A case study on toluene removal by PDMS-modified metal organic frameworks compared to activated carbon.

Luqman Hakim Mohd Azmi1,2,3,*, Elwin Hunter-Sellars1, Bradley Ladewig4, Daryl Williams1

1 Surfaces and Particle Engineering Lab, Department of Chemical Engineering, Imperial College London, Exhibition Road, SW7 2AZ, London, United Kingdom.
2 Barrer Centre, Department of Chemical Engineering, Imperial College London, Exhibition Road, SW7 2AZ, London, United Kingdom.
3 Grantham Institute – Climate Change and Environment, Imperial College London, Exhibition Road, SW7 2AZ, London, United Kingdom.
4 KIT Institute of Micro Process Technology, Karlsruhe Institute of Technology Germany.

*Corresponding email: l.mohd-azmi17@imperial.ac.uk

Keywords: Metal-organic frameworks, toluene, volatile organic compounds, hydrophobic, adsorption.

1 Introduction
Until now, adsorption by porous materials is the most demonstrated technology used for VOCs abatement. Standard air cleaning devices/filters contain carbon-based sorbents given their low cost, high porosity, and stability. Despite these advantages, they are known as structurally amorphous. The scarcity of precise structural details restricts further optimization studies for enhanced adsorptive performance (Xie et al., 2018). Recently, intense research is concerted on a superior class of adsorbent known as metal-organic frameworks (MOFs); built from metal ions bridged with organic linkers. MOFs are characterized with orderly pore structure, high surface area, versatile reusability, and functionalities for vast application prospects particularly in the field of volatile organic compounds (VOCs) treatment (Wang et al., 2019). However, to achieve effective VOCs removal even with the ubiquitous moisture presence, the material needs to feature high water resistance and surface area. Therefore, realizing the limitations from conventional carbon sorbents and the harms posed by VOCs in our surrounding, it is increasingly relevant to focus on developing water-stable MOFs as a potential alternative. By starting with a hydrophilic and highly porous MOF (MIL-101), this study explores the effects on the toluene capture performance after it has been coated with a hydrophobic silicon-based polymer, polydimethylsiloxane (PDMS).

2 Experimental Section
Materials: SYLGARD 184 silicone elastomer base (PDMS) was purchased from Dow Corning Company. Chromium nitrate nonahydrate (Cr(NO₃)₃·9H₂O) and terephthalic acid (H₂BDC) were all supplied by Sigma-Aldrich. All solvents and chemicals were from reagent grade and used without further purification.

Methods: PDMS was poured into a large petri dish containing thinly spread MOF in a smaller dish. The coating was obtained after heat treatment at 235 °C for 6 hours (Zhang et al., 2014). The synthesis of MIL-101 follows our earlier work (Azmi, Williams and Ladewig, 2020) where 2 g of Cr(NO₃)₃·9H₂O (5 mmol), 0.83 g of H₂BDC (5 mmol) and 0.29 mL of acetic acid (5 mmol) were mixed in a Teflon-liner and heated at 220 °C for 8 hours. The resultant solid powder was washed with copious...
amounts of water, dimethylformamide and ethanol before left dried in vacuo overnight at 220 °C. The accessible porosity of the tested materials was probed using N₂ gas adsorption at 77 K on Micrometrics 3Flex Surface Analyzer. Vapor adsorption isotherms of water and toluene (200 sccm) were measured in an Intelligent Gravimetric Analyzer (IGA-002, Hiden Analytical Ltd.) and Dynamic Vapor Sorption (Resolution, Surface Measurement Systems) instrument at 303 K respectively.

3 Results and Discussion
After modification, when exposed to maximum water relative humidity (RH) at 0.8 P/P₀, Si-MIL-101 demonstrates 60% lower total water uptake (Figure 1) than its predecessor, although the surface area was reduced by ~40% (Table 1). Further reduction of the residual 20% water uptake is attributed to the Si coating presence. Our complementary surface analysis (XPS, XRF and EDX) indicate inconsistent Si distribution (17 wt% to 34 wt%) on the crystals, indicating limited coverage. Purportedly homogenous but limited PDMS coverage suggests the need for additional studies to enhance the coating uniformity. In fact, previous successful reports have outlined several key factors for optimization, involving careful selection of PDMS molecular weight and architecture, coating time, experimental parameters (PDMS concentration, state of matter) and cross-linking temperature. The delayed pore filling processes by Si-MIL-101 (represented by the higher shift following the onset P/P₀) also corroborated the minimal hydrophobicity improvement. Figure 2 compares the toluene adsorption isotherms of MIL-101 before and after PDMS modification below 0.1 P/P₀. Within this low-pressure region, the PDMS coating effectiveness is obvious, lagging by only 20% at 0.1 P/P₀ compared to MIL-101 due to the high solvent affinity despite reduced surface area.

Table 1. BET surface area analysis of the MOFs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101</td>
<td>2710</td>
<td>2.2</td>
</tr>
<tr>
<td>Si-MIL-101</td>
<td>1558</td>
<td>1.2</td>
</tr>
</tbody>
</table>

4 Conclusions
The introduction of hydrophobic PDMS lining on the pores of hydrophilic MOF (MIL-101) surface resulted in slight improvement to the hydrophobicity as evident from the water adsorption isotherms. However, the modification is considered only partially successful since the reduced surface area (~40%) is not compensated with higher toluene adsorption capacity. Strategies to achieve better PDMS coating have also been included for future guidance. Based on these preliminary data, further work is ongoing in our lab to optimize the coating protocol.

5 Acknowledgement
Luqman Hakim Mohd Azmi gratefully acknowledges the financial assistance provided by Yayasan Khazanah, the Malaysian Government sovereign wealth fund body for his PhD studies.

6 References
Azmi, L. H. M., Williams, D. and Ladewig, B. P.
