CO_2 Capture VPSA Pilot Unit using MIL-160(Al) and MIL-91(Ti): experimental and simulations study

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Nowadays, power generation and carbon-intensive industries (cement plants, steel plants, petrochemicals plants …) are responsible for around 50% of anthropogenic CO_2 emissions to our atmosphere that mainly contributes to global warming. Since several decades, CO_2 capture techniques were investigated to envisage CO_2 storage and chemical reuse. Absorption-regeneration amine-based process, the benchmark solution, suffers from high energy penalties that leads adsorption process a promising alternative thanks to improvement of process design and development of new materials. Among these materials, MOFs appears as very promising material for both gas separation and purification. However, the performances of these hybrid materials in carbon capture technologies have not been fully evaluated and fine-tuning is still needed for adsorption processes at large scale in real industrial conditions. In this context, the H2020-MOF4AIR project (https://www.mof4air.eu/) aims to develop and promote the use of MOFs for CO_2 capture in energy and industrial sectors. 14 partners are involved in the project, to develop the process of CO_2 capture with MOFs from the material synthesis to an industrial pilot scale.

Several MOFs have been studied to be used in a Vacuum Pressure Swing Adsorption (VPSA) process. MIL-160 (Al)[1,2] ($Al(OH)(O_2C–C_4H_2O–CO_2)$) which is an easily scalable 3D Al-based MOF showing pore size between 4 to 6 Å, and MIL-91(Ti)[3] ($TiO(O_3PCH_2NHC_4H_8NHCH_2PO_3)$) which is a 3D high hydrophilic bis-phosphonate with ultramicropores (3.5 x 4Å) have been selected after several experimental measurements at small scale proving their capacity to keep CO_2 capture properties in real conditions (presence of impurities as water, NO_x, SO_2) and including, if it's

necessary, pre-treatment steps. They were upscaled at 200g-scale and shaped in 2mm-pellets with 3% of PVB by wet granulation. The adsorption performances have been evaluated by CO_2 and N_2 pure component adsorption isotherms and breakthrough curve measurements with CO_2/N_2 (15/85) mixture. From these data, a complete simulation of VPSA process using the Linear Driving Force model and IAST was performed on Aspen Adsorption® software to evaluate the performances of CO_2 capture processes with MIL-160(Al) and MIL-91(Ti) on a laboratory scale (1 Nm^3/h of flue gas, 15% CO_2, 85% N_2, dry). Three different configurations were simulated for this study: (i) a 2-stage VPSA process with 2 columns (Skarstrom cycle with 5 steps including pressure equalization)[4] and a 1-stage VPSA process with 3 columns with (ii) 5 steps[5] or (iii) 6 steps[6] including rinse and purge. These configurations have been investigated and optimized to study the influence of some variables and reach the targets of such a process: CO_2 purity of 95% and recovery of 90% with the lowest energy consumption. After a first optimization of these processes based on a design of experiments (adsorption time, purge time, purge flowrate, rinse time, rinse flowrate, pressure levels, column volume, L/D ratio, …), the targets are reached for 2-stage VPSA process and close for 1-stage VPSA process with 5 steps but with a higher energy consumption (>800 $kJ/kgCO_2$). The best results were obtained with the 1-stage VPSA process with 6 steps where the targets were reached with a lower energy consumption (<500$kJ/kgCO_2$) than the 5 steps configuration. Moreover, these results are experimentally confirmed by measurements on a 3-column VPSA lab scale pilot to treat a CO_2/N_2 (15/85) flow of 1 Nm^3/h with columns of 1.1 liters (L/D ratio of 4.3) confirming the potential of these two MOFs for CO_2 capture by VPSA processes.

References:

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