

CO₂ CAPTURE IN 3D-PRINTED CARBON-BASED MONOLITH BY ADSORPTION

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Motivation and Objective

CO₂ capture from post-combustion streams (mainly consisting of CO₂ and N₂) in coal-fired power plants has become a worldwide research topic over the past decade since it plays a vital role in mitigating global warming. Accordingly, this carbon source accounts for at least 73 % of annual energy sector emissions [1,2]. Therefore, this work aims to evaluate the applicability of hierarchically structured 3D-printed porous carbon monoliths as adsorbents for CO₂ capture from post-combustion streams.

Methodology

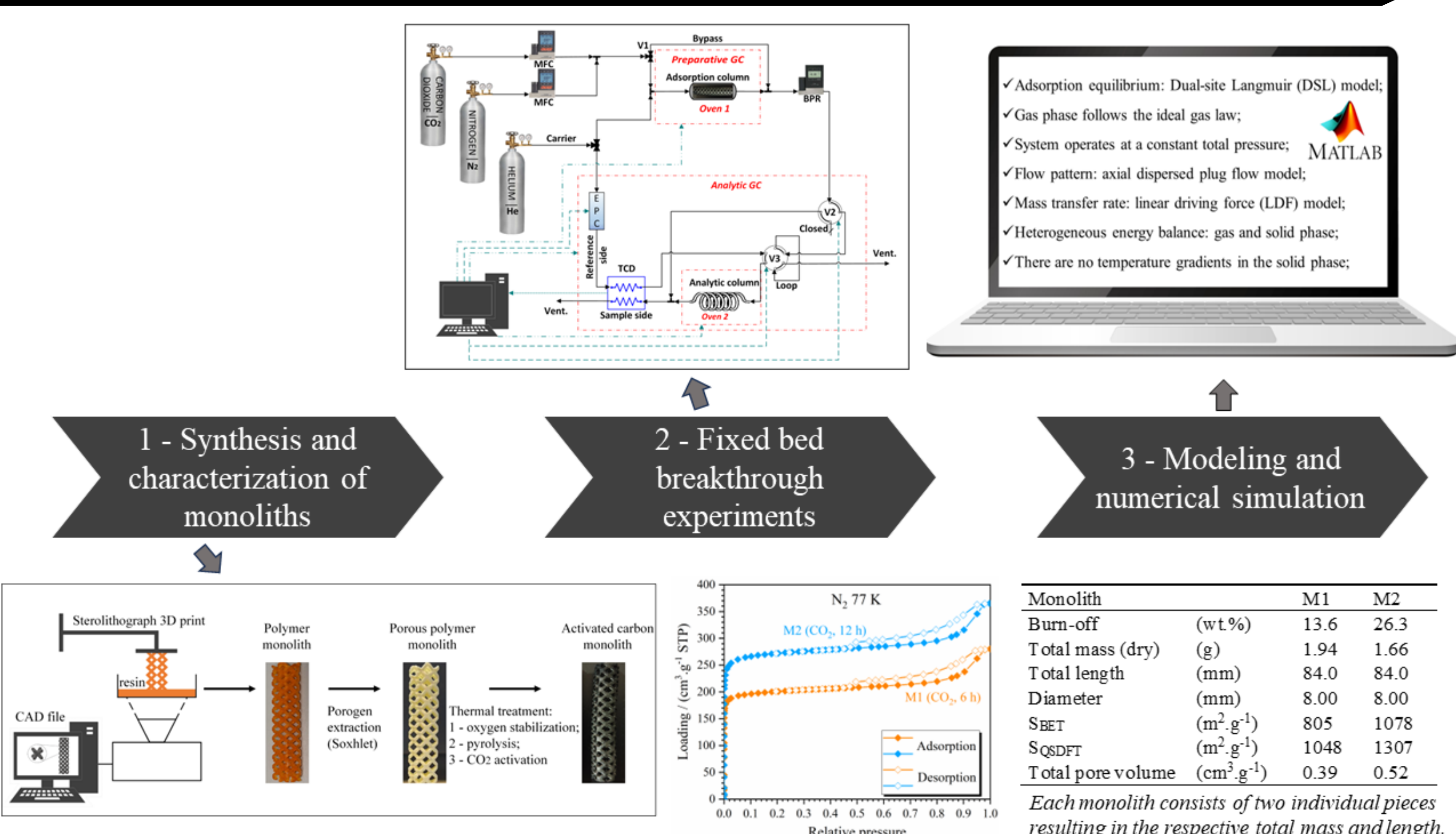


Figure 1. Schematic overview of the methodology used to synthesize and evaluate the performance of 3D-printed monoliths.

1 - 4 steps: (i) resin preparation: two monomers, 35 % pentaerythritol tetraacrylate and 35 % divinylbenzene, an inert porogen 30 % bis(2-ethylhexyl) phthalate, an initiator, 10 mg.mL⁻¹ phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide, and a dye, 0.4 mg.mL⁻¹ sudan1; (ii) photopolymerization: stereolithographic 3D print of a porous polymer open cell structure comprising 8 tetragonal cubic centered unit cells; (iii) porogen extraction: Soxhlet extraction with acetone (at 373 K for 24 h); and (iv) thermal treatment: Oxygen stabilization in the air (at 573 K for 6 h), pyrolysis in N₂ (at 1173 K for 0.3 h) and CO₂ activation (at 1133 K) for 6 h (M1) and 12 h (M2) [3].

2 - Chromatographic-based fixed bed adsorption apparatus to measure breakthrough curves. For multicomponent experiments, each minute (with a 6-way sampling valve), a sample of the column outlet is directed to a capillary column (HayeSep N, mesh 80/100) and then is analyzed in a thermal conductivity detector (TCD).

3 - The equilibrium data is modeled by the Dual-site Langmuir (DSL) adsorption equilibrium isotherm. Then, the fitted parameters are used in a mathematical model based on the fundamental material and energy conservation laws, coupled with a lumped kinetic mass transfer rate (linear driving force model).

Adsorption Equilibrium Isotherms

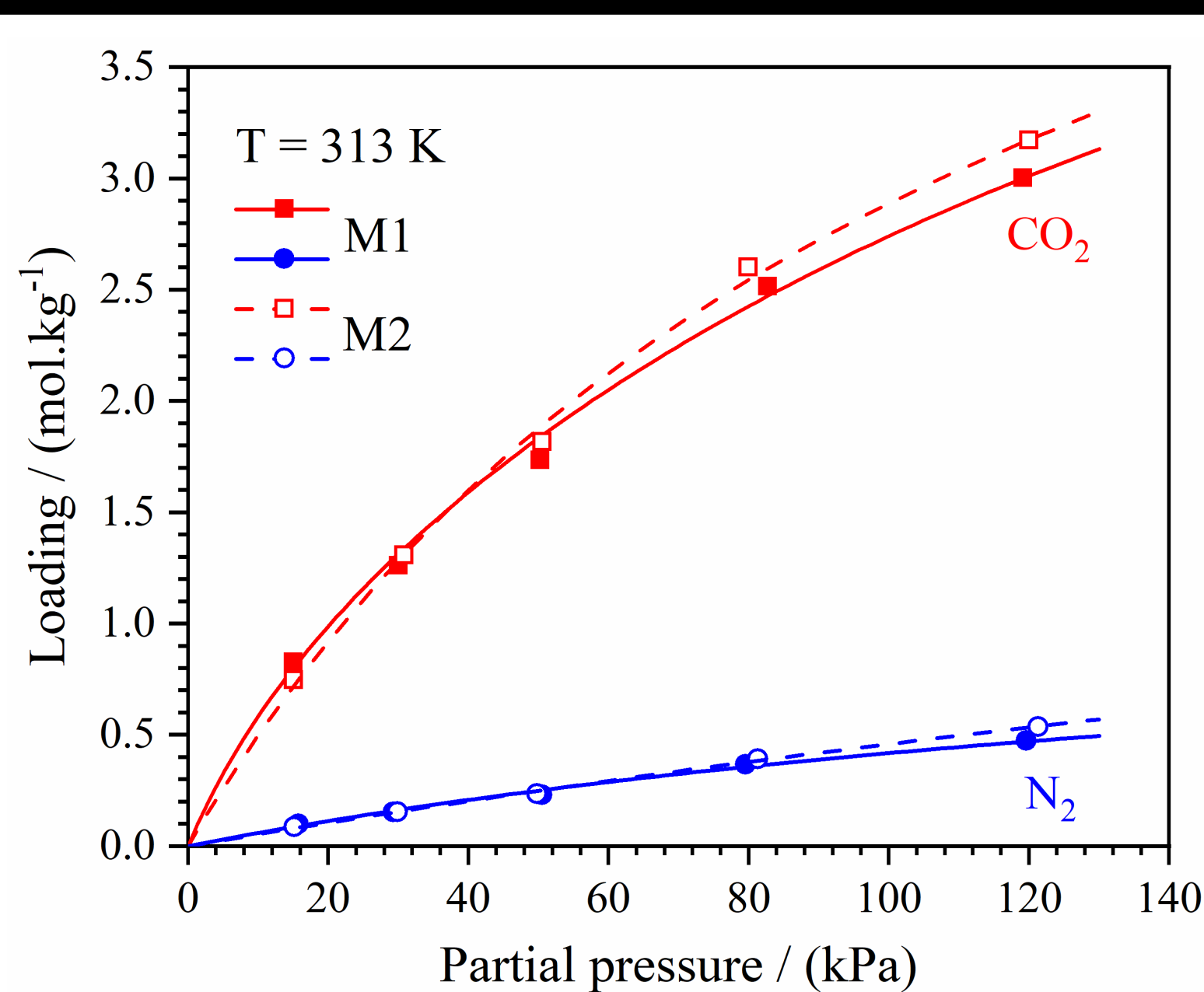


Figure 2. Adsorption equilibrium isotherms of CO₂ and N₂ at 313 K. Points: experimental data. Lines: DSL model predictions

Adsorption capacity

- CO₂ >>> N₂
- CO₂ loadings up to 3.2 mol.kg⁻¹
- N₂ loadings ≤ 0.5 mol.kg⁻¹

Isotherm shape

- CO₂: type I (favorable nature for adsorption)
- N₂: linear

$$q = \frac{q_{sat1,i} b_{1,i} p_i}{1 + b_{1,i} p_i} + \frac{q_{sat2,i} b_{2,i} p_i}{1 + b_{2,i} p_i}$$

Table 1. Model parameters for the sorption of CO₂ and N₂

DSL Parameters	M1		M2	
	CO ₂	N ₂	CO ₂	N ₂
$q_{sat,1}$ (mol.kg ⁻¹)	0.75	1.29	3.07	2.99
$q_{sat,2}$ (mol.kg ⁻¹)	5.95	-	3.33	-
b_1 (1.kPa ⁻¹)	5.77×10^{-2}	0.48×10^{-2}	1.05×10^{-2}	0.18×10^{-2}
b_2 (1.kPa ⁻¹)	0.55×10^{-2}	-	0.65×10^{-2}	-

Separation Performance

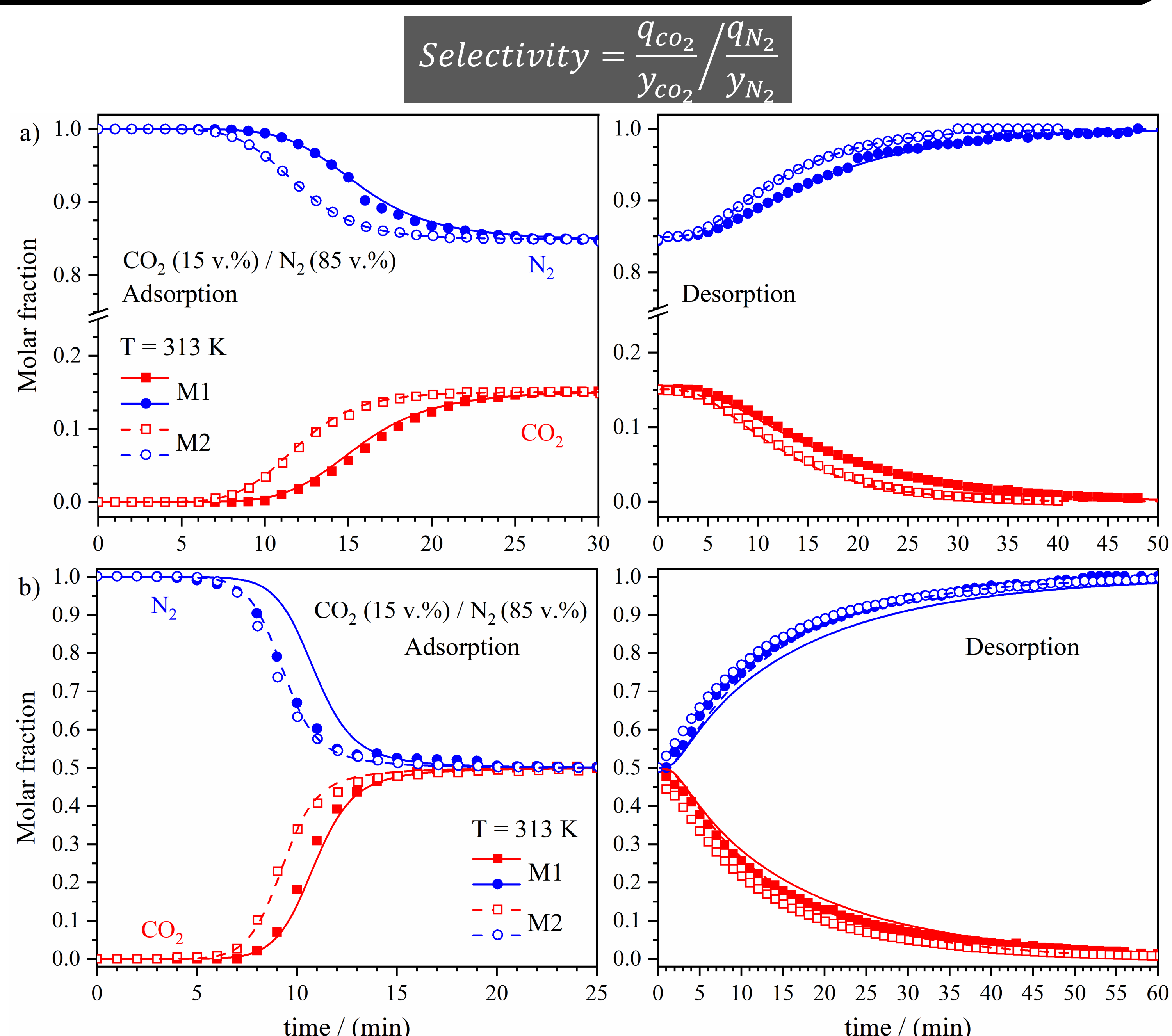


Figure 3. Breakthrough curves for a binary mixture of CO₂/N₂ at 313 K and 100 kPa (column saturated with pure N₂): a) mixture ratio 15/85 v.%, and b) mixture ratio of 50/50 v.%. Points: experimental data. Lines: numerical simulations.

The calculated selectivities resulted in 18 and 24 for (M1) compared to 10 and 9.9 for M2, respectively. The numerical simulations found mass transfer coefficients around 0.070 and 0.075 s⁻¹ for CO₂ in M1 and M2, respectively. Comparing the materials, both showed similar adsorption capacities. However, the loadings are slightly higher in M2, especially for N₂, which means that the additional microporosity created during the CO₂ activation most favored the adsorption of N₂, thus decreasing the separation performance in M2.

Conclusions

The adsorption studies demonstrated that the 3D-printed carbon-based materials, especially M1, perform significantly for the separation of CO₂/N₂. Considering the relevance of the above findings, this work provides an important reference for using structured materials not only in the field of CO₂ capture but also for separating any useful compound mixtures.

Acknowledgments and References

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[1] M. Bui et al., Carbon capture and storage (CCS): the way forward, Energy Environ. Sci. 11 (2018) 1062-1176.

[2] S. Lawson et al., Development of 3D-printed polymer-MOF monoliths for CO₂ adsorption, Ind. Eng. Chem. Res. 59 (2020) 7151-7160.

[3] H. Stedinger et al., Activated carbon in the third dimension - 3D printing of a tuned porous carbon, Advanced Science. 6 (2019) 1901340.