Furfuryl alcohol-derived carbon monoliths for CO2 capture:
adsorption isotherm and kinetic study

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Abstract. Porous carbon monoliths have been synthesized using furfuryl alcohol as a carbon precursor in the nanocasting technique. The highest surface area of 1225 m²g⁻¹ was found for the carbon monolith exhibited the micropore volume of 0.85 cm³ g⁻¹. The various functional groups have been obtained on the surface of the adsorbent which increases its basicity as confirmed from the XPS analysis. The dynamic CO₂ uptake was 1.0 mmol g⁻¹ at 30°C using temperature swing adsorption set up under 12.5% CO₂ flow. The effect of various adsorption temperatures along with CO₂ concentrations on the adsorption capacity was also investigated. The increase in the CO₂ uptake capacity by rising the temperature from 30°C onwards to 100°C confirms the involvement of exothermic and physisorption process. Also, the experiments for five adsorption-desorption cyclic runs were conducted for the regeneration study, indicating the good stability and reusability of the samples.

1. Introduction
The CO₂ greenhouse gas emissions are very harmful to the environment which plays a major role to enhance global warming. The burning of fossil fuels is the main cause of the increasing CO₂ emissions. The estimated CO₂ concentration in the year 2100 is 570 ppm [1] which will be the major threat to the human life. Therefore, the reduction in the CO₂ levels is very necessary to solve the environmental problems.

Porous carbons are considered as well known and effective candidates for the CO₂ capture. It exhibits the wide availability, low cost, and fast adsorption kinetics as compared to other materials. The different synthesis processes are implicated for the synthesis of porous carbons like direct carbonization, nanocasting, sol-gel, physical and chemical activation. Among the various methods, nanocasting is known as the best suitable technique due to the possibilities of varying the porosity/surface area of the carbons. It includes the precursor impregnation in the template, carbonization and then elimination of template [2].

The carbons in the form of the macroscopic level (monolithic form) have lot of advantages as compared to its powder form. The monoliths (meso and microporous) exhibits a lot of significant properties such as easy to deal, mass transfer, fast heat as well as high contacting efficiency [3-5] during the CO₂ adsorption. The presence of micropores trapped the CO₂ molecules effectively whereas, mesopores helps for the diffusion of CO₂ in low resistant pathways[6]. In this regard, porous monolithic carbons (single-rock like) are developed and used for the CO₂ adsorption studies under dynamic conditions. The pore size distribution curves and HRTEM analysis shows the presence of
micropores. Whereas, the XPS analysis are confirmed the presence of the different functionalities on the adsorbent surface.

2. Experimental

2.1 Synthesis

The schematic diagram (Figure 1a) shows the preparation of meso/microporous carbon monoliths. For the synthesis of the monolithic silica template, 9.54 X 10^{-4} M of polyethylene glycol was dissolved in the water (9 ml) and then nitric acid (30%) was added slowly. The 8.1 ml of tetraethylorthosilicate and octadecyltrimethylammonium bromide (0.2M) was taken in the resulted solution and kept for stirring (15 min). The solution was then taken in the microplates and heated for 48 h at the temperature of 40-50°C for the gel formation. The gel form monoliths were then kept in the NH4OH solution (1M) at 80 °C overnight and washed thrice with HNO3 (0.1 M) and H2O each. The silica monoliths were obtained after drying at 50 °C (96 h) and then kept for calcination (550 °C, 5 h). The synthesized monoliths were then impregnated with furfuryl alcohol solution with oxalic acid along with trimethyl benzene (FA/oxalic acid -250, ratio in moles). The monoliths were treated at 50 °C and then 100 °C (24h) in the oven for polymerization. The obtained monoliths were carbonized at 950 °C (4 h) with the 2 °C/min heating rate. Finally, the carbon monoliths were acquired by the complete removal of the template (silica) by treating with hydrofluoric acid (10%, by volume).

![Figure 1.](image)

Figure 1. The schematic diagram for the preparation process of monolithic carbons

2.2 Apparatus

The Microtec Belsorp Mini–II, Japan instrument was used for the N2 sorption isotherms and surface area for the samples. The morphology of the monoliths was examined by SEM (scanning electron microscope, JEOL JSM – 6510 LV) and HRTEM analysis (high-resolution transmission electron microscopy, JEOL JEM-2100). The investigation of various functional groups exists in the adsorbents was done by using X-ray photoelectron microscopy, PANALYTICAL X’Pert PRO. The CO2 capture experiments were carried out using custom made temperature swing adsorption system equipped with the online gas chromatograph of Agilent 7890A. The CO2 adsorption capacity, \( q_t (\text{mmol g}^{-1}) \) estimated by using Eq. (1). In which, m is the adsorbent weight (g), t (min) denotes the time in min, \( Q \) is the CO2 flow rate in ml min\(^{-1}\) and \( C_0 \) and C are the inlet and outlet CO2 concentrations.

\[
q_t = \frac{1}{m} \int_0^t Q(C_0 - C) \, dt
\]

3. Results and discussion
Figure 2. (a) N₂ sorption isotherms and (b) the pore size distribution curves for the monoliths; (c) HRTEM micrograph inset with the SEM image and (d) XPS spectra for the carbon monolith (inset: de-convoluted spectra of the O1s region).

Table 1. The adsorption capacity exhibited by the carbon monolith at different conditions

| CO₂ concentration (%) | CO₂ adsorption (in mmol g⁻¹) |
|-----------------------|-----------------------------|
|                       | 30 °C | 50 °C | 75 °C | 100 °C |
| 5                     | 0.33  | 0.21  | 0.18  | 0.15  |
| 7.5                   | 0.52  | 0.34  | 0.26  | 0.22  |
| 10                    | 0.79  | 0.55  | 0.35  | 0.28  |
| 12.5                  | 1.0   | 0.72  | 0.57  | 0.49  |

The N₂ adsorption-desorption isotherms for the monolithic silica and carbon samples are shown in figure 2a. The silica monolith shows the type IV isotherm whereas, carbon monolith shows the type I isotherm which confirms the presence of micropores. The specific surface area for the silica and carbon monolith is 1225 and 760 m² g⁻¹, respectively. The pore size distribution curves also indicate the existence of pores lies in between 1-2 nm (Figure 2b). The HRTEM image shows the microstructure of the spherical particles of the carbon monoliths which indicating its existence in the nanometer range (Figure 2c). Whereas, XPS spectra (Figure 2d) of the monolithic carbon confirming the existence of C1s and O1s region without the presence of any impurity. The de-convoluted peaks for the O1s region having the binding energies of 531.2eV, 532.3eV and 533.2eV assigned to C=O, C-OH groups, and oxygen in the water, respectively. Also, the C-OH groups increases the surface basicity [7] which can be beneficial to capture CO₂ molecules during adsorption.
Figure 3. (a) CO\textsubscript{2} Breakthrough curves for the silica and carbon monolith; (b) CO\textsubscript{2} adsorption-desorption cycles for the carbon monolith; (c) CO\textsubscript{2} uptake kinetics; and (d) Fitting of the experimental data with the Temkin model at various adsorption temperatures

The breakthrough curves for the monoliths at 30 °C are shown in figure 3a. The maximum adsorption capacity (1.0 mmol g\textsuperscript{-1}) was exhibited by the carbon monolith whereas, silica monolith induced the capacity of 0.26 mmol g\textsuperscript{-1}. This is due to the higher textural properties (S\textsubscript{BET}=1225 m\textsuperscript{2}g\textsuperscript{-1}) of the carbon monolith as well as the presence of basic oxygen functional groups exist on the surface. The CO\textsubscript{2} uptake exhibited by the carbon monolith at various temperatures as well as CO\textsubscript{2} concentrations is shown in table 1. It was seen that the adsorption capacity decreased by increasing the temperature indicating the involvement of physisorption as well as the exothermic process. However, the CO\textsubscript{2} uptake capacity increases by increasing the CO\textsubscript{2} concentration from 5 to 12.5% due to the enhancement of driving force by increasing the concentrations of CO\textsubscript{2}. The experiment runs for the CO\textsubscript{2} adsorption-desorption cycles for carbon monolith at 30 °C under 12.5% CO\textsubscript{2} concentration can be seen in figure 3b. The quick desorption of CO\textsubscript{2} after the adsorption process can be estimated by the sudden fall of C/C\textsubscript{o} after the complete adsorption. The adsorbents showed the excellent recyclability for CO\textsubscript{2}. Therefore, it can be said that the synthesized monoliths can be effective as well as reused for multiple times for the CO\textsubscript{2} capture applications. The fractional order model fitted best with the experimental data and R\textsuperscript{2} value is 0.99 (Figure 3c) using the Eqn.2. Figure 3d shows the fitting of experimental results with the Temkin isotherm model which exhibits the R\textsuperscript{2} value of 0.99 using the Eqn.3. This indicates the heterogeneous surface of carbon monoliths.

\[
q = q_{e} - \left[\frac{1}{((n-1)k_{e}/m)^{n} + (1/q_{e}^{-1})}\right]^{n-1} \tag{2}
\]

\[
q_{e} = B \ln(K_{T}P) \tag{3}
\]

$q_{e}$ and $q_{t}$ are the adsorption capacity (mmol g\textsuperscript{-1}) at a particular time t (minutes) and at equilibrium respectively. $k_{e}$, $m$ and $n$ are the rate constant of fractional order model. $K_{T}$ is the Temkin constant in atm\textsuperscript{-1}, T is the temperature in Kelvin, B is the constant represents the sorption heat.
4. Conclusions
Herein, monolithic carbons were prepared using the nanocasting technique. The obtained carbon monoliths showed the $S_{BET}$ of $1225 \text{ m}^2 \text{ g}^{-1}$ and exhibited the maximum CO₂ uptake (1.0 mmol g⁻¹) which is about 3 times greater than the silica monolith (0.26 mmol g⁻¹). Also, the synthesized monoliths exhibited good stability after five recycle runs of adsorption-desorption. The Temkin isotherm model fitting shows the heterogeneity on the surface of the monoliths. Thus, the synthesized monoliths in the present study can be used in the practical applications in CO₂ separation from flue gas in the coal fired power plants.

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| First name | Surname | Institution | Email address | Title (Prof/ Dr./student) | Research Interests |
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| Soumen     | Basu    | Thapar Institute of Engineering and Technology, Patiala 147004, Punjab, India. | soumen.basu@thapar.edu | Dr. (Associate Professor) | Preparation of metal oxides porous carbons for CO₂ capture. |
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