

Mesoporous carbon supported MgO for CO₂ capture and separation of CO₂/N₂

Harshitha Burri*, Rumana Anjum*, Ramesh Babu Gurram**, Harisekhar Mitta***, Suresh Mutyala****, and Madhavi Jonnalagadda*,†

*Department of Chemistry, Government Degree College for Women, Karimnagar, Telangana, India

**Catalysis Laboratory, Indian Institute of Chemical Technology, Hyderabad-500007, India

***State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian-116023, China

****Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Guangdong 515063, China

(Received 3 February 2019 • accepted 23 July 2019)

Abstract—Mesoporous carbon derived from pongamia pinnata fruit hulls was used as support to incorporate magnesium oxide for the study of CO₂ adsorption and separation of CO₂/N₂. All synthesized adsorbents were characterized by PXRD, N₂ adsorption-desorption isotherms, Raman and SEM with EDX techniques. Characterization results revealed the existence of magnesium oxide on mesoporous carbon. CO₂ adsorption on MgO incorporated mesoporous carbon was higher than bulk mesoporous carbon, due to the electrostatic interaction between magnesium oxide and CO₂. High CO₂ adsorption capacity 1.68 mmol/g was obtained for 10 wt% MgO incorporated mesoporous carbon at 298 K, 1 bar compared to remaining loadings, because of the high content of MgO. However, the N₂ adsorption capacity decreased with the increase of MgO content due to a decrease in surface area and no interaction of the N₂ molecule with the adsorbent. The selectivity of CO₂/N₂ was higher on 10 wt% MgO incorporated mesoporous carbon and the value was 40. The heat of CO₂ adsorption was 36 KJ/mol at low coverage of CO₂, and CO₂ adsorption capacity was constant in each adsorption cycle over the same adsorbent.

Keywords: MgO, Mesoporous Carbon, CO₂ and N₂ Adsorption, Selectivity, Heat of CO₂ Adsorption

INTRODUCTION

Carbon dioxide is one of the environmental pollutant gases causing global warming. It is produced by the consumption of fossil fuel, high growth of petrochemical, automobile industries, and power plants [1]. CO₂ concentration can be minimized by the development of an alternative energy source until commercial energy sources have to use for the production of energy. Carbon dioxide in the atmosphere can be reduced by carbon capture and separation. In power plants, a large amount of CO₂ is liberated that is absorbed by the use of liquid amine solutions. However, a large amount of energy is required for the regeneration, and volatile organic compounds are liberated which damage the pipeline system [2]. Adsorption is one of the best techniques to reduce the concentration of CO₂. In this process, energy consumption and damage to the pipeline system are less. So far, commercially available carbon materials [3], zeolites [4], clays [5] and silica materials [6] have been used for CO₂ capture and separation.

Activated carbon is one of the most abundant carbon materials [7]. However, large-scale synthesis is hindered because of the non-renewable source. Porous carbon was synthesized from renewable sources such as waste tea [8], coffee grounds [9], cotton stalk [10],

peach stone and olive stone [11,12], biodiesel solid residue [13] and rice husk [14]. Pongamia pinnata fruit hulls are also a source for the porous carbon synthesis. Bio-oil is produced from pongamia pinnata seeds. During the production of bio-oil, pongamia pinnata fruit hulls are thrown without any commercial use. From the fruit hulls, we have synthesized mesoporous carbon to capture CO₂. CO₂ adsorption capacity on mesoporous carbon can be enhanced by the incorporation of basic metal oxides, amine or heteroatom which generates basic sites to capture CO₂.

Iron oxide-doped MCM-41 has shown CO₂ adsorption capacity 0.87 mmol/g at 298 K, 1 bar [15]. CeO₂ incorporated mesoporous carbon showed CO₂ adsorption 1.77 mmol/g at 303 K, 1 bar [16]. Cu₂O and NiO incorporated porous carbon showed high CO₂ adsorption capacity compared to bulk porous carbon [17,18]. S-doped microporous carbon has shown 3.7 mmol/g of CO₂ adsorption at 298 K, 1 bar [19]. N-enriched activated carbon from *Procambarus Clarkii* shells has shown 2.55 mmol/g of CO₂ adsorption at 298 K, 1 bar [20]. MgO modified mesoporous silica has shown 1.34 mmol/g of CO₂ at 303 K [21]. Similarly, MgO supported titanium oxide showed 0.48 mmol/g of CO₂ adsorption at 298 K [22]. In all reported adsorbents, the CO₂ adsorption capacity was higher due to electrostatic interaction between a metal oxide and CO₂. In this article, we studied CO₂ adsorption on mesoporous carbon and magnesium oxide incorporated mesoporous carbon in low pressure at 298 K. Moreover, the selectivity of CO₂/N₂, the heat of CO₂ adsorption and multiple CO₂ adsorption cycles was studied.

†To whom correspondence should be addressed.

E-mail: madhavi0521@gmail.com

Copyright by The Korean Institute of Chemical Engineers.

EXPERIMENTAL

1. Materials

All analytical grade chemicals such as magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O), Orthophosphoric acid (H₃PO₄) were purchased from all commercial sources and used without further purification. Laboratory purified double distilled water was used for the synthesis of adsorbents. Ultra-high pure gases such as helium, carbon dioxide, nitrogen were purchased from local suppliers in India.

2. Synthesis of Adsorbents

Pongamia pinnata fruit hulls were collected from the forest region of Telangana, India. The fruit hulls were dried and crushed into a fine powder, then chemically activated using orthophosphoric acid with 1:1 (w/w%) followed by drying at 100 °C for 12 h, then calcined at 723 K for 4 h in a nitrogen atmosphere. The obtained product was washed with distilled water until neutral pH was obtained, then vacuum dried at 373 K for 12 h. Finally, we got mesoporous carbon [23]; it was denoted as MC. Magnesium oxide incorporated mesoporous carbon was synthesized by the impregnation method. The desired quantity of magnesium nitrate hexahydrate was dissolved in 10 mL distilled water, then 1 g of mesoporous carbon was added to it. The mixture was stirred at room temperature for 1 h, then dried at 373 K for 12 h. The dried product was calcined at 723 K for 4 h in the nitrogen atmosphere. Finally, we got magnesium oxide incorporated mesoporous carbon; it was denoted as xMgO/MC, where x represents the weight percentage of magnesium oxide (x=2, 5 and 10).

3. Characterization

Powdered X-ray diffraction patterns were recorded on Rigaku MiniFlex600 X-ray diffractometer using Ni-filtered Cu K_α radiation ($\lambda=1.54 \text{ \AA}$) in the scan range $2\theta=10\text{--}80^\circ$. N₂ adsorption-desorption isotherms were measured using Micromeritics ASAP 2020 surface area and porosity analyzer at 77 K. Prior to adsorption study, about 0.1 g of sample was degasified at 473 K for 4 h under vacuum. The specific surface area was calculated by the BET method. Total pore volume at a relative pressure of 0.99 and micropore volume by the t-plot method was calculated from N₂ adsorption-desorption isotherms. Raman spectra were recorded using LabRAM HR800 Raman spectrometer having laser wavelength 514 nm. Morphological image with metal composition was obtained from ZEISS Sigma 300 Scanning electron microscope analyzer.

4. CO₂ and N₂ Adsorption Measurement

CO₂ and N₂ adsorption isotherms were measured on Micromeritics ASAP 2020 analyzer at low pressure 0–100 kPa at 298 K. Sample temperature was controlled by the thermostatic bath which was connected to water circulating jacket. Free space of the sample was measured using helium gas. About 0.1 g of sample was degasified similar to N₂ adsorption-desorption isotherm measurement at 77 K, then cooled to room temperature for the study of CO₂ and N₂ adsorption isotherms. The selectivity of CO₂/N₂ was calculated using the initial slope of each isotherm by Henry's Law. The heat of CO₂ adsorption was calculated by the Clausius-Clapeyron equation using adsorption isotherms measured at 283, 298 and 303 K. Multiple CO₂ adsorption cycles were also carried out, after desorbing adsorbed CO₂ at 473 K for 2 h under vacuum.

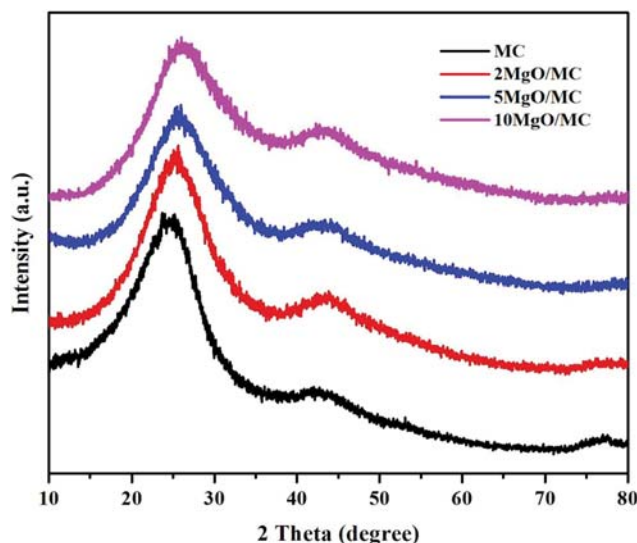


Fig. 1. XRD patterns of MC and MgO incorporated MC.

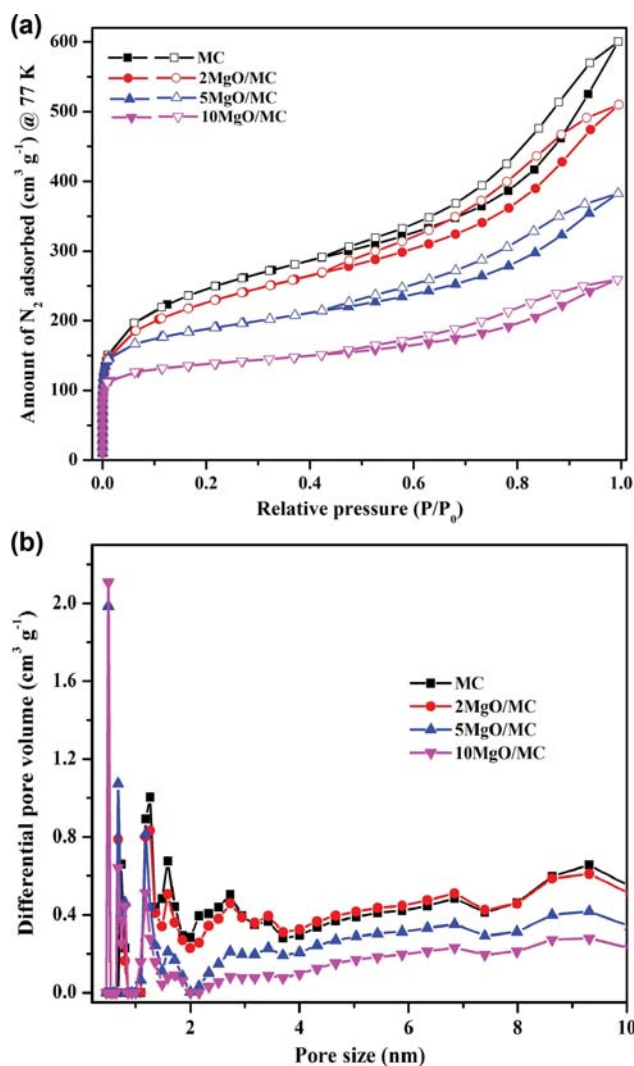


Fig. 2. (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of MC and MgO incorporated MC.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of mesoporous carbon and MgO incorporated mesoporous carbon samples are shown in Fig. 1. MC shows two broad diffraction peaks at $2\theta=24.2^\circ$ and 43.66° having planes (002) and (100), respectively, which are characteristic peaks of mesoporous carbon [24]. Moreover, MgO incorporated mesoporous carbon samples also show diffraction peaks similar to mesoporous carbon and no diffraction peaks related to MgO appeared. It indicates that MgO was well-dispersed over mesoporous carbon. However, the intensity of major diffraction peaks of MC decreased with the increase of MgO loading and shifted towards higher angle. Similar results have been reported on nickel loaded MCM-41 for hydrogen storage [25].

From N_2 adsorption-desorption isotherm, the porosity of carbon material can be found. Fig. 2 shows N_2 adsorption-desorption isotherms of MC and MgO incorporated MC at 77 K. Textural properties are presented in Table 1. MC shows a large amount of N_2 uptake below the relative pressure of 0.1 and a hysteresis loop above the relative pressure of 0.4. The isotherm pattern of MC is similar to type-I and type-IV of classification of porous materials by IUPAC [26], which represent that MC has micro and mesopores. The specific surface area, total pore volume and pore size of MC were $840\text{ m}^2/\text{g}$, $0.94\text{ cm}^3/\text{g}$, and 4.4 nm , respectively. Similarly, MgO incorporated MC samples show the same isotherm pattern similar to MC. But, the amount of N_2 uptake is less. As the content of MgO increased, the amount of N_2 uptake was decreased. Hence, a change in textural properties has been observed. The specific surface area was decreased to $421\text{ m}^2/\text{g}$, the total pore volume $0.34\text{ cm}^3/\text{g}$ and pore size 3.8 nm . However, micropore surface area and micropore volume were increased, which indicates that incorporated MgO has occupied mesopores of MC.

Raman analysis is used to determine the crystallinity of carbon material. Fig. 3 shows the Raman spectra of MC and 10MgO/MC. Mesoporous carbon shows two Raman bands at 1325 cm^{-1} and 1580 cm^{-1} which correspond to D-band and G-band, respectively [27]. D-band represents disordered carbon and G-band represents graphitic carbon. The ratio of the intensity of bands (I_D/I_G) represents the degree of graphitization. In mesoporous carbon, the intensity of G-band is higher than D-band. It represents that mesoporous

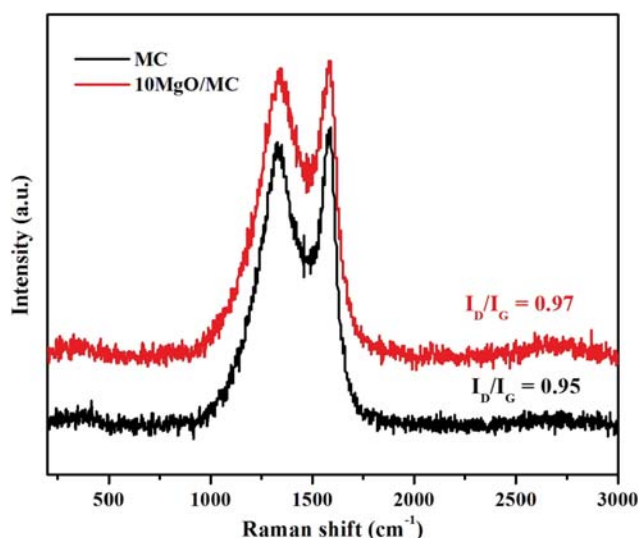


Fig. 3. Raman spectra of MC and MgO incorporated MC.

carbon has a graphitic nature. The I_D/I_G value was 0.95 for MC and 0.97 for 10MgO/MC. By incorporation of MgO, the graphitic nature of MC decreased [28]. Morphology with the elemental composition of MC and 10MgO/MC is shown in Fig. 4. MC shows irregular shaped carbon particles (Fig. 4(a)). Same morphology was replicated in 10 wt% MgO incorporated mesoporous carbon, which indicates that magnesium oxide was homogeneously distributed over carbon surface (Fig. 4(b)). The amount of magnesium was calculated from EDX and the value was 4.92 wt%.

Fig. 5(a) shows single component adsorption isotherm of CO_2 on MC and MgO incorporated MC samples in low pressure at 298 K. With the increase of CO_2 pressure, the amount of CO_2 adsorption capacity was increased. CO_2 adsorption capacity was 0.9 mmol g^{-1} for MC, 1.0 mmol g^{-1} for 2MgO/MC, 1.5 mmol g^{-1} for 5MgO/MC and 1.68 mmol g^{-1} for 10MgO/MC at 298 K, 1 bar. The CO_2 adsorption capacity of MgO incorporated MC samples was higher compared to MC because of electrostatic interaction between MgO and CO_2 . With the increase of MgO content, the amount of CO_2 adsorption capacity increased due to the high content of magnesium oxide. It could be confirmed by calculating the amount of

Table 1. Textural properties of MC and MgO incorporated MC

Adsorbent	S_{BET}^a ($\text{m}^2\text{ g}^{-1}$)	S_{micro}^b ($\text{m}^2\text{ g}^{-1}$)	V_{total}^c ($\text{cm}^3\text{ g}^{-1}$)	V_{micro}^d ($\text{cm}^3\text{ g}^{-1}$)	V_{meso}^e ($\text{cm}^3\text{ g}^{-1}$)	V_{meso}^f (%)	Pore size ^g (nm)
MC	840	225	0.93	0.11	0.82	88	4.4
2MgO/MC	743	189	0.79	0.11	0.68	86	4.2
5MgO/MC	591	293	0.59	0.16	0.43	73	4.0
10MgO/MC	421	263	0.40	0.14	0.26	65	3.8

^aMultipoint BET surface area

^bMicropore surface area by t-plot

^cTotal pore volume at $P/P_0=0.99$

^dMicropore volume by t-plot

^eMesopore volume = $V_{\text{total}} - V_{\text{micro}}$

^fMesopore volume (%) = $V_{\text{meso}}/V_{\text{total}}$

^gAverage pore size by BET method ($4V/S.A$)

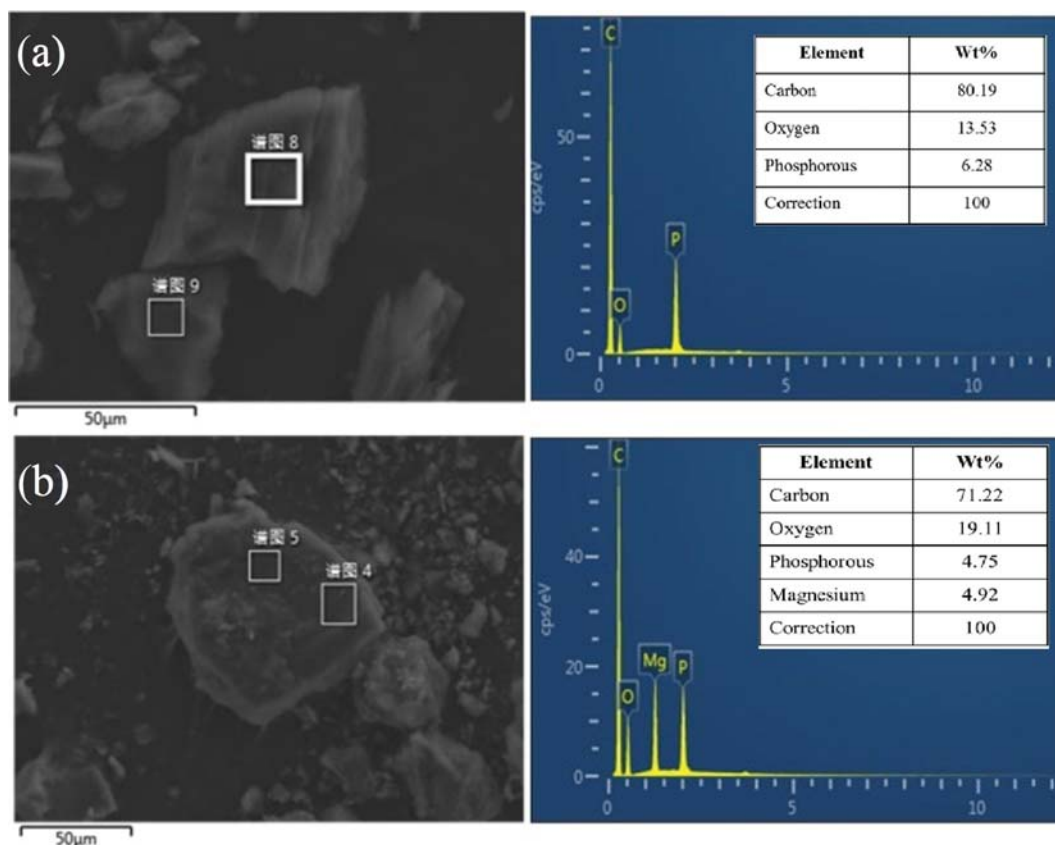
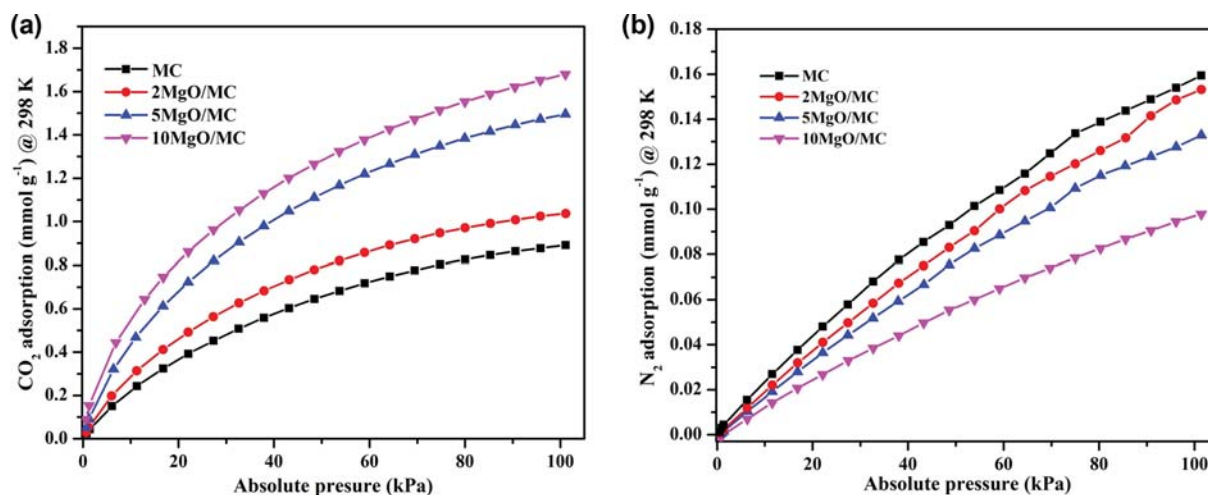


Fig. 4. SEM with EDX of (a) MC and (b) 10MgO/MC.

Fig. 5. (a) CO₂ and (b) N₂ adsorption isotherms of MC and MgO incorporated MC at 298 K.

CO₂ adsorption on unit surface area (Fig. 6(a)). CO₂ adsorption on the unit surface area of MgO incorporated mesoporous carbon samples was higher than porous carbon. Hence, CO₂ adsorption depends on the surface chemistry of the adsorbent instead of surface area. Fig. 5(b) shows N₂ adsorption of synthesized adsorbents under a similar condition of CO₂ adsorption. The N₂ adsorption capacity was 0.16 mmol g⁻¹ for MC, 0.15 mmol g⁻¹ for 2MgO/MC, 0.13 mmol g⁻¹ for 5MgO/MC and 0.09 mmol g⁻¹ for

10MgO/MC at 298 K, 1 bar. The decrease in N₂ adsorption capacity with the increase of MgO content was due to the decrease in surface area.

The difference in adsorption capacity of CO₂ and N₂ is helpful for studying the selectivity of CO₂ over N₂. In industrial flue gas, CO₂ is a major component gas, so it is essential to study the selectivity of CO₂/N₂. It was calculated using the initial slope of each isotherm in low pressure by Henry's law [29]. Fig. 6(b) shows the

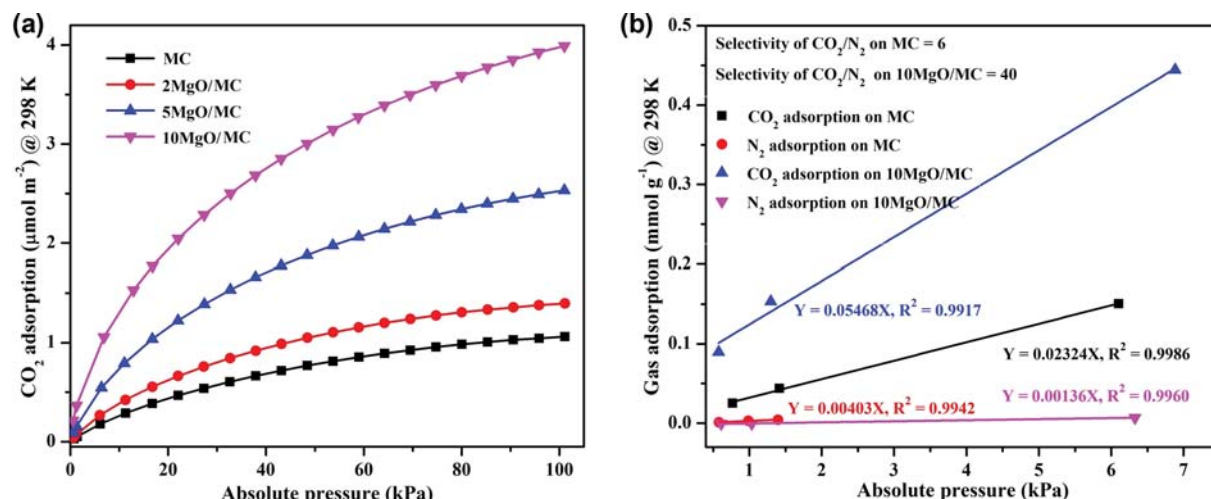


Fig. 6. (a) CO₂ adsorption on unit surface area, (b) selectivity of CO₂/N₂ on MC and 10MgO/MC.

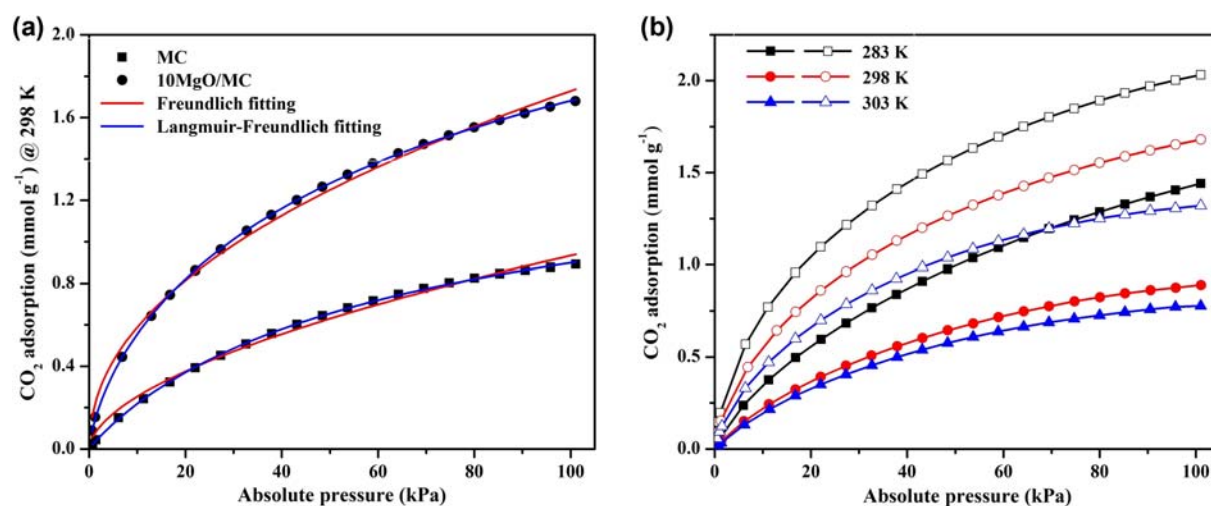


Fig. 7. (a) Fitting curves of experimental CO₂ adsorption data (b) CO₂ adsorption of MC (closed symbol) and 10MgO/MC (open symbol) at different temperatures.

Table 2. Fitting parameters of Freundlich and Langmuir-Freundlich models

Adsorbent	Freundlich model			Langmuir-Freundlich model			
	k_F (kPa ⁻¹)	n	R^2	Q_{max} (mmol g ⁻¹)	K (kPa ⁻¹)	n	R^2
MC	0.0688	1.7666	0.9909	1.4988	0.0195	1.0609	0.9997
10MgO/MC	0.2005	2.1378	0.9942	3.2968	0.0395	1.4077	0.9999

selectivity of CO₂/N₂ on MC and 10MgO/MC. The selectivity value was 6 for MC and 40 for 10MgO/MC. High selectivity value on 10MgO/MC was due to the high adsorption of CO₂. To describe the adsorption of CO₂ on the adsorbent, experimental CO₂ adsorption data of all synthesized adsorbents was fitted with Freundlich and Langmuir-Freundlich models [30]. These models can be expressed as follows.

$$\text{Freundlich model: } Q = k_F P^{1/n} \quad (1)$$

$$\text{Langmuir-Freundlich model: } Q = Q_{max} \frac{K P^{1/n}}{1 + K P^{1/n}} \quad (2)$$

where Q is adsorption capacity at equilibrium in mmol/g, Q_{max} is maximum adsorption capacity in mmol/g, P is pressure in kPa, k_F and K are Freundlich, Langmuir-Freundlich coefficients and n is heterogeneity factor. Fitting curves of experimental CO₂ adsorption data of MC and 10MgO/MC are shown in Fig. 7(a) and fitting parameters are presented in Table 2. Langmuir-Freundlich model was well-fitted with experimental CO₂ adsorption data of both adsorbents with regression coefficient (R^2) higher than 0.999, and Q_{max} was higher on 10MgO/MC.

The interaction between adsorbent and adsorbate can be known by calculating the heat of adsorption using the Clausius-Clapeyron

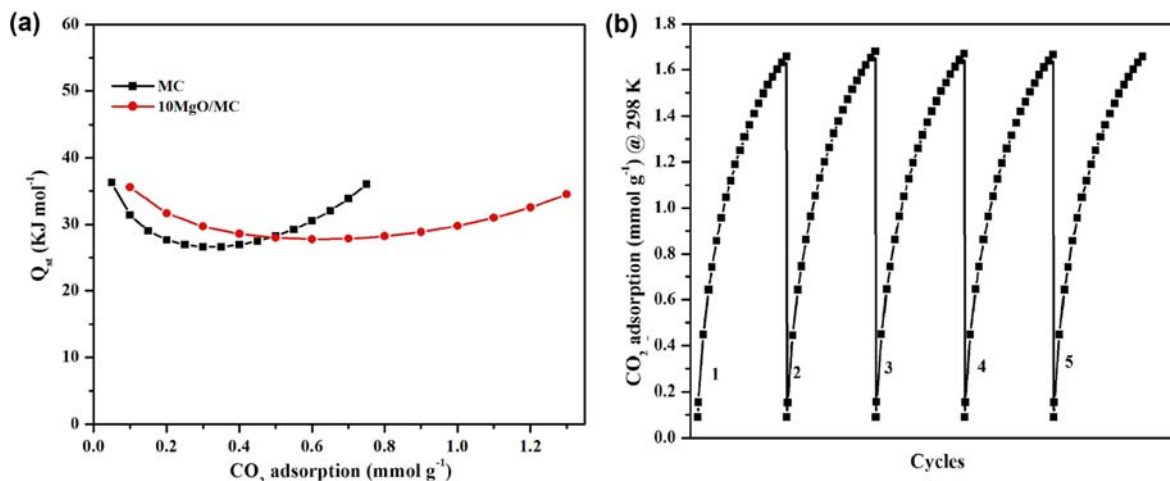


Fig. 8. (a) Heat of CO₂ adsorption on MC and 10MgO/MC, (b) CO₂ adsorption cycles of 10MgO/MC at 298 K.

Table 3. Comparison of CO₂ adsorption capacity and selectivity with reported adsorbents

Adsorbent	CO ₂ adsorption at 298 K, 1 bar (mmol g ⁻¹)	Selectivity (CO ₂ /N ₂)	Reference
NiO/mesoporous carbon	2.02 (303 K)	17.6	[16]
Fe ₂ O ₃ doped MCM-41	0.87	-	[15]
Zeolite-13X	1.70	-	[32]
Karanja seed cake	1.78 (343 K)	-	[33]
MgO/Al ₂ O ₃	1.60 (333 K)	-	[34]
N-doped microporous carbon	1.9	21	[29]
MgO/mesoporous carbon	1.68	40	Present work

equation [31]:

$$\ln P = \frac{-Q_{st}}{RT} + C$$

Here, P is pressure in kPa, T is the absolute temperature in K, R is universal gas constant (8.314 J/K·mol), C is constant and Q_{st} is the heat of adsorption. The partial pressure at different temperatures for the fixed amount of gas uptake can be obtained from the Langmuir-Freundlich model. By drawing a graph between $\ln P$ versus $1/T$ with straight line fitting, we can obtain the slope. Finally, Q_{st} was calculated from the slope. For the calculation of heat of CO₂ adsorption on MC and 10MgO/MC, we measured CO₂ adsorption at 283 K and 303 K also (see Fig. 7(b)). A decrease in CO₂ adsorption capacity was observed on both adsorbents with the increase of temperature. Fig. 8(a) shows the heat of CO₂ adsorption with gas adsorption capacity on MC and 10MgO/MC. The heat of CO₂ adsorption was 36.3–36.0 KJ/mole for MC and 36–34.5 KJ/mole for 10MgO/MC. At low coverage of CO₂, the heat of CO₂ adsorption for 10MgO/MC was higher than MC. It was due to the strong interaction between MgO and CO₂. The Q_{st} was decreased to 34.5 KJ/mole with the increase of CO₂ adsorption. For both adsorbents, the heat of CO₂ adsorption was increased after the minimum with an increase of CO₂ adsorption capacity. It was due to the heterogeneity of the adsorbent.

Adsorption stability of an adsorbent can be known by multiple adsorption cycles. Fig. 8(b) shows multiple CO₂ adsorption cycles of 10MgO/MC at 298 K. Before study of each adsorption cycle, the

adsorbent was degasified at 473 K for 2 h under vacuum. 10MgO/MC showed constant CO₂ adsorption capacity up to five cycles. The CO₂ adsorption of 10MgO/PC was compared with some of the reported adsorbents (Table 3). The CO₂ adsorption capacity value was between the adsorption capacity of NiO supported on mesoporous carbon [16], iron oxide doped MCM-41 [15] and Zeolite-13X [32]. Hence, it is one of the adsorbents that has shown good adsorption capacity and selectivity.

CONCLUSIONS

Mesoporous carbon and MgO incorporated mesoporous carbon samples were used as an adsorbent for the study of CO₂ capture and separation. The presence of MgO on mesoporous was confirmed by all characterization techniques. 10MgO/MC showed high adsorption of CO₂ 1.68 mmol/g at 298 K, 1 bar, which was higher than MC by electrostatic interaction between CO₂ and MgO. High selectivity of CO₂ over N₂ was 40 and heat of CO₂ adsorption was 36 KJ/mole at low coverage of CO₂ on 10MgO/MC. Stable CO₂ adsorption capacity was maintained in each adsorption cycle. Therefore, mesoporous carbon derived from pongamia pinnata fruit hulls can be used as an adsorbent and support to incorporate metal oxides to study CO₂ adsorption and separation.

ACKNOWLEDGEMENT

HB and RA acknowledge the Science and Engineering Research

Board, Department of Science and Technology, New Delhi, India for the financial support (Grant No. EMEQ-283/2014).

REFERENCES

1. S. Hosseini, I. Bayesti, E. Marahel, F. Eghbali Babadi, L. Chuah Abdullah and T. S. Y. Choong, *J. Taiwan Inst. Chem. Eng.*, **52**, 109 (2015).
2. D. Aaron and C. Tsouris, *Sep. Purif. Technol.*, **40**, 321 (2005).
3. M. K. Al Mesfer and M. Danish, *J. Environ. Chem. Eng.*, **6**, 4514 (2018).
4. R. Seabra, A. M. Ribeiro, K. Gleichmann, A. F. P. Ferreira and A. E. Rodrigues, *Micropor. Mesopor. Mater.*, **277**, 105 (2019).
5. J. Pires, M. Bestileiro, M. Pinto and A. Gil, *Sep. Purif. Technol.*, **61**, 161 (2008).
6. C. Knöfel, J. Descarpentries, A. Benzaouia, V. Zelenák, S. Mornet, P. L. Llewellyn and V. Hornebecq, *Micropor. Mesopor. Mater.*, **99**, 79 (2007).
7. B. B. Saha, S. Jribi, S. Koyama and I. I. El-Sharkawy, *J. Chem. Eng. Data*, **56**, 1974 (2011).
8. I. I. Gurten, M. Ozmak, E. Yagmur and Z. Aktas, *Biomass Bioenergy*, **37**, 73 (2012).
9. S. Rattanapan, J. Srikrum and P. Kongsune, *Energy Procedia*, **138**, 949 (2017).
10. H. Deng, G. Li, H. Yang, J. Tang and J. Tang, *Chem. Eng. J.*, **163**, 373 (2010).
11. T. Uysal, G. Duman, Y. Onal, I. Yasa and J. Yanik, *J. Anal. Appl. Pyrolysis*, **108**, 47 (2014).
12. S. M. Yakout and G. Sharaf El-Deen, *Arabian J. Chem.*, **9**, S1155 (2016).
13. X. Zhao, W. Li, F. Kong, H. Chen, Z. Wang, S. Liu and C. Jin, *Mater. Chem. Phys.*, **219**, 461 (2018).
14. Y. Gao, L. Li, Y. Jin, Y. Wang, C. Yuan, Y. Wei, G. Chen, J. Ge and H. Lu, *Appl. Energy*, **153**, 41 (2015).
15. K. C. Chanapattharapol, S. Krachumram and S. Youngme, *Micropor. Mesopor. Mater.*, **245**, 8 (2017).
16. M. Li, K. Huang, J. A. Schott, Z. Wu and S. Dai, *Micropor. Mesopor. Mater.*, **249**, 34 (2017).
17. B. J. Kim, K. S. Cho and S. J. Park, *J. Colloid Interface Sci.*, **342**, 575 (2010).
18. D. I. Jang and S. J. Park, *Fuel*, **102**, 439 (2012).
19. J. Shi, N. Yan, H. Cui, Y. Liu and Y. Weng, *J. Environ. Chem. Eng.*, **5**, 4605 (2017).
20. W. Cai, S. Zhang, X. Hu and M. Jaroniec, *Energy Fuels*, **32**, 9701 (2018).
21. H. Zhao, W. Yan, Z. Bian, J. Hu and H. Liu, *Solid State Sci.*, **14**, 250 (2012).
22. H. Jeon, Y. J. Min, S. H. Ahn, S.-M. Hong, J. S. Shin, J. H. Kim and K. B. Lee, *Colloids Surf., A*, **414**, 75 (2012).
23. M. A. Islam, S. Sabar, A. Benhouria, W. A. Khanday, M. Asif and B. H. Hameed, *J. Taiwan Inst. Chem. Eng.*, **74**, 96 (2017).
24. B. Chen, Z. Yang, G. Ma, D. Kong, W. Xiong, J. Wang, Y. Zhu and Y. Xia, *Micropor. Mesopor. Mater.*, **257**, 1 (2018).
25. S. J. Park and S. Y. Lee, *J. Colloid Interface Sci.*, **346**, 194 (2010).
26. S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
27. W. Tian, Q. Gao, Y. Tan, K. Yang, L. Zhu, C. Yang and H. Zhang, *J. Mater. Chem. A*, **3**, 5656 (2015).
28. S. Cheng, L. Zhang, H. Xia and J. Peng, *Green Process. Synth.*, **6**, 487 (2017).
29. M. Saleh, J. N. Tiwari, K. C. Kemp, M. Yousuf and K. S. Kim, *Environ. Sci. Technol.*, **47**, 5467 (2013).
30. C. Goel, H. Bhunia and P. K. Bajpai, *J. Environ. Chem. Eng.*, **4**, 346 (2016).
31. J. Yan, Y. Yu, C. Ma, J. Xiao, Q. Xia, Y. Li and Z. Li, *Appl. Therm. Eng.*, **84**, 118 (2015).
32. J. McEwen, J. D. Hayman and A. Ozgur Yazaydin, *Chem. Phys.*, **412**, 72 (2013).
33. K. Upendar, T. V. Sagar, G. Raveendra, N. Lingaiah, B. V. S. K. Rao, R. B. N. Prasad and P. S. S. Prasad, *RSC Adv.*, **4**, 7142 (2014).
34. S. Zhang, W. Cai, J. Yu, C. Ji and N. Zhao, *Chem. Eng. J.*, **310**, 216 (2017).