CO_2 Capture VPSA Pilot Unit using MIL-160(Al) and MIL-120(Al): experimental and simulation study

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Power generation and carbon-intensive industries significantly contribute to CO_2 emissions, making their reduction crucial. Carbon capture technology is essential for achieving net zero emissions by 2050. However, the current amine-based absorption process has limitations such as high energy demands and solvent degradation. CO_2 separation by adsorption is a promising alternative due to potential lower energy consumption and reduced environmental impact. Novel materials like Metal Organic Frameworks (MOFs) have been developed to improve adsorption-based carbon capture, but their performance needs further refinement for large-scale industrial use. 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-160(Al) ($Al(OH)(O_2C–C_4H_2O–CO_2)$) which is an easily scalable 3D Al-based MOF showing pore size between 4 to 6 Å [1][2], and MIL-120(Al) – $Al_4(OH)_8(C_{10}O_8H_2)$ xH_2O (x=4.8~5) showing pore size of 4.7 to 5.4 Å [3] were investigated. As represented in Table 1, MIL-120(Al) exhibits higher working capacity, selectivity and bulk density than MIL-160(Al) which could lead to better performance in process for this material. Nevertheless, previous studies have shown that process performance and adsorption metrics are not always clearly related [4][5]. Both MOFs, synthesized at kg-scale and shaped into pellets, were tested on a lab-scale pilot (3 columns of 1.1L) using a 3-bed 6-step cycle (adsorption, heavy reflux, co-current evacuation, counter-current evacuation, light reflux, light product pressurization) with a flue gas composition of 15/85 CO_2/N_2 at 1 Nm^3/h [5]. 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) and MIL-160(Al) can achieve purity and recovery higher than 90%. Investigation of the performance of these MOFs was completed by simulation of the laboratory scale VPSA pilot using Aspen Adsorption. Kinetic measurements, breakthrough curves and pilot experiments were also used to determine the parameters of a linear driving force model and adjust the heat transfer coefficients [6]. Simulation was used to study the effect of the different parameters studied. Concentration and adsorbed amount inside the column were studied in-depth by simulation to understand the difference between the two materials and the link with other properties such as adsorption isotherms, kinetic, heat of adsorption and bulk density.

Table 1: Adsorption metrics of MIL-160(Al) et MIL-120(Al).

	MIL-160(Al)	MIL-120(Al)
Working capacity (0.15 to 0.015 bar CO_2, 30°C) [mmol/g]	0.91	1.49
CO_2/N_2 IAST selectivity (30°C, 1bar, 15/85 CO_2/N_2) [/]	34	94.7
Heat of adsorption [kJ/mol]	30	36
Bulk density [kg/m^3]	419	684

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