# ABSTRACT

Metal organic frameworks have gained considerable attention in recent years. Due to their high surface area and pore volume they are being widely evaluated for potential applications in several areas including adsorptive separations, gas storage and catalysis. Early adsorption studies on MOFs concentrated on hydrogen storage; this was followed by evaluation of their potential for $CO_2$ and methane adsorption. Only recently adsorption of other gases is being investigated for their potential applications in adsorptive separations.

The aim of this work is two-fold; apart from systematic measurement and analysis of these frameworks for adsorption of several carefully gases with industrial potential, this work also aims to correlate the adsorptive behaviour of the gases to their physical properties. In order to achieve this objective, adsorbate gases themselves, experimental temperature and pressure were carefully chosen for these measurements.

Two different frameworks *viz.* Cu-BTC (HKUST-1) and Cr-BDC (MIL-101) were studied. Gravimetric experiments for measurement of pure gas adsorption were systematically carried out using a magnetic suspension balance (Rubotherm). Gases like $N_2$, $O_2$, Ar, CO, $CO_2$, $CH_4$, $C_3H_8$ and $SF_6$ with varying physical properties (e.g. molecular diameter, polarizability, dipole-quadrupole moments) were chosen as probes for studying adsorption properties of these MOFs concerned. These studies were carried out at selected temperatures between 283 to 353 K and pressures ranging between 0-100 bar.

It was observed in literature, synthesis of MOFs under different reaction conditions (i.e. temperature) and post synthesis treatments yield samples with different specific surface areas and pore-volume. This difference affects the overall adsorption properties of the framework. Under these circumstances it has often been a practice to use a "scaling-factor" to match isotherms obtained in different laboratories or comparing experimental data with simulation results. The results obtained in this work showed that such scaling factor may not be unique; it changes with loading, but rather independent of temperature, pressure or the adsorbate. At the zero pressure limit it would be equal to the ratio of Henry constants.

The isotherms on Cu-BTC could be well described by Langmuir, Virial or Virial-Langmuir type models; however that on Cr-BDC required a Dual Site Langmuir type model. Cr-BDC is known to have heterogeneity to adsorption with active metal centers and sites inside the pores of super tetrahedra being the two major locations for adsorption. The enthalpy of adsorption at low loading was directly related to polarizability of the adsorbates as in case of zeolites; CO and $CO_2$ however were exceptions due to their polarity. For all gases considered, the enthalpies of adsorption were found to be lower than those on purely siliceous zeolite like silicalite, suggesting that only moderate interaction exists between the gas and the frameworks.

Comparative adsorption study of three different gases viz. CO, $CO_2$ and $CH_4$ on Cu-BTC and Cr-BDC frameworks up to high pressures indicates that the polarity of the gas molecules plays an important role in determining their adsorption behaviour. In the low loading region the difference between enthalpies of adsorption for all three gases are modest for Cu-BTC whereas they are more pronounced in case of Cr-BDC. This behaviour is attributed to availability of accessible open metal centers for electrostatic interactions. Due to these electrostatic interactions, CO which has dipole moment initially adsorbs more than a non-polar molecule like $CH_4$. However, as the open metal centers needed for electrostatic interactions are occupied the effect of these interactions decreases and methane (which has slightly higher polarizability than CO) starts to adsorb more after this region. Due to large pore volume of Cr-BDC, the loading for gases at our highest experimental pressure does not seem to approach saturation as in case of Cu-BTC. The adsorption behaviour for these three gases can be well correlated to the temperature, pressure and polarity.

$CO_2$+$CH_4$ binary adsorption was studied on Cu-BTC at at 305 K and for pressures up to 10 bar using an infinite dilution gas chromatographic method; appropriate thermodynamic analysis using Virial-Langmuir model was performed on these experimental results. Based on this analysis, cross virial coefficients for adsorption were estimated. The results indicate that that within 10 bar the adsorption of $CO_2$+$CH_4$ mixture on Cu-BTC follows Ideal Adsorbed Solution Theory closely. The selectivity value lies between 5.7 and 7.2.

The results presented in this work indicate that MOF materials have high capacity (or at least comparable to those on zeolites) for a variety of gases; on the other hand they only have modest enthalpies of loading unlike in case of polar zeolites. Both these properties make them attractive candidates for applications in adsorptive separations.