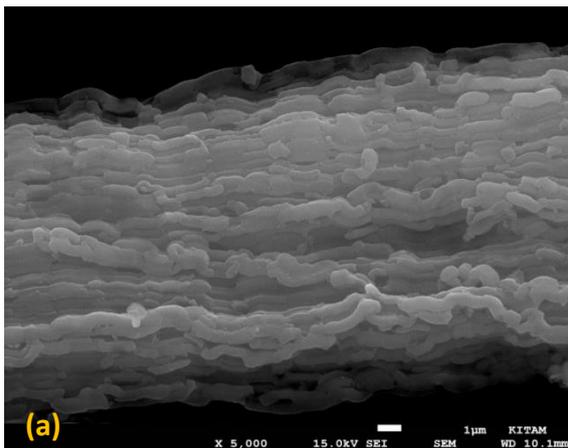


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Figure 2 XRD Patterns of SBA-15 and CMK-3

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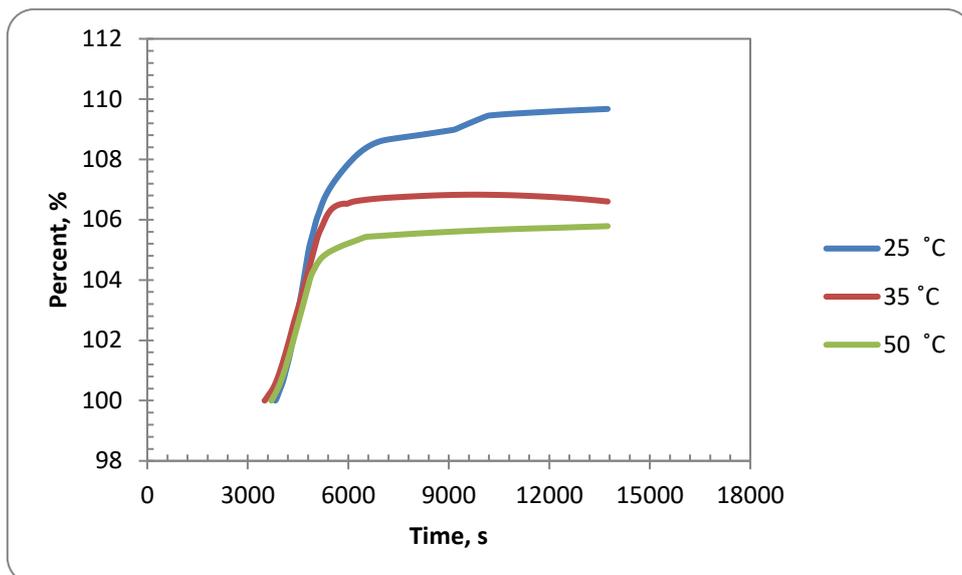


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Figure 3 SEM images of (a) SBA-15 and (b) CMK-3

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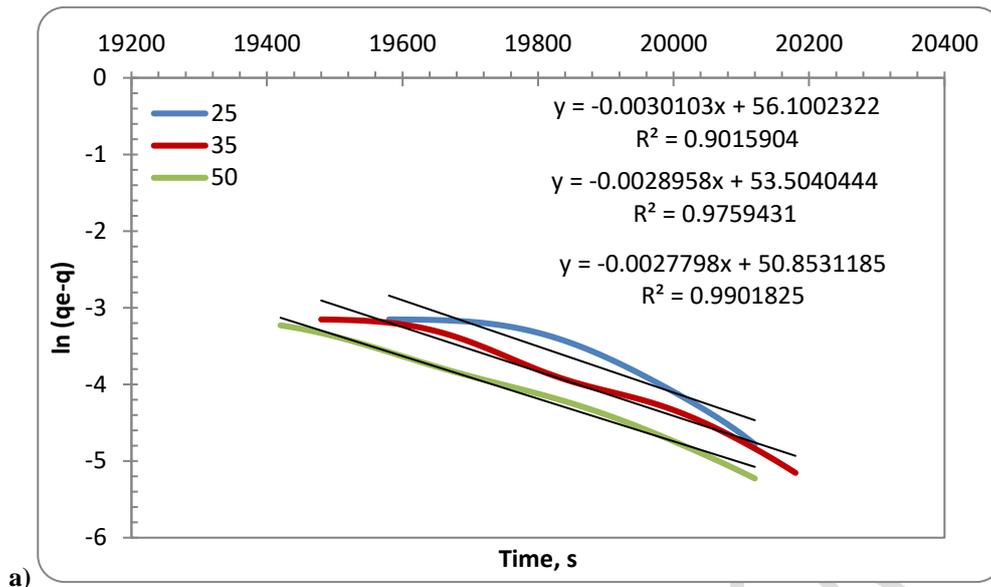
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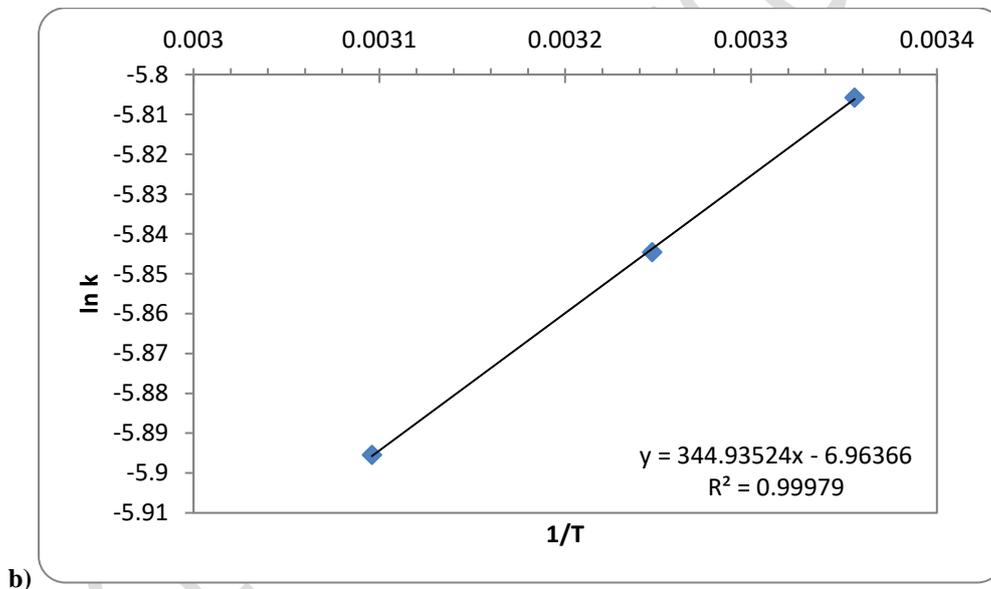
Figure 4 CO₂ adsorption capacity of CMK-3 with various temperatures

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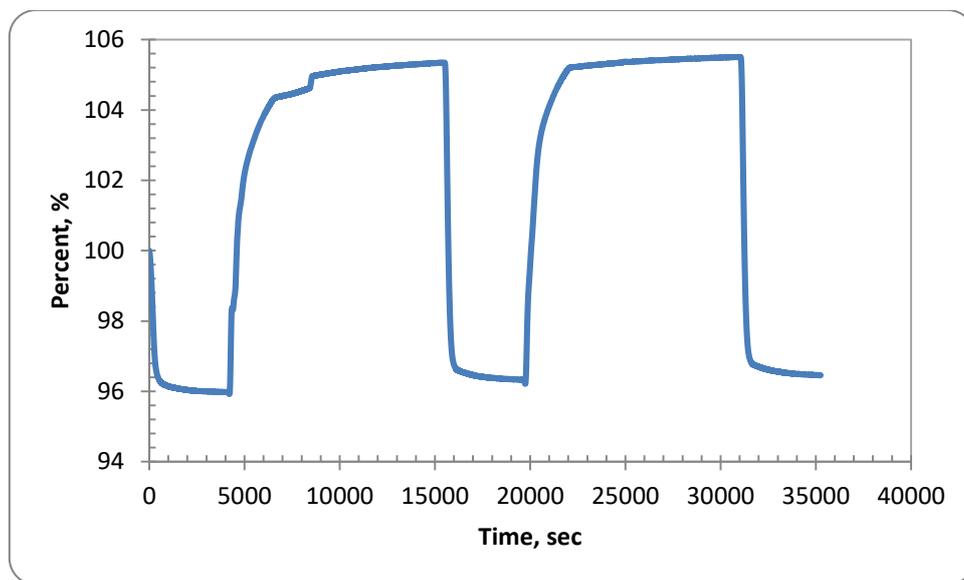
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Figure 5 a) Kinetic plot of pseudo first order model with various temperatures **b)** Arrhenius plot for

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activation energy calculation

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Figure 6 CO₂ adsorption and desorption capacity of CMK-3

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