Chapter 5

Adsorptive Removal of Industrial Toxicants over Metal Organic Frameworks

5.1. Introduction:

It is now increasingly evident that a new kind of warfare is emerging in the world. Conventional warfare and battlefields are left behind, and despite the existence of various examples of unconventional warfare applications, particularly in the second half of the 20\textsuperscript{th} century; the 21\textsuperscript{st} century seems to becoming a more intense era of unconventional-asymmetric war. During World War I chemical agents such as phosgene, chlorine, sulfur mustard, diphosgene (trichloromethylchloroformate), diphenylarsine, chloropicrin, and diphenylchloroarsine were used offensively by both the Allies and the Axis to produce mass casualties. Apart from chemical agents described above, used as incapacitating agents or weapons of mass casualty, also have important uses as industrial chemical intermediates or are the end products of non-weapons manufacturing processes. Recently, the definition of Weapons of Mass Destruction (WMD) has included nuclear, biological and chemical (NBC) weapons. Now, however, the coverage has been extended by inclusion of radiological, and the term CBRN was adopted. However, today’s concern is not limited to classical CBRN war and/or terrorism, in other words, the sources of CBRN are not only the misuse of military means or the production of one’s own CBRN weapons, but also the deliberate or unintentional release of toxic industrial chemicals (TICs), which have great potential of hazard and even mass destruction capability. A typical example showing the threat potential of the accidental release of TICs
and dimensions of a chemical plant accident and its outcomes is the Bhopal, India event\(^1\). During the night of December 2-3, 1984, the world’s worst industrial accident took place in the city of Bhopal, at a pesticide-manufacturing factory, owned by the US-based multinational Union Carbide. Approximately 40 tons of toxic gas, namely methyl isocyanate) (MIC), leaked from the plant into the surroundings, i.e., densely populated area. The gaseous cloud caused immediate lung and eye problems. Estimates of the mortality and morbidity in the aftermath vary. Greenpeace reported that 16,000 died and half a million were injured\(^1, 2\).

Industrial chemicals have become an integral part of daily life in modern society following the industrial revolution that started after World War II. They are developed and used for peaceful conditions and to improve quality of human life, and exist in numerous qualities and quantities. A TIC is defined as any substance that is produced and used by industry for various purposes and that, because of its chemical, physical or biological properties, poses a potential risk for life, health, the environment, or property when not properly contained\(^3\). Median lethal toxicity of TICs is 10-100 times lower than the classical chemical warfare agents, but their availability in quality and quantity is much higher. While the most frequently used CWAs number about 70, approximately 70,000 TICs are produced, used and stored in large amounts and circulated around us by hundreds of thousands of vehicles, and/or they enter our environment as toxic wastes\(^1\). Therefore, the likelihood of exposure to them in large amounts is relatively high. Industrial accidents are defined as unexpected and unwanted events caused by spilling out of hazardous substances in the course of production, storage or transportation. They occur unexpectedly, unpredictably
and fast, and any combination of these makes the event more complex and demanding. For example, Ammonia, a naturally occurring soluble alkaline gas, is a colourless irritant with a sharp odour. It is widely used in industrial processes, including oil refining as well as the production of explosives, refrigerants, fertilizers, and plastics. Ammonia is also used as a fixative in photographic, blueprinting, and duplicating processes. It is a particularly significant airborne environmental hazard in swine and poultry confinement areas. Another source of exposure can be from well-known ammonium-based cleaning agents. Ammonia is transported daily by rail and road across the country. Chlorine, a greenish to yellowish compound, is another irritant gas. Chlorine was used as a chemical warfare agent during World War I because of its heavier-than-air capacity to occupy low-lying areas such as trenches. Chlorine is widely used in the paper and pulp mill production industries. Accidental exposure to chlorine can occur in the household or anywhere bleach is mixed with acidic cleansers in an unventilated room. Other common sources of exposure are swimming pools, where an imbalance in mixing or dilution can result in increased release of chlorine gas. Since World War I over 200 major incidents involving mild to toxic chlorine exposure have occurred worldwide. Intentional exposures are not limited to the battlefield. Poorly water soluble smokes such as tear gas has been used for many years in the riot control operations. Hydrogen cyanide (HCN) is one of the gases most toxic to humans. It may be encountered in industrial processes as sodium or potassium cyanate or as acrylonitrile. Exposures to the salts may occur during the extraction of gold, in electroplating, or in photographic processes. HCN can be manufactured as a by-product during the synthesis of acrylonitrile, which is a more common industrial hazard used in the production of
synthetic rubber and as a fumigant. In spite of on-going efforts to reduce or prohibit unconventional warfare, the period after World War II witnessed a growing interest in WMD, and there are many examples of applications in conflicts in many areas of the world\textsuperscript{6}.

In a chemical warfare scenario, the use of the chemical defence equipment is a must to survive and execute the assigned responsibilities. However, the equipment can not be used directly after production and can only be used when these are certified through the tests and evaluations. In order to evaluate the Chemical defence equipment, it will require working with the CWAs, which are highly toxic and can cause the casualties and incidents. Therefore, generally the equipments, especially the protection equipment which are tested against the higher concentrations are tested against the non toxic chemicals simulating the chemical warfare agents. Though carbon tetra chloride is used as simulant to evaluate the NBC Canisters and Filters against the nerve and blister agents, it is classified as hazardous substance in the Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) list of pollutants, because of its confirmed carcinogenic and hepatotoxic properties. For these reasons, strict regulations are to be abided by the local regulation authorities and governments on the protection of the environment and air quality, industrial plants need to eliminate or reduce the content of toxic chemicals in gaseous effluents prior to their release into the atmosphere. As the chemical industry continues to grow, the filtration of toxic chemicals is a major focus in current sorbent development. Efforts are on-going to develop materials having higher removal capability for specific chemicals, such as hydrogen cyanide\textsuperscript{7}, ammonia\textsuperscript{8}, cyanogen chloride\textsuperscript{9}, arsine\textsuperscript{10, 11}, hydrogen sulfide\textsuperscript{12}, and methyl
bromide\textsuperscript{13}, etc. Indeed, many of these materials provide substantial removal capabilities; however, many of the efforts focus on optimization against a single toxic gas. In particular, materials capable of providing protection against chemicals for broad spectrum, to include acidic and basic gases in support of military and National Institute for Occupational Safety and Health (NIOSH) Chemical Biological Radiological and Nuclear (CBRN) filtration devices are sought\textsuperscript{14,15}.

Highly porous structures possessing functionalized active sites are essential for retention of light vapours. MOFs are especially interesting in the field of adsorption, separation and storage of gases and vapours. In the last ten years MOFs have been extensively studied for the removal of various toxic and volatile organic compounds. Adsorption of ammonia has been studied on HKUST-1, MOF-74, MIL-47, IRMOF-1, IRMOF-10, and IRMOF-16\textsuperscript{16}. Lieder et al. investigated the effects of adsorption of ammonia on the MIL-53 using solid state NMR spectroscopy\textsuperscript{17}. In MIL-53 it was observed that there is a linear increase of the quadruple coupling constant of the framework aluminium atoms in dehydrated MIL-53 as a function of the proton affinity of the adsorbates for the nitrogen bases of acetonitrile, ammonia, and pyridine. In addition to pure materials, composites containing MOFs have also been synthesized. Petit et al. studied ammonia adsorption of several MOFs and MOF/graphite oxide (GO) composites for use in air purification applications\textsuperscript{18-25}. NO interacts strongly with coordinatively unsaturated sites (CUSs) of MOFs, such as those found in Cu–BTC, MOF-74, and MIL-88\textsuperscript{26-28}. Cu–BTC shows an NO adsorption capacity of 3 mmol g\textsuperscript{-1} at 1 bar and 298 K\textsuperscript{29}. Hamon et al. studied several MIL-series MOFs, including MIL-53 (Al, Cr, Fe), MIL-47 MIL-100 (Cr), and MIL-101 (Cr), for
H$_2$S adsorption at a temperature of 303 K$^{30}$. Song et al. developed a POM–MOF composite from Cu–BTC and the Keggin-type POM CuPW$_{11}$O$_{39}$ and investigated its utility as a catalyst using hydrogen sulfide and various organic thiols$^{31}$. Peterson et al. reported on the removal of several toxic gases, including cyanogen chloride, a highly toxic chemical used as a chemical warfare agent, using composites made from Cu–BTC and zirconium hydroxide$^{32}$. The number of studies that have examined dynamic gas separations using MOFs is limited$^{33-35}$. Work done by Yaghi and co-workers$^{33, 36}$ on TICs such as sulfur dioxide and ammonia shows that MOFs have good potential to become next-generation filter media. Cu-BTC (HKUST-1) and Mg-MOF-74 have displayed high ammonia adsorption capacities (greater than 5mmol/g) due to the unsaturated metal centres; nevertheless, their structures collapse upon exposure to humid environments$^{36-37}$. Stability of MOFs under humid environments is a fundamental requirement for their use in CBRN filters. Recently, Decoste et al. have reported the first review article summarizing TICs removal from air by using MOFs$^{38}$.

This particular study is concerned with assessing the capability of novel materials to purify breathing air. To that end carbon tetrachloride (CCl$_4$) is selected as an industrial toxicant as well as a simulant of nerve and blister agents. Further cyclohexane (C$_6$H$_{12}$) was also studied as another industrial toxicant an alternative to CCl$_4$ as the later one is hepatotoxic.
5.2. Breakthrough Experiments:

Breakthrough experiments is an competent means of evaluating the efficacy of a adsorbent to remove a chemical and typically more applicable to filters, which operate in dynamic flow through conditions. This information is used to determine the protection afforded by a particular filter in an air-purifying respirator or a collective protection system. The basic concept of the breakthrough experiment is the introduction of a sorbate through a packed adsorbent bed. As the sorbate begins eluting from the packed bed, the protection afforded by the adsorbent can be determined by the time it takes the chemical to reach a predetermined toxic limit, known as the breakthrough time ($t_b$). It is imperative that developmental materials be evaluated against a wide range of low- and high-volatility chemicals to determine an envelope of protection. Adsorbents used in air purification applications are commonly evaluated for total capacity and/or breakthrough time ($t_b$). The total capacity of a material is typically based on an adsorption isotherm, which measures the amount of the chemical of interest that sorbs on the material as a function of pressure at a constant temperature.

**Theory:** Initially, when a contaminated gas stream passes through a packed sorbent bed, most of the contaminant, the adsorbate, is adsorbed in the vicinity of the inlet to the bed. The gas then passes on with little further adsorption taking place. Later, when the inlet part of the adsorbent becomes saturated, adsorption takes place deeper inside the bed. As more gas passes through and adsorption proceeds, the so-called mass transfer zone (MTZ) moves forward until the breakthrough point is reached. If the flow of gas is continued, the exit
concentration from the bed will rise gradually until it reaches the level of the inlet concentration. At this point, the bed is fully saturated. The simplest case, when the gas stream is challenged with one organic vapour, is illustrated in Figure 5.1. The service life of the filter bed is regarded as the time when the exit concentration has reached an unacceptable level. When packed beds of adsorbents are used for removing gases and vapours from air streams, it is essential to know their efficiencies and service lives to facilitate application, design and maintenance decisions.

![Idealized breakthrough curve of a fixed bed adsorber](image)

Figure 5.1 Idealized breakthrough curve of a fixed bed adsorber

Performance of carbon bed in NBC filtration system depends upon the adsorption capacity/kinetic saturation capacity of used adsorbent and the rate of
adsorption or reactive removal of the contaminants. Adsorption capacity/kinetic saturation capacity depends on parameters such as temperature, concentration, bed geometry, flow rate of gas mixture, particle size and reactivity of the adsorbents surface\(^\text{39}\). Of these, flow rate of gas mixture was observed to be one of important parameters which affect the rate of adsorption prominently. In this regard, Jonas and Svirbely\(^\text{40}\) and Wood and Moyer\(^\text{41}\) have reported that at lower flow rates the rate of adsorption was low while the rate of adsorption increased with increasing air flow rates. Those observations were attributed to diffusion of vapour molecules and the same was found to be the rate limiting process. In order to understand this and the effect of above-mentioned parameters, Jonas and Svirbely\(^\text{40}\) have utilized the modified Wheeler equation\(^\text{42}\). The Wheeler equation was derived from a continuity equation of mass balance between gas entering an adsorbent bed and the sum of gas adsorbed plus that penetrating through the bed and assumes that the rate controlling process is a first order and irreversible. The modified Wheeler equation is given below:

\[
\begin{align*}
t_b &= \frac{W_e W}{Q C_{in}} - \frac{W_e \rho_b}{K v C_{in}} \ln \left( \frac{C_{in} - C_{out}}{C_{out}} \right)
\end{align*}
\]

Equation 5.1 Modified Wheeler Jonas Equation

\(t_b\) = breakthrough time [min]

\(W\) = weight of the MOF [g]

\(W_e\) = Kinetic adsorption capacity of the MOF for the vapour [g/ g\(_{\text{MOF}}\)]

\(C_{in}\) = filter inlet concentration of the vapour [g/cm\(^3\)]

\(Q\) = volumetric flow rate [cm\(^3\)/min]

\(\rho_b\) = bulk density of the MOF [g\(_{\text{MOF}}$/cm\(^3\)]
$k_v = \text{overall adsorption rate coefficient [min}^{-1}]$

$C_{\text{out}} = \text{chosen breakthrough concentration [g/cm}^3\text{]}$

When Wheeler-Jonas is applicable to an adsorption process (e.g. physisorption), plotting breakthrough time versus inlet/outlet concentration gives a straight line, with equation $y = b - ax$.

$$t_b = \frac{W e W}{QC_{\text{in}}} - \frac{W e \rho_b}{k_v C_{\text{in}}} \ast \ln \left( \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{out}}} \right)$$

$$y = b - a \ast x$$

A breakthrough test is an experiment determining essential parameters of an adsorption process (e.g. physisorption). The parameters ($W$, $C_{\text{in}}$, $Q$, $\rho_b$, $C_{\text{out}}$) figuring in the Wheeler-Jonas equation are fixed for a specific breakthrough test. The parameters, $W_e$ and $k_v$, essential for determining the safety margins of the filter, can then be calculated applying Wheeler-Jonas, more specifically via equation 5.2, 5.3.

$$b = \frac{W e W}{QC_{\text{in}}}$$

$$a = \frac{W e \rho_b}{k_v C_{\text{in}}}$$

Equation 5.2

Equation 5.3
5.3. Experimental:

5.3.1. Chemicals/ Instruments:

Carbon tetra chloride and cyclohexane were procured from M/s sd Fine Chemicals. Mini RAE 3000 VOC monitor form M/s RAE systems, USA was used for the monitoring of CCl\(_4\) and C\(_6\)H\(_{12}\) vapours. KDS dual syringe pump series 200 and 100ml, 250 ml capacity gas flow meters were bought from Sigma Aldrich India.

5.3.2. Test rig for breakthrough Study:

Figure 5.2 represents the experimental test set up for the breakthrough study of CCl\(_4\) and C\(_6\)H\(_{12}\) vapours. A blower was used as an air source and air flow was controlled by a flowmeter. Relative humidity (RH) was controlled by passing the air through a water chamber. The required concentration of Analytes were generated by injecting a controlled amount of CCl\(_4\) and C\(_6\)H\(_{12}\) using an auto syringe pump into the mixing chamber, maintained at 80°C and 50°C for CCl\(_4\) and C\(_6\)H\(_{12}\) respectively and then mixed with an air stream containing the required moisture content to achieve a predetermined concentration. The completely mixed stream then passed through a adsorbent bed, filled on a weight basis in a 6 mm internal diameter tube approximately 20-80 mg of MOF materials were being used for each test. Breakthrough time and breakthrough concentration (10 ppm) were monitored at the outlet of the MOF bed with the VOC monitor RAE 3000 equipped with a photo ionization detector. Details of experimental conditions are tabulated as follows:
Table 5.1 Experimental conditions of breakthrough experiments

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of MOFs</td>
<td>20-80 mg</td>
</tr>
<tr>
<td>Test flow rate</td>
<td>75- 250 ml/min</td>
</tr>
<tr>
<td>CCl₄ inlet conc.</td>
<td>5.3- 15.38 mg/L</td>
</tr>
<tr>
<td>C₆H₁₂ inlet conc.</td>
<td>2.6- 7.8 mg/L</td>
</tr>
<tr>
<td>Breakthrough conc.</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Temperature</td>
<td>25± 5°C</td>
</tr>
<tr>
<td>Relative Humidity (RH)</td>
<td>30± 5 %</td>
</tr>
</tbody>
</table>
Figure 5.2. Breakthrough Test Rig

1- Air blower
4- Water column
6- Auto syringe pump
8- Heating mantle
14- Adsorbent bed

2, 3, 11, 12, 15- Control valve
5, 13- Gas flowmeter
7, 9- Mixing Chamber
10- Temperature & RH sensor
16- VOC Monitor
5.4. Results and Discussion:

HKUST-1, MIL-101 and copper nitrate impregnated MIL-101 were evaluated against CCl₄ and C₆H₁₂ under dynamic conditions. The effects of mass of MOFs, analyte concentration and air flow mixture have been studied on the breakthrough behaviour of the analytes. Figure 5.3 and 5.4 represent comparison of breakthrough behaviour of HKUST-1, MIL-101 and copper nitrate impregnated MIL-101 for CCl₄ and C₆H₁₂ respectively. The weight of the MOFs, test flow and concentration of CCl₄ and C₆H₁₂ were maintained 0.05g, 100ml/L and 5.3 mg/L of CCl₄ and 2.6 mg/L of C₆H₁₂ for this experiment. The breakthrough time of CCl₄ was found to be 5 min, 12 min, and 4 min, and of C₆H₁₂ was found to be 5 min, 10 min and 3 min for HKUST-1, MIL-101 and copper nitrate impregnated MIL-101 respectively.

![Breakthrough behaviour of CCl₄ on different MOFs](image)
5.4.1. Kinetics of adsorption of CCl₄ and C₆H₁₂ on MOFs:

Amongst the three adsorbents used for the dynamic adsorption study copper nitrate impregnated MIL-101 shows minimum adsorption capacity towards the analytes. To explore how $t_b$ values vary with mass of the adsorbent breakthrough experiments were conducted at 5.3 mg/L of CCl₄ and 2.6 mg/L of C₆H₁₂ concentration and 150 mL/min flow rate for both the analytes. It was observed that with the increase of weight of the adsorbents the $t_b$ values also increased (Figure 5.5- 5.10) and different weight showed a straight line whose slope is proportional to $W_e$ values and intercept is related to $k_v$. 

![Figure 5.4 Breakthrough behaviour of C₆H₁₂ on different MOFs](image)
Figure 5.5 Effect of sorbent weight on breakthrough behaviour of CCl₄ on HKUST-1

Figure 5.6 Effect of sorbent weight on breakthrough behaviour of C₆H₁₂ on HKUST-1
Figure 5.7 Effect of sorbent weight on breakthrough behaviour of CCl₄ on MIL-101

Figure 5.8 Effect of sorbent weight on breakthrough behaviour of C₆H₁₂ on MIL-101
Figure 5.9 Effect of weight variation on breakthrough behaviour of CCl$_4$ on copper nitrate impregnated MIL-101

Figure 5.10 Effect of sorbent weight on breakthrough behaviour of C$_6$H$_{12}$ on copper nitrate impregnated MIL-101
The details of the $W_e$ and $k_v$ values are given in table 5.2 and 5.3. Among all the MOFs MIL -101 shows better adsorption capacity for CCl$_4$ and C$_6$H$_{12}$. The reason behind increase in the uptake capacity of MOFs as weight increases is availability of more binding sites for sorption, which also resulted in a broadened mass transfer zone.

Table 5.2 Effect of weight variation on adsorption kinetics of CCl$_4$ on MOFs

<table>
<thead>
<tr>
<th>MOFs Parameters</th>
<th>HKUST-1</th>
<th>MIL-101</th>
<th>Copper nitrate impreg. MIL-101</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic saturation capacity ($W_e$) (g/g)</td>
<td>0.078</td>
<td>0.176</td>
<td>0.074</td>
</tr>
<tr>
<td>Kinetic rate constant ($k_v$) (min$^{-1}$)</td>
<td>28905</td>
<td>16590</td>
<td>18305</td>
</tr>
</tbody>
</table>

Table 5.3 Effect of weight variation on adsorption kinetics of C$_6$H$_{12}$ on MOFs

<table>
<thead>
<tr>
<th>MOFs Parameters</th>
<th>HKUST-1</th>
<th>MIL-101</th>
<th>Copper nitrate impreg. MIL-101</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic saturation capacity ($W_e$) (g/g)</td>
<td>0.037</td>
<td>0.096</td>
<td>0.037</td>
</tr>
<tr>
<td>Kinetic rate constant ($k_v$) (min$^{-1}$)</td>
<td>15934</td>
<td>6957</td>
<td>16712</td>
</tr>
</tbody>
</table>

Based on the dynamic adsorption data the dead layer (minimum amount of adsorbent required to get any protection as at the dead layer or below it
instantaneous breakthrough will occur) and effective loading have been calculated. Table 5.4 describes dead layer and effective loading for different adsorbents and analytes. The dynamic loading was calculated from these data for the studied adsorbents. MIL-101 with an effective loading of 1.14 mol/kg clearly outperforms the other two adsorbents.

Table 5.4 Effective loading and dead layer of CCl₄ and C₆H₁₂ on different MOFs

<table>
<thead>
<tr>
<th>Parameters</th>
<th>MOFs</th>
<th>HKUST-1</th>
<th>MIL-101</th>
<th>Copper nitrate impreg. MIL-101</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dead layer (g)</td>
<td>CCl₄</td>
<td>0.010</td>
<td>0.011</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>C₆H₁₂</td>
<td>0.012</td>
<td>0.020</td>
<td>0.028</td>
</tr>
<tr>
<td>Effective Loading (mol/kg)</td>
<td>CCl₄</td>
<td>0.51</td>
<td>1.14</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>C₆H₁₂</td>
<td>0.44</td>
<td>1.14</td>
<td>0.45</td>
</tr>
</tbody>
</table>

5.4.2. Effect of concentration of carbon tetra chloride and Cyclohexane on the adsorption capacities of MOFs

To investigate the impact of concentration of CCl₄ on the adsorption capacities of MOFs $t_b$ values for different weight were determined at 5.3, 10.25, 15.38 mg/L concentration of CCl₄ in gas mixture at 150 mL/ min flow rate for HKUST-1 and for MIL-101 concentration of CCl₄ was kept same while the flow rate maintained at 100 mL/min. Figure 5.11 and 5.12 show the effect of
concentration of CCl₄ on the adsorption capacities of HKUST-1 and MIL-101 respectively.

Figure 5.11 Effect of Concentration on breakthrough behaviour of CCl₄ on HKUST-1

Figure 5.12 Effect of Concentration on breakthrough behaviour of CCl₄ on MIL-101
Effect of concentration of C₆H₁₂ on the adsorption pattern of MOFs breakthrough test were performed for different weight at 2.6, 5.2, 7.8 mg/L concentration of C₆H₁₂ in gas mixture at 150 mL/min flow rate for HKUST-1 and for MIL-101 concentration of C₆H₁₂ was kept same while the flow rate maintained at 100 mL/min. Figure 5.13 and 5.14 show the effect of concentration of C₆H₁₂ on the adsorption capacities of HKUST-1 and MIL-101 respectively.

![Graph showing breakthrough time vs weight for different concentrations of C₆H₁₂]

Figure 5.13 Effect of concentration on breakthrough behaviour of C₆H₁₂ on HKUST-1
Figure 5.14 Effect of concentration on breakthrough behaviour of C₆H₁₂ on MIL-101

The \( t_b \) values were plotted against different weights of MOFs at respective CCl₄ concentrations, and then the kinetic parameters were determined. The effect of concentration of CCl₄ on the kinetic parameters is shown in Table 5.5 and the effect of concentration of C₆H₁₂ on the kinetic parameters is shown in Table 5.6. In copper nitrate impregnated MIL-101 at higher concentration, i.e., instantaneous breakthrough occurred, therefore, effect of concentration was not studied in impregnated MOF.

With the increase in CCl₄ concentration from 5.3 to 15.38 mg/L, \( W_e \) values increased from 0.078 to 0.189 and 0.131 to 0.258 g/g while \( k_v \) values decreased from 28905 to 16731 and 12387 to 3932 min\(^{-1}\) (Table 5.5) for HKUST-1 and MIL-101 respectively.
Table 5.5 Effect of concentration on adsorption kinetics of CCl₄ on MOFs

<table>
<thead>
<tr>
<th>MOFs</th>
<th>CCl₄ conc. mg/L</th>
<th>Kinetic saturation capacity (Wₑ) (g/g)</th>
<th>Kinetic rate constant (kᵥ) (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td>5.3</td>
<td>0.078</td>
<td>28905</td>
</tr>
<tr>
<td></td>
<td>10.25</td>
<td>0.141</td>
<td>19288</td>
</tr>
<tr>
<td></td>
<td>15.38</td>
<td>0.189</td>
<td>16731</td>
</tr>
<tr>
<td>MIL-101</td>
<td>5.3</td>
<td>0.131</td>
<td>12387</td>
</tr>
<tr>
<td></td>
<td>10.25</td>
<td>0.230</td>
<td>5323</td>
</tr>
<tr>
<td></td>
<td>15.38</td>
<td>0.258</td>
<td>3932</td>
</tr>
</tbody>
</table>

On the other hand, in case of C₆H₁₂ increase in concentration from 2.6-7.8 mg/L, Wₑ values increased from 0.037 to 0.119 and 0.081 to 0.21 g/g, while kᵥ values decreased from 15934 to 8935 and 5176 to 3724 min⁻¹ (Table 5.6) for HKUST-1 and MIL-01 respectively.

Table 5.6 Effect of concentration on adsorption kinetics of C₆H₁₂ on MOFs

<table>
<thead>
<tr>
<th>MOFs</th>
<th>C₆H₁₂ conc. mg/L</th>
<th>Kinetic saturation capacity (Wₑ) (g/g)</th>
<th>Kinetic rate constant (kᵥ) (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td>2.6</td>
<td>0.037</td>
<td>15934</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>0.089</td>
<td>8855</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>0.119</td>
<td>8935</td>
</tr>
<tr>
<td>MIL-101</td>
<td>2.6</td>
<td>0.081</td>
<td>5176</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>0.132</td>
<td>5821</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>0.210</td>
<td>3724</td>
</tr>
</tbody>
</table>
Chapter 5

On increasing the concentration of analyte, the kinetic saturation capacity increased, indicating that when analyte concentration was more, more amount of adsorbate molecule come in contact with the adsorbent thus increasing the kinetic saturation capacity. As the number of molecules increased, the number of collisions also increased and the rate of diffusion increased, thereby resulting in the increase of $W_e$ values.

5.4.3. Effect of flow rate of carbon tetrachloride and cyclohexane on the adsorption capacities of MOFs:

Figure 5.15- 5.20 are showing the effect of flow rate on the adsorption properties of MOFs at 5.3 mg/L concentration of CCl$_4$ and 2.6 mg/L concentration C$_6$H$_{12}$. The flow rate was varied from 75 to 250 mL/min, and the values of $t_b$ were plotted versus weight at each flow rate.

![Figure 5.15 Effect of flow rate on breakthrough behaviour of CCl$_4$ on HKUST-1](image_url)
Figure 5.16 Effect of flow rate on breakthrough behaviour of CCl₄ on MIL-101

Figure 5.17 Effect of flow rate on breakthrough behaviour of CCl₄ on copper nitrate impregnated MIL-101
Figure 5.18 Effect of flow rate on breakthrough behaviour of C₆H₁₂ on HKUST-1

Figure 5.19 Effect of flow rate on breakthrough behaviour of C₆H₁₂ on MIL-101
Figure 5.20 Effect of flow rate on breakthrough behaviour of C_6H_{12} on copper nitrate impregnated MIL-101

The results are incorporated in Table 5.7 and 5.8. Accompanied by increase in flow rate from 75 to 250 mL/min, k_v values were found to be decreased.

Table 5.7 Effect of flow rate on adsorption kinetics of CCl_4 on MOFs

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Air mix flow rate mL/ min</th>
<th>Kinetic saturation capacity (W_e) (g/g)</th>
<th>Kinetic rate constant (k_v) (min^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td>150</td>
<td>0.078</td>
<td>28905</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.097</td>
<td>12255</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.104</td>
<td>15157</td>
</tr>
<tr>
<td>MIL-101</td>
<td>75</td>
<td>0.102</td>
<td>25092</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.131</td>
<td>12386</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.176</td>
<td>16590</td>
</tr>
<tr>
<td>Copper nitrate impreg. MIL-101</td>
<td>75</td>
<td>0.048</td>
<td>22998</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.054</td>
<td>16584</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.074</td>
<td>18305</td>
</tr>
</tbody>
</table>
Table 5.8 Effect of flow rate on adsorption kinetics of $C_6H_{12}$ on MOFs

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Air mix flow rate mL/min</th>
<th>Kinetic saturation capacity ($W_e$) (g/g)</th>
<th>Kinetic rate constant ($k_v$) (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td>150</td>
<td>0.037</td>
<td>15934</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.056</td>
<td>8843</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.070</td>
<td>8731</td>
</tr>
<tr>
<td>MIL-101</td>
<td>75</td>
<td>0.067</td>
<td>4387</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.081</td>
<td>5176</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.096</td>
<td>6957</td>
</tr>
<tr>
<td>Copper nitrate impreg. MIL-101</td>
<td>75</td>
<td>0.018</td>
<td>39436</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.026</td>
<td>16537</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.037</td>
<td>16712</td>
</tr>
</tbody>
</table>

Results showed that with increase in flow rate $W_e$ also increases which indicates that this is a purely physisorption phenomena. With increase in flow rate, the breakthrough curves became steeper and the breakthrough time decreased. This behaviour may be due to insufficient residence time of the analytes in the column and diffusion limitations of the analytes into the pores of the sorbent at higher flow rates. Even though more shortened mass transfer zone (usually preferable) was observed at the highest flow rate, the maximum breakthrough time for $CCl_4$ and $C_6H_{12}$ were actually observed at the low flow rate.
5.5. Conclusion:

HKUST-1, MIL-101, copper nitrate impregnated MIL-101 were evaluated against carbon tetra chloride and cyclohexane. The effect of weight, concentration of analytes and flow rate were studied. The order of protective potential against CCl$_4$ and C$_6$H$_{12}$ is as follows: MIL-101 > HKUST-1 > Copper nitrate impregnated MIL-101. Breakthrough behaviour of C$_6$H$_{12}$ is found to be similar with CCl$_4$ and indicative of pure physisorption phenomenon. As concentration of CCl$_4$ and C$_6$H$_{12}$ increases kinetic saturation capacity is also found to be increasing which may be attributed to the fact that when the concentration increases the number of molecules increase; as a consequence, number of collisions increase and thereby rate of diffusion increases. This is resulted into higher adsorption capacity. The same trend has been followed when effect of flow rate variation was studied. The impregnated MOF is found to be less significant for this study.

At this point, individual MOFs have shown efficacy towards specific gases; however, a full set of design rules has yet to be established to synthesize MOFs with the ability to remove a broad spectrum of toxic gases. The modification of MOFs can be exploited to design such materials, which has always been a challenge for activated carbons and other traditional filtration media.
References:


