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CO_2 capture at laboratory pilot-scale by vacuum pressure swing adsorption using MIL-120(Al)

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Currently, power generation and carbon-intensive industries are responsible for a significant part of anthropogenic CO_2 emissions, which contribute to global warming, making the reduction of CO_2 emissions from industrial sources critical. Carbon capture technology is one of the key solutions to achieve net zero emissions by 2050. However, the most mature technology, absorption-regeneration amine-based process, faces several limitations, including high energy demands, solvent degradation, and toxicity. Among alternative separation technologies, CO_2 separation by adsorption is one of the most promising solutions due to its potentially lower energy consumption, reduced costs, and minimal environmental impact compared to amine-based absorption processes. Over the past two decades, novel materials have been developed to enhance the efficiency of adsorption-based carbon capture, with Metal Organic Frameworks (MOFs) showing great potential for gas separation and purification. Despite this, the performance of MOFs in carbon capture applications has not yet been fully explored, and further refinement is necessary for large-scale adsorption processes under industrial conditions. One key challenge is the scalability of the MOFs which need to be produced at large scale for industrial applications. MOFs need to retain their adsorption properties when shaped and produced at tons scale, while being cost-effective compared to traditional adsorbents for CO_2 capture such as zeolite 13X or activated carbons.

In the framework of H2020-MOF4AIR project (https://www.mof4air.eu/) which aims to develop and promote the use of MOFs for CO_2 capture in energy and industrial sectors, several MOFs have been evaluated for use in a Vacuum Pressure Swing Adsorption (VPSA) process. Among these, MIL-120(Al) – $Al_4(OH)_8(C_{10}O_8H_2)\ xH_2O$ (x=4.8~5) represented in Figure 1, was investigated [1]. MIL-120(Al) exhibited higher working capacity and similar heat of adsorption for CO_2 compared to the benchmark material zeolite 13X (Table 1). Bulk density and CO_2/N_2 selectivity are also high for the MIL-120 making it an interesting candidate for CO_2 capture. Moreover, due to its favorable chemical composition (cost-effective precursors and a high metal-to-ligand ratio) and a green kg-scale synthesis optimized in-house (conducted in water at ambient pressure), the estimated production cost at the kiloton scale (~13 $/kg) is significantly lower compared to other MOFs [1].

Both adsorbents, zeolite 13X and MIL-120(Al), were tested on a home-made VPSA lab-scale pilot system design to process a CO_2/N_2 mixture at a flow rate of 0.5 to 1.5 Nm^3/h with two or three working columns of 1.1 liters and adjustable pressure levels for adsorption and evacuation. The pilot can reproduce the most common steps encountered in (V)PSA cycles (adsorption, co- and counter-current evacuation, light and heavy reflux, pressure equalization, pressurization, …) making it able to perform almost all 2 or 3-bed cycles of the literature for CO_2 capture.

Zeolite 13 was firstly tested as a benchmark, using a 3-bed 6-step cycle (adsorption, heavy reflux, co-current evacuation, counter-current evacuation, light reflux, light product pressurization) [2] with a flue gas composition of 15/85 CO_2/N_2 at 1 Nm^3/h. The process was optimized to achieve a CO_2 purity of 85.9% and a recovery of 84.1% at an adsorption pressure of 2 bar and a desorption pressure of 0.1 bar [3]. Then 3 kg of shaped MIL-120(Al) beads were subsequently prepared and tested on the VPSA pilot using a 15/85 CO_2/N_2 mixture at a flow rate of 1 Nm^3/h. A design of experiments was employed to investigate five variables: adsorption time (100-400 s), reflux time (40-300 s), co-current evacuation time (20-40 s) and pressure (0.4-0.6 bar), and light reflux flow rate (0.1-0.3 Nm^3/h). Adsorption pressure was maintained at 2 bars, and counter-current evacuation pressure at 0.1 bar for all tests. Under these optimized conditions, MIL-120(Al) achieved a CO_2 purity of 93.1% and a recovery rate of 91.6%, outperforming zeolite 13X.

Investigation of the performance of this MOF was completed by simulation of the laboratory scale VPSA pilot using Aspen Adsorption. The flow through the bed is represented by the axial dispersed plug flow model assuming there is no radial effect in the bed. The bed is non-isothermal with heat balance for the solid, the gas and the wall. Data obtained from adsorption isotherm measurements were used to fit the Toth model for CO_2 and N_2 with a good agreement with experimental data (R^2>99.9%). The mixture adsorbed amounts are predicted by IAST using pure component isotherms. Kinetic measurements and breakthrough curves were also used to determine the parameters of a linear driving force model and adjust the heat transfer coefficients.

This simulation model is able to reproduce the results of the VPSA pilot with a mean error of 2.8% and 2.1% for purity and recovery. A surrogate model including adsorption pressure, counter-current evacuation pressure, feed flow rate, feed composition, in addition to the variables studied experimentally was constructed from VPSA simulations. The surrogate model was then used to find the optimum energy consumption and productivity for a given CO_2 concentration providing a complete overview of MIL-120(Al) performance. This simulation model could be used to have a complete techno-economic study of a CO_2 capture plant using MIL-120(Al) at kiloton scale.

Table 1: Comparison of zeolite 13X and MIL-120(Al) at adsorbent scale

	Zeolite 13X	MIL-120(Al)
Adsorbed amount at 0.15 bar 25°C [mmol/g]	2.73	1.96
Working capacity (0.015 to 0.15 bar) 25°C [mmol/g]	1.35	1.46
IAST selectivity (1bar, 25°C, yCO_2 = 0.15)	860	105
CO_2 heat of adsorption [kJ/mol]	41.2	41.0
Bulk density (shaped) [kg/m³]	750.8	683.8

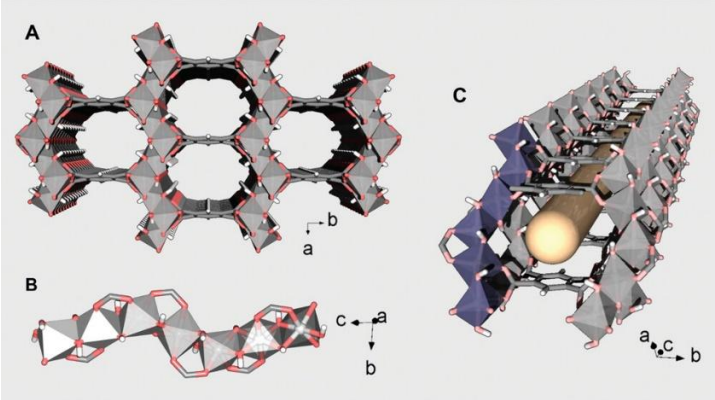

Figure 1: Crystal structure of MIL-120(Al) from [1]. A) General view along [0 0 1] B) Constitutive Al hydroxo-chains built of trans-cis edge sharing $Al(OH)_4O_2$ octahedra. C) Representation of one channel. Color code: $Al(OH)_4O_2$, gray polyhedra; C, gray; O, light red; H, white.

References

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