18-23 MAY 2025 PORTO-PORTUGAL
FOA15
15TH FUNDAMENTALS OF ADSORPTION

Experimental study of adsorption and desorption of carbon dioxide/nitrogen using microwave radiation on modified MOFs (Metal Organic Frameworks) with graphene oxide

N. Heymans [(1)], R. V. Pinto [(2)], A. Houzé [(1)], S. Devautour-Vinot [(3)], M. Muschi [(2)], F. Nouar [(2)], G. Mouchaham [(2)], C. Serre [(2)], G. De Weireld [(1)]

[(1)] *Thermodynamics and Mathematical Physics Unit, University of Mons (UMONS), Place du parc 20, 7000 Mons, Belgium.*
[(2)] *Institut des Matériaux Poreux de Paris, Ecole Normale Supérieure, ESPCI Paris, CNRS, PSL University, 75005 Paris, France*
[(3)] *ICGM, Université de Montpellier, CNRS, ENSCM, 34095 Montpellier, France*
nicolas.heymans@umons.ac.be

Combating climate change is the primary challenge of the 21st century, particularly in relation to the rising concentration of greenhouse gases. According to recent estimates, the industrial (steel, cement, lime, etc.) and energy production sectors account for nearly 60% of anthropogenic emissions, with 35 $GTCO_2$.eq per year [1]. Reducing emissions is therefore a necessity. In recent decades, a variety of capture and conversion methods have been studied. Among them, adsorption methods have become an increasingly promising alternative, especially due to their potential low energy consumption and high operational flexibility. One of their main challenges lies in optimizing the regeneration of the adsorbent, either through pressure (Pressure Swing Adsorption) or temperature (Temperature Swing Adsorption). The latter configuration provides more thorough regeneration but at the cost of longer cycles, resulting in lower productivity. Conventionally, the adsorbent is heated either directly with a heat transfer fluid or indirectly. In the first configuration, the issue is the low thermal capacity of the gas, while in the second, it is the poor heat transfer from the outside of the column [2]. To address this, new heating methods are emerging (Joule heating, induction heating, …), with one of the most promising being the use of microwaves (Microwave Swing Adsorption) [3]. Unlike conventional heating, which relies on thermal conduction and often leads to energy loss, microwaves penetrate directly into materials, allowing for faster and more efficient heating. Additionally, microwave-assisted adsorption processes can significantly reduce treatment times and improve the overall efficiency of the process. However, despite these advantages, the application of microwaves in adsorption processes also presents challenges, particularly regarding precise temperature control, heating uniformity, and the compatibility of adsorbent materials with microwave energy.

Metal Organic Frameworks (MOFs) are increasingly investigated for their versatility and their strong selectivity towards CO_2 as adsorbents. The aim of this study is to evaluate them in microwave-assisted capture applications. Without modification, MOFs exhibit low electrical conductivity and thus low microwave heating. By combining them with graphene oxide (GO), one can drastically enhance their microwave adsorption. Some adsorbents were selected among the MOFs based on their potential for CO_2 selectivity and adsorption capacity in post-combustion applications, their water stability, and their scalability through single-step synthesis. A series of composites were prepared with varying GO contents, and it was observed that incorporating 5 wt% GO via in situ synthesis resulted in composites exhibiting semi-conducting behavior [4]. CALF-20, MIL-120(Al) and MIL-91(Ti) are among the five MOFs studied with and without the 5 wt% of GO.

First, the adsorption properties of the MOFs were characterized through CO_2 and N_2 adsorption isotherm measurements. These measurements were conducted on a gravimetric setup from 0 to 1 bar and at temperatures ranging from 20 to 50°C. Then an experimental setup was developed to measure adsorption and desorption breakthrough curves for their study.

This setup, shown in Figure 1, consists of a generator from the Sairem group, capable of delivering microwaves in the range of 2400 to 2500 Hz with power up to 200 W. The borosilicate column (internal diameter of 18.5 mm and height of 40 mm) containing the adsorbent (3-5g) is placed in a cavity that acts as a waveguide, reducing energy losses (such as leaks or reflections back into the generator). The

temperature in the column is measured remotely using an infrared sensor (pyrometer) to avoid interference with the microwaves. Finally, the gas circulating through the column is analyzed using a mass spectrometer. A parametric study was conducted, starting with the impact of graphene oxide by measuring the adsorption capacity on MOFs without GO and then with 5% GO. A slight decrease in adsorption capacity was observed, proportional to the presence of GO, which is nearly inert regarding CO_2 capture. However, when exposed to microwave radiation, no significant temperature increase was observed for the samples without GO. Next, the desorption temperature was varied from ambient (with a simple nitrogen flush) to 60°C. Heating was performed by applying microwaves at 2400 Hz and a power of 20 W. As the temperature increased, a faster desorption was initially observed. Depending on the adsorbent, there seems to be a threshold temperature beyond which no further improvement in desorption is observed. For MIL-91 5wt% GO, this threshold is around 50°C. The flowrate of adsorption has been fixed to 4NL/h. The influence of the nitrogen flow rate in desorption was also investigated, ranging from 2 to 5 NL/h. As expected, a faster desorption was observed as the nitrogen flow rate increased. For MIL-91 at 50°C, desorption was completed in 13 minutes at 2 NL/h compared to 4 minutes at 5 NL/h. Finally, varying the CO_2 concentration from 10% to 50% led to the same conclusions regarding the influence of temperature and nitrogen flow rate on desorption.

At the conclusion of this study, it appears that coupling GO with MOFs slightly reduces their adsorption capacity but enables their regeneration via microwaves. Indeed, results show a drastically increased desorption time for the adsorbent without GO. It also appears that the desorption time is substantially reduced in an MSA process compared to its TSA equivalent using heated gas [4]. Finally, there exists an optimal flow rate and concentration for each system, minimizing the desorption time and the amount of purge gas required. This represents a considerable advantage for the use of MOFs in a complete CO_2 capture process.

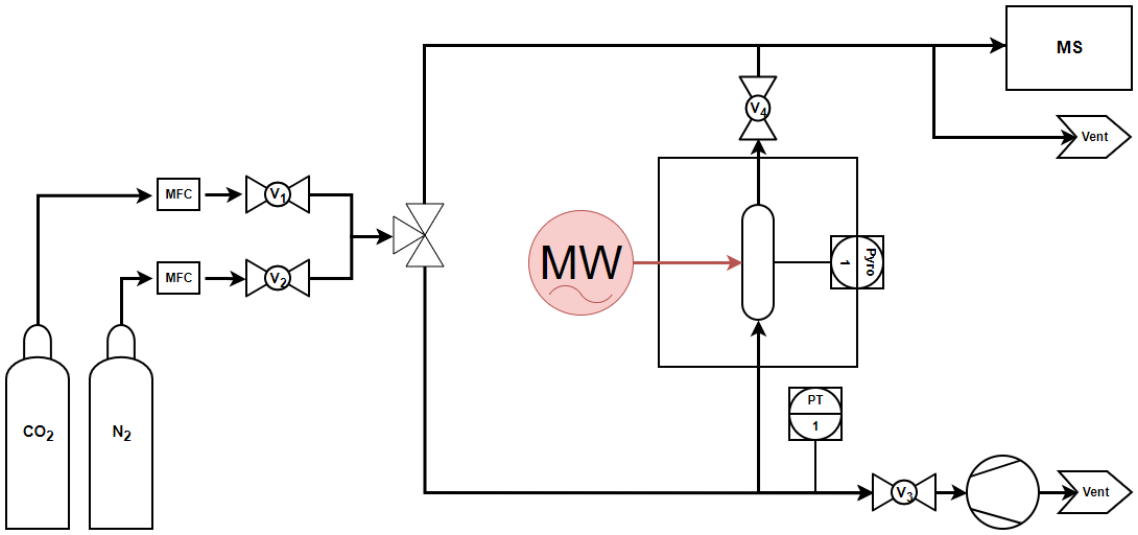

Figure 1. Schematic of **e**xperimental device for breakthrough curves measurements

References

[1] IPCC (2023).
[2] N. Tlili, G. Grévillot, and C. Vallières, "Carbon dioxide capture and recovery by means of TSA and/or VSA," *International Journal of Greenhouse Gas Control*, vol. 3, no. 5, pp. 519–527, Sep. (2009).
[3] B. Verougstraete *et al.*, "Advancements and challenges in electric heating for enhanced temperature swing adsorption processes," *Sep Purif Technol*, vol. 353, p. 128522, Jan. (2025).
[4] M. Muschi *et al.*, "Metal–organic framework/graphene oxide composites for CO_2 capture by microwave swing adsorption," *J Mater Chem A Mater*, vol. 9, no. 22, pp. 13135–13142, Jun. (2021).