3.1. Introduction:

Despite the greatly reduced threat of Cold War superpower conflict, the threat of chemical, biological, radiological, and nuclear attack still remains severe and credible. There is now renewed interest to develop biological and chemical reaction systems to neutralize a variety of chemical warfare agents (CWAs). In last few years scientific community showed their interests on establishing rapid and reliable decontamination processes for the nerve agents, sarin (GB) and VX and for the blister agent sulfur mustard (HD). Sulfur mustard was used during WWI and WWII, and in the Iran Iraq war of the 1980’s. Sulfur mustard is known for persistence in the environment, especially at the bottom of the ocean. The terrorist organization Aum Shinrikyo used sarin (GB) in the Tokyo subway in March, 1995, killing 13 civilians and VX in 1994 to kill a disgruntled ex-member. Established criteria emphasized that, for a decontamination/neutralization process to be effective, it must generate nontoxic reaction products, be rapid and controlled in a medium that is environmentally secured. In the years between 1994 and 1997, Bellamy reported that HD vapor adsorbed on the 13X zeolite and the modified resins could be degraded. Sulfonium ion of $\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}^+\text{S}^+(\text{CH}_2\text{CH}_2\text{OH})_2$ (CH-TG) over 13X zeolite and divinyl sulfide (DVS) over the resins were identified by NMR. In
Bartarm and Wagner\textsuperscript{10} stated in a patent that an activated alumina is able to neutralize the droplets of HD, GD (3,3-dimethyl-2-butyl methylphosphonofluoridate or soman), GB (isopropyl methylphosphono fluoridate or sarin) and VX (O-ethyl S-2 (diisopropylamino)ethyl methylphosphonothioate). The extensive reviews on decontamination procedures published in 1992\textsuperscript{6} and 2007\textsuperscript{11} were mostly focused on liquid or soluble decontamination agents (mostly alkaline and oxidizing solutions); minor attention was paid to heterogeneous decontamination system. Moreover, chemical solutions cannot be effectively used for decontamination of CWAs available as gases. Adsorbents such as impregnated carbon\textsuperscript{12}, nanometal oxides\textsuperscript{13,14} have been used for the degradation of CWAs, but the main drawback is they usually take a longer time to degrade, sometimes half-life value observed up to few days. Therefore, there is a need to find out solid phase decontaminants which can clean the contaminated surface/air effectively and rapidly due to inbuilt adsorption capacity towards CWAs with high efficiency.

Metal organic frameworks (MOFs), a new class of hybrid porous solids, are potentially a type of prominent porous adsorbents with ordered three-dimensional frameworks via strong metal–ligand bonds, stable at relatively high temperatures and can exist in an empty guest free state\textsuperscript{15-18}. Since their discovery, MOFs received lots of significant attentions in their potential applications in gas storage, separation, heterogeneous catalysis, sensing, drug delivery, and ionic conductivity\textsuperscript{19-23}, in addition to their wide range of classic applications in gas storage and separation, MOFs have been explored in the area of defence interests, for example adsorptive removal of CCl\textsubscript{4}, detection of
highly explosives and aromatic compounds, adsorption of DMMP and nitric oxide etc.\textsuperscript{24-27}. HKUST-1 has been used as a Lewis acid catalyst in many reactions such as acetalization of aldehydes with methanol, quinoline synthesis, $\alpha$-pinene oxide rearrangement, trimethylsilyl azide addition to carbonyl compounds\textsuperscript{28-31}, etc. Encouraged by its adsorption and guest molecule binding properties, it was thought to find out applicability of MOFs for the degradation of simulants of sulfur mustard and sarin such as 2-chloroethylphenyl sulfide (CEPS), 2-chloroethyl ethyl sulfide (CEES) and diethyl chloro phosphate (DECIP), diethyl cyano phosphonate (DECNP) respectively (Figure 3.1).

\begin{center}
\begin{tabular}{ll}
CEES & CEPS \\
\includegraphics[width=0.3\textwidth]{CEES.png} & \includegraphics[width=0.3\textwidth]{CEPS.png} \\
DECIP & DECNP \\
\includegraphics[width=0.3\textwidth]{DECIP.png} & \includegraphics[width=0.3\textwidth]{DECNP.png}
\end{tabular}
\end{center}

\textbf{Figure 3.1 sulfur mustard and sarin simulants}

The study of degradation kinetics of the simulants on the MOFs will help in developing a next generation NBC filtration systems containing high surface
area MOF capable of degrading the physisorbed CWAs in \textit{in-situ} thus avoiding
the cross contamination of the environment.

3.2. Experimental:

3.2.1. Materials:

Chloroform, dichloromethane, heptane, pentane and CEES were
purchased from Sigma–Aldrich chemicals Pvt. Ltd. CEPS and DECNP were
purchased from Alfa-Aesar, DECIP, bis(trimethylsilyl)trifluoro acetamide was
bought from Acros Organics. All the chemicals were used without further
purification.

\textbf{Caution:} Since the chemicals mentioned above, are highly toxic in nature,
therefore, these experiments should only be performed by trained
personnel using applicable protective gear and in high-quality fuming
hood.

3.2.2. Screening test for the reactivity of MOFs for the toxicants:

All the synthesized MOFs, i.e., bare and impregnated ones were exposed
to the toxicants to check the reactivity against sulfur mustard and sarin
simulants. Details of the reaction procedure are discussed in the following
section. It was found that amongst all the MOFs, HKUST-1 was found to be
reactive over the toxicants. Therefore, further reaction parameters were studied
with KHUST-1 only. Along with bare MOFs impregnated MOFs were also
studied for their chemical reactivity with the toxicants. Details of the results are
discussed in the following sections.
3.2.3. Reaction Procedure and kinetics of degradation of toxicants:

50 mg MOF was spiked with 40µL carbon tetrachloride containing 5µL of CEES, CEPS, and 40µL chloroform containing 5µL of DECIP and DECNP (incipient volume) in glass tubes separately and agitated for 5 min in vortex mixer for the homogeneous distribution of toxicants over the MOF. These tubes containing reaction mixture were allowed to stand at room temperature and each tube was taken out for kinetics studies at regular intervals of time. For kinetics of degradation, residual toxicants were extracted in carbon tetrachloride/chloroform and the solutions were subjected to GC/FID (gas chromatograph coupled with flame ionization detector) analysis using split less injection technique. GC spectra were obtained periodically to monitor the reaction in-situ. All Gas chromatographic analyses were performed in programming mode from 40 to 250°C at a rate of 10°C/min to determine the amount of remaining toxicants on a Chemito 8610 gas chromatograph equipped with BP-5 column (5% phenyl methyl silicon capillary column of 30m. length, 0.3 mm internal diameter). The detector and injection port were maintained at 280 and 220°C respectively. To understand the kinetics of degradation first order plots were made by plotting log (remaining agent conc.) on Y axis against time in hours on X axis. Rate constant (k) was calculated from the slope of the straight line and half-life calculated by following the equation \( t_{1/2} = \frac{0.693}{k} \). The same procedure was followed for all the MOFs.

For the degradation experiments in solution the graphs were made by plotting the per cent of agent degraded on Y axis and time on X axis.
Calculations for the composition of toxicants are based on relative peak areas. Recovery determinations are based on starting amount of toxicants and calculated amounts of CEES and other toxicants based on a five-point linear calibration vs. the amount of toxicant recovered in the controls using averaged values.

3.2.4. Effect of solvents and co-adsorbed moisture on the degradation of toxicants:

To identify the solvent suitability reactions were also carried out with different solvent such as tetrahydrofuran (THF), chloroform, heptane and pentane in similar way. The effect of the atmospheric moisture adsorbed by HKUST-1 on the degradation of the CEES was studied by exposing the HKUST-1 at different relative humidity for 1 h. The effect of the co-adsorbed moisture of the MOF has also been studied by adding 2 µL of water in the HKUST-1 prior to the reaction with CEES. To understand the role of the surface area and porosity same reaction procedure was followed with copper acetate monohydrate.

Effect of co-adsorbed moisture on the degradation of sulfur mustard and sarin simulants was also studied by adding 10 µL of water to the MOF prior to the reaction with the toxicants. Thereafter, extracting the residual toxicant after 20 min as stated in the reaction procedure.
3.2.5. Reusability of MOF:

The reusability of MOF was verified with HKUST-1. The MOF was tested by recovering the MOF after completion of the kinetics study from every cycle. The insoluble MOF was treated with the methanol and agitated for 5 min in vortex mixer to remove every portion of the unreacted toxicant adsorbed on the HKUST-1. This process was repeated for 5 times thereafter, the MOF was filtered out, dried and reused without further purification for the second run. The procedure was repeated and the efficiency of the MOF was checked up to the 4th cycle.

3.2.6. Identification of reaction products:

In order to investigate the reaction products 50 mg of toxicants exposed MOFs were extracted after 2 h of reaction with 5.0 mL of methanol in well-stoppered test tubes. The reaction mixtures were centrifuged and transferred to other tubes. This process was repeated for five times. Then the extracts were then purged with nitrogen gas to concentrate the extracted reaction products and were silylated by bis-(trimethylsilyl) trifluoroacetamide and analyzed by GC/MS (gas chromatograph coupled with mass spectrometer) instrumental techniques. GC/MS (6890N GC coupled with 5973 inert MS detector) of Agilent Technologies, USA was used for characterization of reaction products. It was equipped with HP-5 MS column of 30m×0.25mm×0.25m dimensions. Temperature programming [50°C (2 min hold) to 280°C (10 min hold) at 10°C/min] with split injection technique (10:1) was used to perform the study. Injection port and GC/MS interface, MS source and quadruple analyzer were kept at 280, 230 and 150°C, respectively. The degradation kinetics was studied
by exposing MOFs to CEES, CEPS, DECIP and DECNP under ambient conditions.

### 3.3. Results and Discussion:

#### 3.3.1. Kinetics of degradation of sulfur mustard and sarin simulants over unimpregnated MOFs:

Amongst all the synthesized MOFs only HKUST-1 has shown reactivity towards sulfur mustard and sarin simulants. First the MOFs were exposed to CEES and DECIP. It was found that HKUST-1 is reactive against both the toxicants, so to understand the nature of reaction further two more simulants (CEPS as sulfur mustard simulant and DECNP as a sarin simulant) were taken for comparative study. Kinetics plots shown in Figure 3.2- 3.5 exhibited that initial degradation of toxicants were faster followed by a steady state reaction indicating the first order reaction.
Figure 3.2a Kinetics of degradation of CEES

Figure 3.2b Percentage of degradation of CEES
Figure 3.3a Kinetics of degradation of CEPS

Figure 3.3b Percentage of degradation of CEPS
Figure 3.4a Kinetics of degradation of DECIP

Figure 3.4b Percentage of degradation of DECIP
Figure 3.5a Kinetics of degradation of DECNP

Figure 3.5b Percentage of degradation of DECNP
The fast initial reaction is attributed to the rapid adsorption and distribution of the toxicants within the pores and its interaction with the accessible reactive sites. The limited surface reaction occurs when the sites are exhausted, obviously, replacing the initial fast reaction by a steady state reaction. Result indicates the degradation of CEES is faster than CEPS. The half-life for the degradation of CEES and CEPS was found to be 16.11 and 75.27 min respectively (Table 3.1). DECNP was found to be degraded relatively faster than DEClP possessing the half-life of 42.98 min (Table 3.1). The order for degradation of studied simulants of sulfur mustard was: CEES > CEPS and for sarin was: DECNP > DEClP. No degradation of toxicants was observed with blank solution having no MOF.

Table 3.1 Kinetics data for the degradation of CEES, CEPS, DEClP and DECNP on HKUST-1

<table>
<thead>
<tr>
<th>Toxicants</th>
<th>Rate constant ((k)) (\text{min}^{-1})</th>
<th>Half Life ((t_{1/2})) (\text{min})</th>
<th>% of degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEES</td>
<td>0.043</td>
<td>16.11</td>
<td>91% in 40 min.</td>
</tr>
<tr>
<td>CEPS</td>
<td>0.009</td>
<td>75.27</td>
<td>83% in 80 min.</td>
</tr>
<tr>
<td>DEClP</td>
<td>0.011</td>
<td>60.18</td>
<td>83% in 120 min.</td>
</tr>
<tr>
<td>DECNP</td>
<td>0.016</td>
<td>42.98</td>
<td>87% in 60 min.</td>
</tr>
</tbody>
</table>

Kinetics study indicated that the degradation of CEES is faster than CEPS which is in accordance with neighboring group participation phenomenon. The slow degradation of CEPS is because of resonance involvement of lone pair of sulfur atom in phenyl ring, which in turn decreases neighboring group participation hence decreases leaving group tendency of Cl\(^-\). In case of CEES,
the ethyl group attached to sulfur atom acts as electron releasing group which increases the electron density on sulfur atom. The increased electron density on sulfur atom results in increase of neighboring group participation and makes Cl$^-$ to a better leaving group as shown in scheme 1. Kinetics study also indicated that DECNP was degraded fast than DEClP. The fast degradation of DECNP is due to better leaving tendency of CN$^-$ as compared to Cl$^-$ of DEClP. Moreover, the orders of the degradation of the toxicants are in line with their vapour pressure (Table 3.2). Toxicants with higher vapour pressure will diffuse more rapidly and result into faster rate of degradation.

Table 3.2 Vapour pressure and molecular diameter of CEES, CEPS, DEClP and DECNP on HKUST-1.

<table>
<thead>
<tr>
<th>Toxicants</th>
<th>CEES</th>
<th>CEPS</th>
<th>DECIP</th>
<th>DECNP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor pressure (mm Hg/25°C)</td>
<td>3.789</td>
<td>0.043</td>
<td>0.10</td>
<td>0.158</td>
</tr>
<tr>
<td>Molecular Diameter (Å)</td>
<td>6.98</td>
<td>8.6</td>
<td>12</td>
<td>10</td>
</tr>
</tbody>
</table>

On the other hand the effect of molecular size of the toxicant on the adsorption over MOF cannot be ruled out. The reason for the slow degradation of CEPS than CEES and DEClP than DECNP lies in the fact that larger the size of the molecule slower will be the adsorption (Table 3.2). Molecular diameter was calculated using the equation\(^{32}\). The molecular size of CEPS is greater than CEES and DECIP is greater than DECNP. Therefore, toxicants having bigger size cause slow adsorption and degradation of CEPS and DECIP relatively to their counterpart due to steric hindrance. Kinetics study also indicated that the
degradation of DECNP is faster than CEPS which are not in accordance with their molecular diameter based adsorption. The fast degradation of DECNP is attributed to better leaving tendency of CN\(^{-}\) which results into fast hydrolysis of the DECNP.

The high surface area of the MOF was found to be facilitating the faster degradation of toxicants. The role of the surface area and porosity was further confirmed by reaction of CEES with copper acetate monohydrate which is having similar coordination environment as of HKUST-1 but very low surface area (< 5 m\(^2\)/g). Result indicates insignificant degradation (approx. 7%) of CEES in 3h by copper acetate monohydrate whereas MOF degraded more than 91% in 40 min (Figure 3.6).

![Figure 3.6 Kinetics of degradation of CEES with HKUST-1 and copper acetate monohydrate](image)

Figure 3.6 Kinetics of degradation of CEES with HKUST-1 and copper acetate monohydrate
3.3.2. Kinetics of degradation of sulfur mustard and sarin simulants over impregnated MOFs:

Table 3.3 represents percentage of decontamination of CEES over the impregnated MOFs. It is found that what was assumed that KMnO₄, Active chlorine compound would act as strong oxidizing agent which would in turn result into degradation CEES, did not happen. In case of KMnO₄, KOH results were varied every time while repeated experiments were done, therefore, no inference could be done from results. The active chlorine compounds impregnated MOF was also found to be inefficient in decontamination of the toxicants. This may be due to unstable nature of active chlorine compounds.

**Table 3.3 Decontamination of CEES by impregnated MOFs**

<table>
<thead>
<tr>
<th>Impregnant</th>
<th>Weight Percentage</th>
<th>Percentage of Degradation of CEES</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMnO₄</td>
<td>15%</td>
<td>---</td>
</tr>
<tr>
<td>Sodium dichloro isocyanurate</td>
<td>15%</td>
<td>30% in 3h</td>
</tr>
<tr>
<td>KOH</td>
<td>15%</td>
<td>-----</td>
</tr>
<tr>
<td>Cu(NO₃)₂•2.5 H₂O</td>
<td>20%</td>
<td>83% in 3h</td>
</tr>
<tr>
<td>CuCl₂•2 H₂O</td>
<td>20%</td>
<td>28% in 3h</td>
</tr>
<tr>
<td>CuSO₄•5H₂O</td>
<td>20%</td>
<td>-----</td>
</tr>
</tbody>
</table>
According to Pearson’s hard–soft acid–base principle\textsuperscript{33} S-compounds tend to be intermediate to soft bases, and the soft S-compounds prefer to interact with intermediate or soft Lewis acid sites, such as Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, or Ag\textsuperscript{+}, therefore, three different copper salts were chosen for impregnation. When the different copper salt impregnated MOFs were exposed to CEES it was found that only copper nitrate impregnated MOF was able to decontaminate CEES. Figure 3.7- 3.8 showed the kinetic plot of decontamination of CEES, CEPS respectively by copper nitrate impregnated MOF. Results exhibited that initial degradation of toxicants was faster followed by a steady state reaction indicating the first order reaction. The rate constant (k) and half-life (t\textsubscript{1/2}) were found to be 0.019 min\textsuperscript{-1}, 0.007 min\textsuperscript{-1} and 35.9 min, 92.4 min.

![Figure 3.7a Kinetics of degradation of CEES on impregnated MIL-101](image_url)
Figure 3.7b Percentage of degradation of CEES on impregnated MIL-101

Figure 3.8a Kinetics of degradation of CEPS on impregnated MIL-101
It was observed not only copper ion but also the anion it is attached to, has an impact on the reaction. In literature it is found that copper nitrate get sublimed when heated to over 80°C which is not possible in case of copper sulfate and copper chloride. The plausible cause that Copper nitrate impregnated MIL-101 is capable of decontaminating CEES can be attributed to the fact that after impregnation when the MOF is heated in vacuum oven at 100°C then copper nitrate is sublimed and get into the pores of MIL-101 and become available to come into contact with CEES. In case of copper sulfate and copper chloride, they don’t get sublime on heating rather they got transformed into copper oxide, therefore, decontamination was not observed till experiments carried on up to 3 h.

None of the impregnated MOFs show any decontamination when exposed to sarin simulants.
3.3.3. Effect of solvents on the degradation of toxicants:

The degradation of the toxicants using various solvents indicates that the solvents of low polarity are beneficial for the use of HKUST-1 because of the low solubility in such solvents. However, in presence of the donor type solvents such as THF competing for the adsorption at the copper site, the reaction of the toxicants showed no degradation even after 4 h of reaction time indicating the possibility of coordination of THF with copper site resulting into blockage of the active sites of the HKUST-1. Other solvents such as chloroform, heptane and pentane were also found to be compatible for degradation reaction similar to carbon tetrachloride.

3.3.4. Effect of co-adsorbed moisture on the degradation of sulfur mustard and sarin simulants:

Effect of co-adsorbed moisture on the degradation of sulfur mustard and sarin simulants was studied by adding 10 µL of water to the MOF prior to the reaction with the toxicants. Thereafter, extracting the residual toxicant after 20 min as stated in the reaction procedure. The degradation obtained for CEES and CEPS with the HKUST-1 containing 10 µL of water was found to be 67 and 38% only whereas, activated MOF having negligible moisture indicated 83 and 72 % degradation of the CEES and CEPS respectively. The reason for the decreased degradation of CEES and CEPS by the MOF containing moisture is due to the blockage of the active sites of the MOF by the adsorbed water molecules. Probably the high moisture in MOF results into the formation of a thin film of water into the pores of MOF. As CEES and CEPS are lipophilic in nature hence, they form the droplets and results into slower spreading of water insoluble CEES
and CEPS on MOF. This slower spreading results into the slow diffusion of CEES and CEPS into the pores which in turn results into slower degradation of CEES and CEPS\textsuperscript{34}. The degradation for DECIP and DECNP were found to be 60, 83 % on MOF with the co-adsorbed water and 48, 78% respectively on activated MOF containing negligible moisture. Here the degradation of the nerve agent simulants is enhanced on the MOF having co-adsorbed water. The increased reactivity of the MOF containing water can be attributed to the hydrophilic character of the nerve agent simulants. At high water content, the nerve agent simulants reactivity is at least partially facilitated by facile diffusion of simulants within the pores of the MOF.

**3.3.5. Reusability of HKUST-1:**

Based on the faster degradation of toxicants, CEES was selected for checking the reusability of the HKUST-1. Reusability test indicated that the MOF can degrade CEES efficiently up to 4\textsuperscript{th} cycle. The fresh samples showed 92% degradation in 2 h whereas in 2\textsuperscript{nd}, 3\textsuperscript{rd} and 4\textsuperscript{th} cycle degradation was found to decrease up to 70, 50 and 45% respectively. Deactivation of MOF is attributed to strong adsorption of products, quite evident from reducing surface area with increased reaction cycles (Table 3.4) and EDAX spectra (Figure.3.9) indicating the presence of sulfur and chlorine. Another reason for the deactivation is the irreversible collapse of the structure; evident from SEM images (Figure 3.10 b-c) due to the migration of the framework metal ions because of the reaction with hydrochloric acid resulted from hydrolysis of CEES with the increased reaction cycles.
Table 3.4 Reusability of HKUST-1 for degradation of CEES

<table>
<thead>
<tr>
<th>No. of cycle</th>
<th>N$_2$BET surface area (m$^2$ g$^{-1}$)</th>
<th>Micropore volume (cc g$^{-1}$)</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^{st}$</td>
<td>1645</td>
<td>0.804</td>
<td>92</td>
</tr>
<tr>
<td>2$^{nd}$</td>
<td>441</td>
<td>0.214</td>
<td>70</td>
</tr>
<tr>
<td>3$^{rd}$</td>
<td>43</td>
<td>0.018</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 3.9 EDAX spectra of HKUST-1

(a) As synthesized HKUST-1, (b) After 1$^{st}$ cycle exposed with CEES,
(c) After 3$^{rd}$ cycle exposed with CEES
Figure 3.10 SEM images of HKUST-1

(a) As synthesized HKUST-1, (b) After 1st cycle exposed with CEES,
(c) After 3rd cycle exposed with CEES

3.3.6. Identification of the reaction products:

In order to understand the reaction pathways the reaction products were analyzed using GC-MS (scheme 1 and 2).

![Scheme 3.1 Reactions products of CEES and CEPS](image-url)
Scheme 3.2 Reactions products of DEClP and DECNP

GC-MS data of the reaction products of CEES, CEPS (Figure 3.11, 3.12) indicated the formation of the hydrolysis products\(^1\,^1\,^2\), i.e., silylated 2-hydroxy ethyl ethyl sulfide (HEES) (m/z at 73, 89, 103, 163, 178) and silylated hydroxy ethyl phenyl sulfide (HEPS) (m/z 45, 59, 73, 91, 103, 137, 167, 211, 226). Similar reaction pathway was observed for the degradation of DEClP and DECNP on HKUST-1. GC-MS data, (Figure 3.13) showed the formation of silylated diethyl phosphate (DEP) (m/z 45, 65, 81, 96, 113, 127, 147, 155, 167) as hydrolysis products of DEClP and DECNP.

![Mass spectrum of Silylated HEES](image)
The formation of reaction products can be explained by detailed understanding of the structure of HKUST-1. The structure is composed of large hydrophilic type central cavities (diameter 9.0 Å) surrounded by small pockets (diameter 5.0 Å), these pores are less hydrophilic as they are encircled by four...
benzene rings\textsuperscript{15}. Each metal corner has two copper atoms bonded to the oxygen of four BTC linkers. In the as-synthesized material, each copper atom is also coordinated to one water molecule that is, two water molecules for each paddlewheel metal corner, corresponding to 8 wt. % water loading. The presence of water molecules in the first coordination sphere of Cu\textsuperscript{2+} ions has suggested the possibility to obtain a coordinative vacancy on Cu\textsuperscript{2+} species. The partial positive charge on the metal sites in HKUST-1 enhances the adsorption properties\textsuperscript{35}. Therefore, toxicant molecules were attracted by the attractive forces and adsorbed in the pores of the MOF by physisorption. Thereafter adsorbed toxicant molecules reacted with chemisorbed water molecules and resulted into the formation of the hydrolysis products.

In case of copper nitrate impregnated MOF no product was found. This is likely because CEES molecules may get chemisorbed over the impregnated MOF by sulfur metal interaction or pi- interaction\textsuperscript{36}.

3.4. Conclusion:

MOFs with and without impregnation of reactive chemicals were explored for their suitability against simulants of CWAs. The kinetics of degradation was monitored using GC/FID. Linearity of the curves showed the kinetics to be following pseudo first order reaction kinetics. Kinetics was found to be initially fast, which gradually slowed down to a steady state.

In summary, it is found that amongst all the synthesized MOFs only HKUST-1 has shown reactivity towards sulfur mustard and sarin simulants. Among the entire impregnated MOFs Only copper nitrate impregnated MIL-101
shows reactivity against sulfur mustard simulants. None of the impregnated MOFs show reactivity towards nerve agent simulants. Incorporation of reactive materials in the pores of a MOF can prove useful for reaction with toxicants; however, this typically results the reduction of removal capacities for other analytes as pores and functional groups are blocked. Furthermore, approaches are needed to make MOFs useful for decontamination of broad spectrum of toxic compounds.

Kinetics of degradation of CWAs simulants were studied against HKUST-1 and the order for degradation of simulants of sulfur mustard was found to be: CEES > CEPS and for sarin was: DECNP > DEClP. Kinetics study indicated that the degradation of CEES is faster than CEPS because of neighboring group participation effect. DECNP degraded faster than DEClP due to better leaving tendency of CN$^-\text{a s c o m p a r e d t o C l}^-$. The molecular diameter and vapour pressure of the toxicants was also found to influence the adsorption properties of the MOF as toxicants having bigger size and lower vapour pressure caused steric hindrance and slow diffusion which in turn results into slow adsorption as well as degradation. The study clearly indicates that the HKUST-1 is a potential material for the degradation of the toxicants via hydrolysis; therefore, HKUST-1 can be effectively used for in-situ degradation of nerve and blister agents. Hydroxy ethyl ethyl sulfide, hydroxy ethyl phenyl sulfide and di ethylphosphate were found to be hydrolysis products through GC/MS. This study can lead to the development of efficient NBC filtration system and decontamination formulation based on MOFs.
References:


