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Experimental study of adsorption and desorption of carbon dioxide/nitrogen using microwave heating (MSA) on modified Metal Organic Frameworks (MOF's) with graphene oxide

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Abstract

Combating climate change is one of key challenge of the 21st century, particularly in relation to the rising concentration of greenhouse gases. According to recent estimates, the industrial (steel, cement, (petro)chemistry, lime, etc.) and energy production sectors account for nearly 60% of anthropogenic emissions, with 40 $GTCO_2$.eq per year [1]. Reducing emissions is therefore a necessity. In two last decades, a variety of carbon capture 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 - PSA) or temperature (Temperature Swing Adsorption - TSA). 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 desorption step can significantly reduce treatment times and improve the overall efficiency of the process. However, despite these advantages, the application of microwaves in thermal swing 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 or no electrical conductivity and thus low or no microwave heating. By combining them with graphene oxide (GO), one can significantly 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]. The MOFs considered in this study are the MIL-91(Ti), MIL-160(Al), CALF-20, MIL-120(Al) and NH_2-MIL-53(Al) with and without the 5 wt% of GO.
First, the adsorption properties of the MOFs were characterized through CO_2 and N_2 pure 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. In parallel, an homemade 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 on MIL-91(Ti); CALF-20 and MIL-120(Al), 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 80°C. Heating was performed by applying microwaves at 2450 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 4 NL/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. A similar study has been conducted for the CALF-20 and the MIL-120(Al).
Finally, the influence of adsorbed water regarding both the adsorption capacity and the microwave absorption was investigated. It is shown that water molecules strongly enhance the radiation absorption allowing a regeneration of the sample without graphene oxide where otherwise no absorption is observed. Additionally, some MOF's proved to increase their adsorption capacity of carbon dioxide in presence of water (e.g. CALF-20 with a relative humidity below 25%). This is a promising result for CO_2 capture in wet conditions without the need for a semi-conductive additive.

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 decrease desorption time for the adsorbent with GO compared to the one without GO. It also appears that the desorption time is substantially reduced in an MSA process compared to its "classical" 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.

References

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Keywords: Metal Organic Framework's, Microwave, Graphene oxide, carbon dioxide capture, Microwave Swing Adsorption.

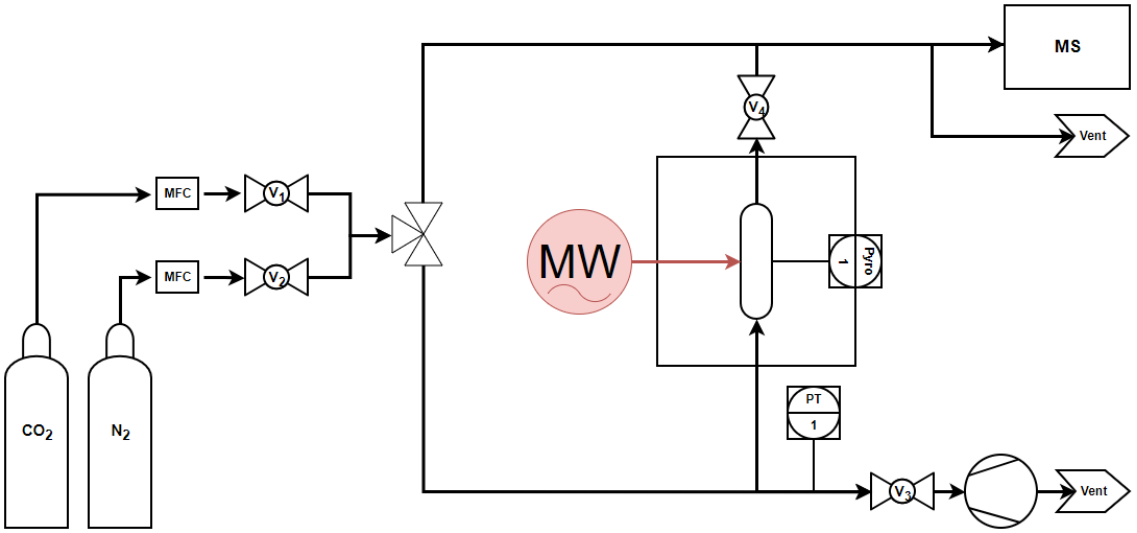

Figure 1: Schematic of experimental device for breakthrough curves measurements