Metal organic framework against chemical warfare agents in gas adsorption

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**NANYANG
TECHNOLOGICAL
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SINGAPORE

**METAL ORGANIC FRAMEWORK AGAINST CHEMICAL
WARFARE AGENTS IN GAS ADSORPTION**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2019

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A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Master in Science

2019

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Abstract

Metal Organic Frameworks (MOFs) are a class of porous materials with highly desirable properties that enabled these materials to deliver excellent results to a wide range of application such as gas storage, gas capture, and catalysis. These properties make MOFs a potential alternative to be deployed as an active adsorbent and decontaminant against chemical warfare agents rather than the conventional approach of using activated carbon.

In this study, two representative MOFs, HKUST-1 and UiO-66, were chosen as test specimen to evaluate its performance by doing a comparison with activated carbon, the widely used adsorbent in chemical protective equipment. The test methodology (**Chapter 2**) includes the synthesis of the two MOFs, and stored them in standard room condition (STP) for a period of six months. These aged MOFs were then exposed to a constant stream of HD vapour at a concentration of 5 mg/m^3 , for a period of 24 hours to determine its adsorption capacity and its first breakthrough volume.

The test results (**Chapter 3**) illustrated the structural stability of the two MOFs under prolonged storage in room condition. The aged MOFs retained their structure and crystallinity with indication on the presence of water picked up from the environment during storage. However, the presence of water did not hinder the MOFs from capturing HD vapour for a period of 24 hours. In comparison with activated carbon, the aged MOFs adsorption capacity for HD were as good. For HKUST-1, it outperformed activated carbon by having a significant longer first breakthrough volume.

Despite the promising results, more work has to be done to ensure a wide adoption of MOFs in the area of chemical defense. Recommendation on future work (**Chapter 4**) includes the extension of this study to the different classes of chemical agents and toxic gases, such as the nerve agents and toxic industrial chemicals (TICs). Studies are needed to demonstrate the catalytic degradation reaction will occur in the vapour phase for a wide range of chemical agents and toxic gases. Novel MOFs could also be designed to include useful functionalities, such as the detection of CWAs, to yield smart materials for deployment in the three aspects of mitigation efforts in chemical defense.

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List of Abbreviations

ACh - Acetylcholine

AChE – Acetylcholinesterase

AEGL – Acute Exposure Guideline Limit

BET – Brunauer-Emmett-Teller

BTC - Benzene-1,3,5-Tricarboxylic Acid

CEES – 2-chloroethylethylsulfide

CWAs – Chemical Warfare Agents

DIFP – Diisopropylfluorophosphate

DMMP – Dimethylmethylphosphonate

GB – Sarin, Isopropyl Methylfluorophosphate

GD – Soman, Pinacolyl Methylfluorophosphonate

HD- Sulfur Mustard, Bis (2-chloroethyl) Sulfide

HN-1 – Nitrogen Mustard-1, Bis (2-chloroethyl) Ethylamine

HN-2 – Nitrogen Mustard-2, Bis(2-chloroethyl) Methylamine

HN-3 – Nitrogen Mustard-3, Tris(2-chloroethyl) Amine

MOFs – Metal Organic Frameworks

OPCW – Organisation For The Prohibition of Chemical Weapons

PPE – Personal Protective Equipment

PXRD – Powder X-Ray Diffraction

SEM – Scanning Electron Microscope

TICs – Toxic Industrial Chemicals

VX – 2-(Diisopropylamino)ethyl]-O-ethyl methylphosphonothioate

Chapter 1: Introduction

1.1 Research Motivation

A new class of crystalline material named metal organic frameworks (MOFs) has emerged in the field of materials science and chemistry. This material has highly desirable intrinsic properties such as high porosity and large surface area which has stirred enormous interest in the study of MOFs and its applications such as storage media for gases, catalysis, and sensors^[1]. In the recent five years, MOFs and its related application publication has experienced an exponential growth. With a better understanding of the behaviour of such material, the scientific community has also created well-known MOFs that not only possessed the mentioned desirable properties but also made improvement on their thermal and moisture stability.

This piqued the interest of exploring the use of this new class of material in the application of chemical defense against toxic chemicals such as chemical warfare agents (CWAs) and toxic industrial chemicals (TICs). CWAs such as Sarin (GB), Sulfur Mustard (HD) and 2-(Diisopropylamino)ethyl]-O-ethyl methylphosphonothioate (VX), are highly toxic chemicals that were used in past wars and conflicts^[2] to strike fear, injure, incapacitate or even kill. Whereas, TICs are common industrial chemicals which have a lethal concentration and time value (LCt50) of less than 100,000 mg.min/m³ in any mammalian species. The production quantities are exceeding 30 tonnes per year at any one production factory or chemical plant. These chemicals are stored, handled and transported for downstream industrial processes.

The potential immediate application of MOFs could be an active adsorbent which not only absorbs but also catalyzed the degradation of these adsorbed toxic gases. The ability to function as both a high capacity adsorbent and a catalyst allows it to be an excellent candidate in replacing activated carbon used in personal protective equipment (PPE) and decontamination products. Future application could be expanding to the detection of toxic chemicals as they could be integrated into system such as the PPE, vehicles and important facility installation to achieve defense against chemical threat in a multi-functional approaches, such as the highly envisioned smart PPE for our first responders.

However, due to chemical warfare agents inherent high toxicity and its access limitation, many reported studies use chemical agent simulants to do their experimental work on MOFs instead of the actual agents in their study^[3]. These simulants usually have certain similar properties, such as the same functional groups but with toxicity that are much lower than the actual agent. Although testing with simulants can be ideal for initial screening with a safer approach, it can never be a complete representation of the actual agent. To understand the true dynamic of MOFs against CWAs in realistic scenarios, testing with the actual agents is imperative. With the evaluation and test done on real agents, valuable insights and information on the agent fate and its degradation products can be determined. Although there are some studies reported the use of MOFs tested with liquid CWAs, the tests done were not extensive enough, therefore, is inconclusive.

Furthermore, to fully adopt the use of MOFs against CWAs, the gaseous state of CWAs should be taken into consideration as one of the testing parameters, especially so if MOFs were to be used in protective gears such as in respiratory canisters, air filter and as a layer in a chemical protective suit. Although several reports of studies attempted to cover this area by using other toxic industrial chemicals (TICs)^[4], till date, there is no report of MOFs testing against actual gaseous CWAs.

This arises the motivation and agenda of this research which is to derive an approach to study the adsorption capacity of MOFs against gaseous CWAs. In this study, a system is designed to generate a steady stream of gaseous CWA, namely HD vapour, to determine the effectiveness and the adsorption capacities, which determines the protective index of the selected MOFs, namely HKUST-1 and UiO-66. With the system established in this study, paves the beginning and the fundamentals of screening MOFs, including future novel MOFs with different gaseous CWAs.

1.2 Chemical Warfare Agents

1.2.1 Introduction

Chemical warfare agents (CWAs) are highly toxic chemicals designed to incapacitate enemy trooper by inflicting harm, discomfort or even death through their chemical interaction with the human body. The first use of chemicals in wars started in World War 1, and ever since then, many variations of chemical agents have been developed with variation in their mechanism and toxicity.

On 29 April 1997, the chemical weapons convention was in-forced. This was the world's first agreement on the disarmament and the elimination of the use of chemical weapons, also known as the weapons of mass destruction, within a stipulated time-frame^[5]. As of the date of this report is written in 2019, 193 states have been committed to this convention, and 96% of the chemical weapons stockpile has been destroyed. However, even with the convention in place, there were still report of the use of CWAs in several incident such as the use of nerve agent, Sarin, in Syria in August 2013^[6].

On the other hand, there is a growing concern on the unconventional warfare against terrorism, which mainly targets the civilians and the innocent. The well-known case happened in 1995, where Sarin was used to strike a terrorist attack on the Tokyo subway system by a cult group known as Aum Shinrikyo^[7]. The concern of high-risk terrorist attacks with CWAs escalated after September 11, 2001, terrorist attack in the United States, especially from the Jihadist^[8].

Therefore, research on the detection and mitigation against CWAs are still valid, and is of an important concern. Much attention has been given to CWAs such as the nerve agents Sarin (GB), Soman (GD), and the vesicant, mustard gas (HD) due to its ease of accessibility.

CWAs are widely classified into various classes namely, nerve agents, vesicant agents, blood agents, choking agents, riot control agents, psychomimetic agents and toxins. Among these classes of agents, the nerve and vesicants agents are the two main classical agents. In the following sections, the nerve agents and vesicants agents will be described in details.

1.2.2 Nerve Agents

Nerve agents are chemicals that belong to the organophosphate family that can target and interfere with our nervous system to inflict harm. Agents such as Sarin (GB, Isopropyl methylfluorophosphate), Tabun (GA), Soman (GD) and GF are known to be the G-series which are hazardous when exposed via inhalation or percutaneous route. Another class of nerve agent are the V-series, such as VE, VG, VM and VX, are less of a percutaneous compare to the G-series. However, there are known to be more persistent in the environment.

Figure 1: The nerve agents

Nerve agents being anticholinesterase compounds, disrupt signal transmission from the nervous system to muscles by interacting with the serine hydroxyl residue in the esteratic site of the AChE. This results in a halt in the normal function to hydrolyse the acetyl choline presence, resulting in an accumulation of the neurotransmitter, acetylcholine (ACh). Depends on the route of exposure and the concentration level, the following type of symptoms can be observed namely, the muscarinic, nicotinic or central nervous system effects. Muscarinic effects symptoms such as miosis, excessive sweating, and salivation^[9]. Nicotine effects symptoms occur in motor systems such as muscle fasciculation and paralysis. Central nervous system effects such as confusion, incoherent speech and loss of respiratory control that could lead to death^[10].

Figure 2: The mechanism of nerve agents on acetylcholinesterase^[11]

Antidotes to nerve agents poisoning are atropine (anticholinergic) and pralidoxime. Central nervous system symptoms can be treated with diazepam, especially if convulsion has occurred^[12]. However, reactivation of AChE by dephosphorylation once the nerve agent and enzyme complex “aged”, which often associates with the loss of an alkyl or alkoxy group. $T_{1/2}$ is often used to indicate the time required for 50% of the enzyme become resistant to reactivation. For example in the case of red blood cell cholinesterase, GD ages the most rapid, where $t_{1/2}$ is 1.3 minutes^[13]. The ageing $t_{1/2}$ for GA, GB and VX are 46 hours, 5 hours^[14], and 48 hours^[15] respectively.

1.2.3 Vesicant Agents

Vesicant agents are a group of chemical agents that cause tissue blistering, therefore they are also known as the blistering agents. It targets not only the skin but also able to cause an irritation to the eye and the respiratory tract, and in serious cases could lead to death. Chemicals that belong to the vesicant family are Sulfur Mustard [bis(2-chloroethyl) sulfide], Nitrogen Mustards [HN-1: Bis(2-chloroethyl) ethylamine, HN-2: Bis(2-chloroethyl)methylamine and HN-3: Tris(2-chloroethyl)amine] and Lewisites. These cytotoxic alkylating class of CWAs, are used to inflict pain or injuries to incapacitate or reduce troops fighting efficiency.

Figure 3: The vesicant agents

For HD and HN-x series, the mechanism involves the formation of an onium cation, followed by a nucleophilic attack by the base of nucleic acids or the sulhydryl groups in proteins and peptides^[16]. Whereas, Lewisites apply its toxicity with the arsenic binding to the sulhydryl containing proteins to prevent pyruvate oxidation^[17]. The symptoms displayed for vesicant agents can be classified under acute and stochastic effects. For acute effects upon exposure will exhibit ulceration and edema on skin. The victim may also feel nausea and fever. Stochastic effects after an ocular exposure are conjunctivitis that could lead to blindness and chronic bronchitis after an inhalation exposure^[18].

Figure 4: HD Mechanism of Action^[19]

Currently, there are no effective antidotes for mustards vesicants agents, HD and HN-X series, although there are reviews on the use of antioxidants as an antidotes^[20]. Therefore mitigation efforts have to depend on the prevention, effective decontamination, and the treatment of the signs and symptoms due to the toxication. On the other hand, Lewisites relies on a chelation therapy drug, Dimercaprol (2,3-dimercaptopropanol), for lewisities poisoning despite its undesirable side effects^[21].

HD was selected to be the agent to be studied for the evaluation of MOFs against CWAs vapour. It is the most utilised chemical as a weapon of destruction of the past century. Being a bialkylating agent, it can alter DNA structures which could result in cell death and elevated risk of cancer development. Due to the ease of synthesising and its toxicity potency, it remains as a relevant military and civilian threat to date.

1.3 Existing Means Technology For Mitigation

1.3.1 Protection

The current approach for air purifying material for protection against toxic chemicals is with the use of activated carbons, which is mainly based on physio-absorptivity properties, primarily due to Van Der Waals forces, of pores found in activated carbons. Despite its superb performance in removing certain organic and inorganic contaminants, it has its weaknesses that need to be addressed.

Figure 5: Example of the layers found in a chemical protective suit^[22]

Firstly, activated carbon has been known to poor absorptivity for highly volatile chemicals with low molecular weight such as hydrogen cyanide, hydrogen sulfide and ammonia gas. Secondly, the purification of air based solely on adsorption does not prevent these materials from behaving as secondary emitters once they are contaminated.

Although there are efforts invested into developing modified activated carbon such as impregnation, or the substitution of other class of materials, such as metal oxides, for absorbing and the degradation of CWAs, issues such as low capacity and slow reaction kinetic hampered its adoption for application.

Therefore, an ideal adsorbent to be used in protective gear should be equipped with the dual functionality of not only filtering but also the ability to degrade toxic chemicals into benign products to prevent secondary contamination.

1.3.2 Decontamination

Current decontamination approaches used for neutralising chemical agents are unable to achieve 100% destruction of these toxic chemicals. Some conventional approaches including the use of a copious amount of water added with surfactants and/or the use of corrosive decontaminants such as hypochlorite. Such procedures generate secondary waste and can be time-consuming. Furthermore, sensitive equipment such as data storage devices such as a computer, which could contain useful forensic information, will be destroyed in the process of decontamination. The following table list the common decontamination approaches:

Decontamination Approaches	Material Used	Remarks
Enzymatic	Acetylcholinesterase	Enzymes are highly specific to the nerve agents. However, it has a shorter shelf-life and required a more stringent storage condition.
Chemicals	NaOH, hypochlorite and oxone with surfactants	Easy to purchase, store and prepare. However, it is not as specific and can be corrosive in nature.
Adsorption	Bentonite and activated carbon	Non-specific and usually only adsorption but no decontamination of CWAs.

Table 1: Current decontamination approaches for CWAs

Therefore, an ideal decontaminant has to be reactive to a range of classes of CWAs to destroy the majority of the agents in the shortest possible time to benign products. The application should be able to extend from inanimate objects to personnel decontamination.

In the application of area decontamination, there is yet to be a dynamic solution to resolve chemical contamination in porous surfaces such as concrete and bricks. The remnant chemical agents posed a subsequent contact hazard as well as vapour desorption hazard

within a confined area. Therefore, to assess the area suitability for re-entry after a chemical incident, usually a prolonged vapour sampling, and repeated decontamination efforts are to be expected.

1.3.3 Detection

For the detection and identification of CWAs during operation, the first responder currently employed the use of portable chemical detectors such as AP4C and CAM for detection and HAZMAT ID for the identification. Although such portable detectors are robust and do provide vital information to the first responder out in the field, there are limitations with the use of such detectors to be addressed.

Firstly, detectors based on different detection technology are usually used concurrently to resolve signal interference issue and for cross-verification. This entails that first responders have to carry additional pieces of equipment into a possible contaminated area which could add on to their carry load, and also resulted in concern over post-operation equipment decontamination. Secondly, the detection limit of portable chemical detectors for certain agent is high which signifies that such agent could go undetected at a possible lethal concentration level.

1.3.4 Future Research in Agent Mitigation

With the rise of asymmetric warfare such as terrorism, chemical attack incidents can happened without ample warning. Besides CWAs agents, the possibility of toxic industrial chemicals being used should not be rule out.

To provide our first responders with better protection against a myriad class of toxic chemicals, it is imperative to explore new class of adsorbents to handle a broad spectrum of threats. These materials should ideally be able to cover all three mitigation areas and be able to integrate into various platform to be part of the new age “smart platforms” against chemical threats. This will enable the first responders to rapidly overcome the challenges posed by CWAs, and potentially extended to other chemical threats such as TICs and radionuclides. These materials should ideally be physically and chemically stable for actual field use. It should also be relatively easy to synthesize and therefore, keeping the adoption cost low.

1.4 Metal Organic Framework

1.4.1 Introduction

Metal organic frameworks (MOFs) a porous coordination polymers¹⁻⁴ have piqued a high interest among the scientific committee due to its highly desirable properties such as their high crystallinity, high porosity and large surface area. Surface area as high as 6000 m²/g^[23-24] has been reported. Furthermore, it is highly tunable to incorporate new functionalities to cater for a specific application. These properties were not observed for any traditional materials such as silica, zeolites, and porous carbon, therefore distinguish MOFs as a unique new class of materials.

Metals organic obtained his name from the way it is constructed. A combination of two components between the inorganic nodes and organic linkers. Transition metals are often used as the inorganic component in the synthesis of MOFs which give rise to the different coordination numbers and geometries. For the organic linker, they can be group under neutral, anionic or cationic. The most widely used linkers are the carboxylates anionic linker^[25-28] because during the synthesis process, they can cluster the metal ions as a whole yielding a robust framework.

Majority of reported MOFs can be synthesised in bulk quantities by solvothermal or hydrothermal approach^[29]. In this conventional approach, the precursors are dissolved in either an organic solvent or distilled water. The reaction will take place in a closed bottle or reaction vessels, placed in a reaction oven with temperatures ranges from 80 to 260 °C. Examples of MOFs that can be synthesised via the conventional approach are MOF-5, MOF-177, HKUST-1 and UiO-66^[30].

1.4.2 Review on MOFs Against Toxic Gases

With its unique and highly desirable properties, MOFs have been reported to potential in numerous fields, especially in the applications of gas storage, separation, catalysis and drug delivery^[31]. These applications share similarities in the three mitigation areas for CWAs as described in section 1.3, making MOFs a potential class of materials to be used to resolve the gaps. Many research groups have done studies either on CWAs and its simulants, with the later was the most studied^[32-34].

In the area of detection, one research demonstrated the possibility of using MOF-5 as a luminescence indicator for sensing organophosphate compounds using parathion, which contained similar functional groups as the nerve agents. The mechanism reported was that due to the interactions of the organophosphate compounds with the ligand molecule, will result in a decrease in the photoluminescence of MOF-5^[35].

In the area of protection, one research group tested and compared various MOFs including MOF-5 and HKUST-1 with activated carbon in the removal of toxic gases such as ammonia and sulfur dioxide. It was found that HKUST-1 is more superior in adsorbing ammonia as compared to activated carbon due to the presence of Cu^{2+} open metal sites which behaves as Lewis acids in coordinating with the ammonia, NH_3 , Lewis base^[36]. One research group studied the possibility of integrating MOFs into protective fabrics to complement the semi-permeable chemical protective suit as a self-detoxifying adsorbent^[37]. In the study, post-synthesis modified MOF, UiO-66-LiOtBu, was deposited on silk fibroin fibres and tested against CWA simulants, DIFP, DMMP and CEES, with CEES has the shortest degradation half-life of 8 minutes.

In the area of decontamination, Prof. Farha's group did a comprehensive review in discussing the development of MOFs and summarised the results of these MOFs tested with CWAs and simulants^[38]. In his study, out of the 16 MOFs mentioned, only five of them are tested with the actual agent. This highlighted the need to have more extensive tests to be performed on MOFs with CWAs to better understand the mechanism which could impact future applications and design of MOFs. For example, a study was published reporting the degradation of HD and its simulant, chloroethyl sulfide (CEES), using HKUST-1^[39] which attributed its activity to the Lewis-acidic Cu^{2+} active sites in solvent form. Essential observations were made that could affect future consideration and design of novel MOFs. Firstly, HD was observed to have a slower reaction rate due to its two electron withdrawing

chlorine atoms as compare to CEES having a single chlorine atom. Secondly, is that hydrolysis proceeds slower with increasing humidity due to the blockage of Cu active sites by water molecules absorbed. Lastly, it showed that HKUST-1 will be deactivated by the adsorption of degradation products resulting in decreasing effectiveness after multiple cycles.

Below are the two shortlisted MOFs that used in this study based on the properties and stability that were discussed above namely HKUST-1 and UiO-66.

1.4.3 HKUST-1

In this study, HKUST-1 is one of the MOFs that was chosen for testing against HD vapour. HKUST-1 is sustained by a Copper paddlewheel building unit linked to organic linkers BTC (benzene-1,3,5-tricarboxylic acid), resulting in a binomial 3,4-c twisted boracite net with the formula $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$. This arises to a 3D channel structure which composed of a large cavity of 9.0 Å surrounded by a smaller cavity of 3.5 Å.

Figure 6: Paddlewheel structure adopted by Cu^{2+} cations (blue) and BTC anions within the HKUST-1 framework^[40]

The water ligands are weakly attached to the Cu atom, and can be removed via heating to produce an anhydrous form of $\text{Cu}_3(\text{BTC})_2$ which resulted in a colour change of from blue to purple can be observed as shown below:

Figure 7: The colour change from hydrated to anhydrous HKUST-1

With the loss of water ligand, the Cu metal sites will be freed and exposed, which has been reported to be responsible for its catalytic reaction ^[36] for the hydrolysis of CWAs.

1.4.4 UiO-66

UiO-66 was the second MOF that was chosen for testing against HD vapour. Besides being a potential decontaminant for CWAs, the reason for why it was selected was of its high porosity, high thermal stability, a high stability to hydrolysis, and the ease in synthesising. Their excellent stability is attributed to its strong zirconium to oxygen bond (Zr-O).

The UiO-66 framework features two types of cages. First is in octahedral structure with a diameter of 9Å, and second in the tetrahedral structure with a diameter of 7Å. These cages are significant as they served as a host and are made accessible to the adsorption of CWAs. In a normal situation, they are filled with solvent, which can be activated by first doing a solvent exchange with a more volatile solvent followed by heating under vacuum.

Figure 8: A illustration showing the two cages of UiO-66. (c) the octahedral form in orange, (d) the tetrahedral form in yellow^[41]

In an ideal synthesise, UiO-66 will be constructed from a full 12 connected Zr_6 nodes with the organic linkers, having low Lewis acidic catalytic activity. However, in reality, defect sites are common, yielding the Zr_6 nodes that are terminated with hydroxide or water ligands. Upon the removal of water, Zr metal sites will be exposed and can serve as active Lewis acid sites for the catalytic degradation of CWAs.

1.5 Adsorption and Desorption

1.5.1 Fundamentals and Principles

Adsorption is a process where molecules of gases or liquids or solutes adhere to the surface of a solid. This process involves two primary components, the adsorbate and the adsorbent. The adsorbent is the component provides its surface for the adhesion of adsorbate during adsorption. Whereas, the adsorbate is the component which its molecules get adsorbed onto the surface of the adsorbent. The reverse process of adsorption is known as desorption. Factors affecting these two process are the chemical and physical properties of the adsorbate and adsorbent, the adsorbent's surface area, the method of activating the adsorbent and lastly, the environment such as the temperature and pressure.

There are two mechanisms that explained the adsorption process namely physisorption and chemisorption ^[42]. Physisorption is the adsorption based on Van Der Waals forces of attraction that causes the adsorbate to adhere to the surface of the adsorbent. This physical attraction between these two substances is relatively weaker and therefore can be annulled by the increase of temperature or the decrease in pressure. Whereas, chemisorption is the adsorption based on the formation of chemical bonds between the adsorbate with the surface of the adsorbent. This chemical bond attraction is relatively stronger and therefore cannot be easily be reversed. A full comparison between the two mechanisms is given below:

	Physisorption	Chemisorption
Heat of adsorption	20-40kJ/mol	40-400 kJ/mol
Force of attraction	Van Der Waals forces	Chemical bonding
Temperature	Occurs in low temperature and decreases with high temperature	Occurs in high temperature
Reversibility	Easily reversible	Not easy and mostly irreversible
Specificity	Not Specific	Highly Specific
Type of layers formed	Multi-molecular layers	Monomolecular layers
Activation Energy	Not required	Required

Table 2: Comparison between physisorption and chemisorption

1.5.2 The Adsorption Isotherm

Adsorption process can be described in plots of the mass of adsorbate against a function of pressure at a constant temperature. These plots are known as adsorption isotherm. There are six different types^[43]:

Figure 9: Graph for the different types of Isotherm ^[43]

For Type I isotherm, it represents adsorbents that are microporous solids with a diameter of pore size ≤ 2 nm. The flat portion of the graph depicts that the adsorbate forms a monolayer on the adsorbent surface. Examples of porous materials with such characteristic are MOFs, activated carbon and zeolites.

For Type II isotherm, it represents adsorbents that are non-porous or mesoporous solids with diameter 2 nm to 50 nm. The slightly flat portion of the graph depicts adsorbate forms a monolayer, followed by a spike in adsorption depicts a multi-layer on the adsorbent surface when higher pressure is applied. Examples of such adsorbents are Iron catalyst and the silica gel.

For Type III isotherm, it represents adsorbents that are non-porous or microporous with weak physisorption and chemisorption forces with the adsorbate which resulted in low uptake of adsorbates at low pressure. With the absence of a flat portion in the graph indicates that monolayer formation does not occur. Instead, the adsorption peaks as the pressure increase indicates a multi-layer adhesion to the surface.

For Type IV isotherm, it represents adsorbents that are marcoporous solids with a diameter of >50 nm. At low pressure, the graph resembles a Type II isotherm, which indicates a monolayer followed by a multilayer adhesion to surface. At higher pressure, the saturation level falls below the saturation vapour pressure, which could indicate the condensation of gas

adsorbates in the pores, therefore showing a limiting uptake trend in the plot.

For Type V isotherm, it represents adsorbents that are both microporous and mesoporous solids. Its graph trend is a combination of both a Type III and IV isotherms.

For Type VI isotherm, represent adsorbents that are homogenous non-porous solids. It is step wise trending indicates a multi layer adsorption one after another.

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Chapter 2: Approaches and Methodology

2.1 Chemical Agent Vapour Generation System

To conduct a robust scientific study to evaluate the performance of MOFs against chemical agent vapour, it is imperative to build a robust system to be able to generate and control the vapour concentration with precision. Although there are several established methods of generation such as sparging and via syringe injection into a carrier gas stream, they are considered to be direct contact approaches, and posed its inherent safety concerns in handling these toxic chemicals agents.

A safer approach will be using the indirect contact approach such as using a permeation tube generation or a solid-state vapour generation system. Permeation tube generation involves the generation of vapour through the use of a polymeric tube on which the liquid agent of interest is encapsulated in.

In this study, the permeation tube generation system was chosen to generate a constant concentration of HD gas. The setup will be discussed in details in section 2.1.1 below.

2.1.1 Permeation Tube Generation System

The agent generated by permeation is yield by the slow penetration of the liquid sample through a polymeric membrane^[1]. Therefore, the permeation rate is mostly determined by several of the membrane properties namely its physical characteristic, its permeability with respect to the compound, the temperature it is exposed to, and the partial pressure difference across the membrane. In addition to the membrane properties, the vapour pressure of the compound also plays a signification impact on the permeation rate.

Under stable generation condition, the mass flow will be constantly producing a steady concentration of chemical agent vapour at a set temperature and flow rate of the carrier gas which created a database that it is widely used as a type of calibration means in the chemical industries for their equipment and analytical instruments. However, due to the toxicities and the limited access to CWAs, commercially available data is not available for the agents of our interest. Therefore, to determine the resultant concentration of the HD vapour generated for this study on a set of pre-determined parameters, it has to be quantitated with proper analytical instrumentations and means housed in DSO National Laboratories, Singapore.

Figure 10 : Vapour generation system setup.

To generate the HD vapour, 150 μl of pure HD (purity of 99% GC, synthesised by DSO National Laboratories) was filled in a 10cm long Teflon permeation tube. The permeation tube was placed in a heating oven kept at 70°C . Dry nitrogen gas was used as the span gas to carry the vapour generated inside that permeation cell out.

The agent flow path was coated with sulf-inert coating (Silicotek 2000) on all stainless steel parts. The inert coating is to avoid carryover effect of HD along the flow path that could result to inconsistency in the concentration of HD vapour generated, and to prevent any undesirable side reaction that give rise to agent degradation.

The HD vapour concentration generated was at 5.0 mg/m^3 . Concentration data was captured automatically on a five minutes cycle by an online detector, namely miniature chemical agent monitoring system (MINICAM) as described in section 2.2.1. A secondary analytical approach was deployed to verify the concentration of the HD vapour generated determined by the MINICAM. Air samples were collected manually using air sampling tubes to verify the concentration with the use of a thermal desorption gas chromatography mass spectrometer (TD-GCMS) described in section 2.2.2 and section 2.2.3.

2.1.2 HD Vapour Exposure Guideline Levels

To associate this concentration value to understand its level of harm, one of the guidelines that we could use is the Acute Exposure Guidelines Levels (AEGLs). AEGLs was established by the National Advisory Committee for Acute Exposure Guideline Levels for Hazardous Substances in November 1995, to identify and review hazardous substances to interpret the toxicology based on scientific data. This information has been guiding government agencies and the private sectors worldwide in making an appropriate emergency response when dealing with a chemical incident.

The concentration of HD vapour generated for the purpose of this research study was at 5.0 mg/m³. The objective is to generate a HD vapour at a concentration reasonably high enough to have a strong correlation and significant results in a safe manner. At 5.0 mg/m³. The concentration of HD vapour generated was 1.28 times higher than the Acute Exposure Guidelines Level (AEGLs) of AGEL 3 with an exposure of 10 mins, and it was 18.5 times higher with an exposure time of 8 hours. The individual AEGLs of HD and its corresponding concentration with respect to the time exposure is illustrated in the table below:

	mg/m ³				
	10 minutes	30 minutes	60 minutes	4 hours	8 hours
AEGL 1	0.40	0.13	0.067	0.017	0.0083
AEGL 2	0.60	0.20	0.10	0.025	0.013
AEGL 3	3.9	2.7	2.1	0.53	0.27

Table 3: AEGL values of Sulfur Mustard, HD in mg/m³

AEGLs estimate the concentrations at which the general population will begin to experience health effects if they are exposed to a hazardous chemical for a specific length of time. A chemical may have up to three tiers of AEGL which defines as follows^[2]:

At AEGL 1, it is defined as the airborne concentration of HD in mg/m³, which the general population could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, these effects felt are not disabling nor permanent. They are usually transient and reversible upon one's cessation of exposure.

At AEGL 2, it is defined as the airborne concentration of HD in mg/m³, which the general population could experience an irreversible or other long-lasting adverse health effects which could result in one's impaired ability to escape.

At AEGL 3, it is defined as the airborne concentration (mg/m^3) which the general population could experience life-threatening health effects or death.

Another vital exposure guideline that is widely used by the decision-makers and the first responder will be the exposure limits based on immediately dangerous to life and death (IDLH) guideline^[3]. It is defined as the exposure concentration (mg/m^3) that is likely to cause death, immediate or delayed permanent health effects, or impair an individual's ability to escape from the contaminated environment. For HD vapour, the IDLH exposure guideline is at $0.7 \text{ mg}/\text{m}^3$. The concentration of HD vapour generated for this study at $5.0 \text{ mg}/\text{m}^3$ was therefore seven times higher than the IDLH of HD.

As AEGLs value is time-weighted exposure of up to 8 hours, therefore IDLH will be more applicable for the discussion of the results beyond 8 hours to the exposure duration of 24 hours that were conducted in this study.

2.2 Analytical Instruments

2.2.1 Miniature Chemical Agent Monitoring System

The miniature chemical agent monitoring system (MINICAM) is an automated, portable air monitoring system for volatile organic compounds (VOCs) in the environment or directed gaseous samples. Its working principle is based on the usual benchtop capillary gas chromatography system which is capable of doing both quantitative and quantitation analysis.

The MINICAM series 3001 was used in this study which was developed by the manufacturers to detect CWAs and its simulants. It has a solid bed adsorbent (Tenax TA) preconcentrator and was set to give a readout of every five minutes.

Figure 11: MINICAM detector

2.2.2 Air Sampling Tubes

Figure 12: Stainless Steel, sulfonert coated air sampling tube

Air sampling tubes are inert coated air sampling tube (Markes International, UK) was packed with 150mg of Tenax TA (Supelco Inc., Bellefonte, PA, mesh size of 60/80) adsorbent powder. The sorbent bed was retained with glass wool. The sorbent tubes were conditioned at 300°C for 3 hours at carrier gas flow of 100ml/min before use.

Conditioning involves the continuous flow of high purity gas (either nitrogen or helium) while the air sampling tubes are heated at elevated temperature. There are three stages of conditioning for each cycle of conditioning, which are the purging, heating and cooling phase. Below provide the explanation and consideration in each phase of the conditioning cycle.

1. Purging Phase - Initial phase with high purity gas flows to remove all traces of oxygen from the adsorbent resins inside the sampling tubes for 10 minutes.
2. Heating Phase - Heat will be applied to the tubes at a rate of 5-10°C per minute from room temperature up to the maximum temperature required for conditioning for at least 2 to 4 hours, with the continuous flow of the high purity gas.
3. Cooling Phase - The tubes will be cooled to room temperature (or back to the initial temperature set in the purging phase). Gas flow must be maintained through the adsorbent resin during this cooling cycle.

2.2.3 Thermal Desorption Gas Chromatography Mass Spectrometer

This set of analytical instruments consist of two main portions, a thermal desorber and a gas chromatography coupled with a mass spectrometer detector.

For the first portion, the thermal desorber served as an air sample introduction means where adsorbed compounds in the air sampling tube are thermally desorbed by heating the adsorbent bed with a heater. By changing the direction of flow of the GC carrier gas (helium), via a valve rotation or switching, it will allow analytes to be desorbed, be introduced into the GC column. This equipment contained a cold trap, where desorbed samples are temporarily trapped in a concentration tube cooled (Peltier plate) and then introduced into the column by heating.

The sample tubes were desorbed on the ATD with the primary desorption flow of 30ml/min (Helium) at 250°C/min for 10 minutes with the cold trap held at -25°C with no inlet split. This was followed by a secondary desorption flow of 11.5ml/min (Helium) at 300 °C for 5 minutes with 10ml/min as the outlet split. This gave a split ratio of 30:0:10.

The TD was interfaced with an Agilent GC7890A Gas Chromatography system coupled with detection completed by Agilent MSD5975C Mass Spectrometer. The capillary column used was a DB5-MS Ultra Inert column with dimension as follows: 30m in length, 0.25mm internal diameter and 0.25µm of capillary thickness. The carrier gas is Helium and constant flow of 1.5ml/min was selected throughout the analytical run. The mass spectrometer interfaced was maintained at 280 °C.

The column temperature program was as follows: initial temperature of 40°C (held for 0.5 minutes), followed by a temperature ramping at 20°C/min to 170°C (held for 1 minute) and end off with a temperature ramping at 100°C/min to 280°C (held for 5 minutes). Total run time is 14.1 minutes. The solvent delay was set at 2.50 minutes, and the mass spectrometer was operated in Selected Ions Mode (SIM).

2.3 Metal Organic Framework Synthesis

Both MOFs, HKUST-1 and UiO-66, were synthesised by the solvothermal method. The synthesis process generally involves heating the reaction mixture which contains the metal and the organic linker in solvent in a sealed bottle. The MOF will be built in a self-assembled building block approach and eventually be precipitated out due to its insolubility. Below describes in details the reagents and reaction conditions for the two MOFs.

2.3.1 HKUST-1 Synthesis

HKUST-1 was synthesised by solvothermal method. Benzene 1,3,5-tricarboxylic acid (20mg) and copper(II) nitrate (60mg) were added to 6ml of N,N-dimethylformamide (DMF) with 2ml of Ethanol and 2ml of distilled water. The reaction mixture was stirred by a magnetic stirrer for 15 minutes to ensure complete dissolution. The reaction bottle was then placed in an oven for three days at a temperature of 80 °C yielding the HKUST-1 crystals (~85% yield).

The crystals were activated by immersing with dichloromethane (DCM) and was replaced with fresh DCM three times before it was dried in an oven at 150 °C for 10 hours.

2.3.2 UiO-66 Synthesis

UiO-66 was synthesized by solvothermal method. Zirconium Chloride (13 mg) was added to 15 ml of N,N-dimethylformamide (DMF) with 1ml of hydrochloric acid. The reaction mixture was sonicated for 10 minutes until it has been fully dissolved before Benzene, 1,4-dicarboxylic acid (13mg) was added to the mixture. The reaction was then sonicated for another 10 minutes for complete dissolution before heated at 100 °C for 24 hours yielding the resulting UiO-66 crystals (~80% yield).

The crystals were activated by washing with DMF twice and then with ethanol twice before placing in an oven of 100 °C for drying.

2.4 Metal Organic Framework Characterisation

The aged MOF samples were being tested for its structural integrity and with the following common characterization methodology to ascertain the stability and structure integrity of the MOFs before they were subjected to CWA vapour exposure. The techniques that were employed were powder X-ray Diffraction (PXRD), Thermogravimetric Analysis (TGA), Infrared Spectrometer (IR) and Brunauer-Emma-Teller (BET).

2.4.1 Brunauer–Emmett–Teller Surface Area (BET)

Brunauer- Emmett- Teller (BET) was run to determine the surface area of the MOFs. The principal was based on the physical adsorption of both the external and internal surfaces of the adsorbent by a gas, usually N₂ gas. The amount of gas adsorbed will be based on the temperature and the relative vapour pressure in which an adsorption isotherm of the material will be plotted with the amount adsorbed against the relative vapour pressure.

MOFs samples were recorded on a full microspore gas analyser (Autosorb iQ Quantachrome Instruments) at 77 K at relative pressure up to 1 atm. Specific surface areas were calculated according to the BET method at a relative pressure of P/P_0 of 0.98.

2.4.2 Thermo Gravimetric Analyser (TGA)

A thermogravimetric analysis (TGA) can be used to determine the thermal stability of the MOFs with a function of increased temperature. It measures mass change as a function of heat due to phase transition and eventually to degradation of the adsorbent under study. TGA is also used to detect the presence of any foreign substance, such as moistures, on the surface or in pores that will be released when the temperature is elevated.

MOFs samples were recorded on a TA instrument model, TGA Q500 Thermogravimetric analyser with a heating rate of 10 °C per minute from 25 °C to 800 °C under a continuous flow of N₂ and O₂.

2.4.3 Powder X-ray Diffraction Meter (PXRD)

Powder X-ray diffraction (PXRD) reveals information to ascertain the identity of the material as the X-ray powder pattern is considered as a fingerprint of the sample. When X-ray falls onto a crystal, it will diffract in a pattern unique to its structure. In PXRD, the diffraction pattern is obtained from a powder sample rather than from a crystal, which served as a useful characterisation tool for MOF samples which exist in powder form.

The measurements reported in this work were carried out at room temperature on a Rigaku MiniFlex 300 diffractometer 40 kV, 15 mA for Cu K α ($\lambda = 1.541 \text{ \AA}$) and with a scan speed of 10° per minute.

2.4.4 Infrared (IR) Spectroscopy

Infrared Spectroscopy is useful for structure analysis and function group identification of the materials studied. It works by the principle of molecules at the absorption of IR radiations at a specific wavelength. The wavelength differs structure to structure depends on its symmetry and the functional groups present. Therefore, it is useful for qualitative analysis.

The infrared spectra were recorded from 500 to 4000 cm^{-1} on a Shimadzu model IR Prestige-21 spectrometer using KBr pellets. A background scan was executed with clean KBr pellets prior to the samples scan.

2.4.5 Scanning Electron Microscope (SEM)

SEM uses a high energy electron beam on the specimen that can produce secondary electrons, Auger electrons, characteristic X-ray. The secondary electrons are sensitive to the sample surface therefore able to elucidate the sample morphology.

For this research, all SEM tests were realised by JEOL JSM-7600F field emission scanning electron microscope at 5 kV after sputtering Pt particles on sample surfaces.

2.5 Vapour Challenge

Vapour challenge experiments were carried out by passing the generated HD vapour through the air sampling tube mentioned in section 2.2.2. However, instead of Tenax TA adsorbent, 10 mg of MOFs sample was carefully filled to be substituted as the adsorbent bed.

The initial HD vapour generated at 5.0 mg/m^3 will pass through the tube at a flow rate of 100 ml/min. The samples were made to be exposed to the HD vapour for a stipulated time of 24 hours. The concentration of HD breakthrough was recorded by the MINICAM detector as mentioned in section 2.2.1.

Due to the toxicity of HD, the experimental setup was housed in a fume cupboard with a scrubber system.

Figure 13: A schematic diagram for the vapour challenge

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Chapter 3: Results

3.1 Activated Carbon

Activated carbon has been the gold standard, and the preferred adsorbent for CWAs deployed in personal protective equipment such as on NBC clothing and in gas mask canisters. The comparison of the adsorption result of CWAs from activated carbon and the MOFs will therefore, provide a more significant insight discussion to the study.

Activated carbon (from PicaACT 90, BET surface area $1200 \text{ m}^2/\text{g}$) was packed in an air sampling tube, and subjected to HD vapour challenge for 24 hours. The same test setup was done thrice, and the average result was taken for the discussion of this study. The graph below depicts the average results of the breakthrough profile of concentration (mg/m^3) against time (hours) for the triplicate studies.

Figure 14: HD vapour breakthrough graph for activated carbon

Based on the results established above, it will be used as a baseline for comparison with the other two MOFs specimens, HKUST-1 and UiO-66 in this study.

3.2 HKUST-1

3.2.1 Storage and Thermal Stability

HKUST-1 was aged by storing under standard room condition (25 °C, 1 atm) for six months. The FTIR spectra closely resembled the fresh synthesised HKUST-1. Specifically peaks at 1300 to 1700 cm^{-1} indicating intact co-ordination of trimesic acid with Cu, and peaks at 1646, 1599 and 1450, 1374 cm^{-1} indicating asymmetric and symmetric vibrations of coordinated carboxyl groups^[1].

Figure 15: FTIR for aged HKUST-1

Powder X-ray diffraction (PXRD) analysis was performed for the aged powder. The peak position and relative intensity were similar to literature. Therefore, it can be concluded that there was no degradation in the structural integrity of the crystal framework and it maintained its crystallinity. BET surface area remained at 1803 m^2/g . The total pore volume was 0.678 cm^3/g .

Figure 16: PXRD spectrum of HKUST-1

Thermogravimetric analysis was used to determine the thermal stability of HKUST-1 after prolonged storage. The TGA graph below illustrated a first mass lost between 30 to 100 °C due to loss of water moisture HKUST-1 picked up from the environment during the storage period. The second mass lost between 100 to 200 °C was the loss of water and activation solvent, ethanol that was adsorbed in the internal pores, and bonded to the copper atom. At 350 °C, a sharp drop in mass indicated that the HKUST-1 had degraded as a result of the decomposition of the carboxyl groups which led to complete destruction of the structure above 400 °C. The mentioned thermal behaviour is similar to the fresh synthesized HKUST-1, therefore reinforced that pro-longed storage did not compromise its thermal and structural integrity.

Figure 17: TGA graph for aged HKUST-1

The morphologies of the aged HKUST-1 were characterised by SEM. The crystals expected size and shape can match the fresh synthesized HKUST-1 which is of about 10 – 30 μm in size and its defect-free octahedral crystals remained intact as observed.

Figure 18: SEM images for aged HKUST-1

3.2.2 HD Vapour Challenge

10mg of Aged HKUST-1 was packed in the air sampling tube, and subjected to HD vapour exposure for 24 hours. HD vapour generation was maintained at 70 °C to yield the challenge concentration of 5 mg/m³, at 100 ml/min. The same test setup was done thrice, and the average result was taken for the discussion of this study. The graph below depicts the average results of the breakthrough profile of HKUST-1, with concentration (mg/m³) against time (hours).

Figure 19: HD vapour breakthrough graph for aged HKUST-1

From the graph above, the significant breakthrough happened after 16 hours. Breakthrough time and volume were determined when the filtered air contained 25% and higher concentration of HD with reference from the concentration at time 0. For HKUST-1, the concentration at time 0 was at 0.269 mg/m³ and, the first breakthrough concentration was at 0.350 mg/m³. This corresponds to a total filtered volume of 0.096 m³, and effective uptake capacity of 0.048 g/g.

3.3 MOF UiO-66

3.3.1 Storage and Thermal Stability

UiO-66 was aged by storing under standard room condition (25 °C, 1atm) for six months. The FTIR spectra exhibited similar characteristic peaks as the fresh synthesized UiO-66. Peaks at 1650 cm^{-1} represented the C=O asymmetric stretch of the residual DMF within the pores. The presence of two peaks at 1590 and 1395 cm^{-1} indicated the presence of O=C=O asymmetric and symmetric stretch vibrations respectively in the carboxylate group of H2BDC. A peak around 1500 cm^{-1} represented the C=C vibrations in the benzene ring^[2].

Figure 20: FTIR spectrum for aged UiO-66

The structure of the aged UiO-66 was further evaluated with powder X-ray diffraction, and the peak position and relative intensities were similar to the literature of a freshly synthesised UiO-66 crystal. Therefore, it can be concluded that there was no degradation in the structural integrity of the crystal framework and it maintained its crystallinity. BET surface area is kept at 1489 m^2/g . The total pore volume was 0.654 cm^3/g .

Figure 21: PXRD spectrum of aged HKUST-1

The thermal stability of aged UiO-66 was determined by thermogravimetric analysis. The crystals had its first mass lost from 30-100 °C which was an indication of water moisture lost that UiO-66 adsorbed during the storage period. A sharp drop in mass at 500 °C indicated that the crystals had started to degrade which led to a complete destruction above after 550 °C. The mentioned thermal behavior is similar to the fresh synthesised UiO-66, therefore further supported its excellent shelf-life without compromising its thermal and structural integrity after prolonged storage.

Figure 22: TGA graph for aged UiO-66

The morphologies of the UiO-66 were characterised by SEM. The aged UiO-66 shared the same irregular morphology as reported in the literature. The image below depicted the UiO-66 is disordered and agglomerative. This was expected as benzoic acid was not used in the synthesis as a modulator which will yield more regular and dispersive UiO-66 crystals.

Figure 23: SEM images for aged UiO-66

3.3.2 HD Vapour Challenge

10 mg of Aged UiO-66 was packed in the air sampling tube, and subjected to HD vapour exposure for 24 hours. HD vapour generation was maintained at 70 °C to yield the challenge concentration of 5.0 mg/m³, at 100 ml/min. Below figure illustrate the breakthrough profile of concentration (mg/m³) against time (hours).

Figure 24: HD vapour breakthrough graph for aged UiO-66

From the graph above, the significant breakthrough happened after 6 hours. Breakthrough time and volume were determined when the filtered air contained 25% and higher concentration of HD taking reference from the concentration at time 0. For UiO-66, the concentration at time 0 was at 0.279 mg/m³, and the first breakthrough concentration was at 0.503 mg/m³. This corresponds to a total filtered volume of 0.036 m³, and an effective uptake capacity of 0.018 g/g.

3.4 Discussion

From the above results, it has been demonstrated that both aged HKUST-1 and UiO-66 can adsorbed HD vapour for a good period of 15 hours and 6 hours respectively, and the first breakthrough concentrations were at 0.35 and 0.5 mg/m³ respectively. This was calculated to provide a protection factor of 14x and 10x respectively from the challenge concentration of 5.0 mg/m³. The protection factor defined as the hazard concentration attenuated from the initial exposed concentration as a result of the adsorbent, $\frac{\text{Initial Concentration} (\frac{mg}{m^3})}{\text{Attenuated Concentration} (\frac{mg}{m^3})}$.

Figure 25: HD vapour breakthrough graph for all specimens in full scale

In comparison, activated carbon has its first significant breakthrough at slightly less than 5 hours, make these two MOFs performed better in capturing HD vapour in the early exposure hours. This result is expected based on the larger surface area as compared to activated carbon, with HKUST-1 having the largest BET surface area of 1803 mg/m³. With a larger BET surface area, more surfaces are available for the physical adsorption of the HD vapour. Using the 3 specimens first breakthrough timings, the average adsorption capacities upon the first breakthrough were calculated and tabulated in Table 4.

	BET Surface Area (m²/g)	Average Adsorption Capacity (g HD/ g MOF)
Activated Carbon	1200	0.00075
HKUST-1	1803	0.056
UiO-66	1489	0.016

Table 4: The test specimens' specific area and their average adsorption capacity

The adsorption capacity was computed by firstly the need to determine the amount of HD collected by multiplying the concentration of HD per volume (ng/ml) with the volumetric flow rate of the air passed through the adsorbent bed (ml/min) and the time required (mins) to reach its first breakthrough. The amount of HD will be divided by the weight of the specimen loaded in the air sampling tube to determine the adsorption capacity of the adsorbent specimen.

These average capacities do not reflect the true adsorption capacities of the specimens. To obtain true adsorption of each specimen, the total volume of filtered air computed, should be based on the duration when the effluent HD concentration detected reaches the challenge HD concentration of 5 mg/m³. Due to experimental limitation, the specimens were not challenged with the HD vapour till the full breakthrough occurred, and instead, a 24 hours study is carried out. However, this preliminary adsorption capacities tabulated do provide an insight to show the relationship of BET surface area to the adsorption capacity and illustrated the performances of these materials against HD vapour for a period of 24 hours.

At the end of the test duration of 24 hours, the attenuated HD concentration detected for HKUST-1, UiO-66 and activated carbon were 0.4, 1.1 and 0.6 mg/m³ respectively. At this time point, HKUST-1 still performed better than activated carbon. At the concentration of 0.4 mg/m³ of HD in the filtered air, it was still lower than the IDLH exposure guideline limit of HD vapour at 0.7 mg/m³ as described in section 2.1.2. Therefore, it can be deduced that HKUST-1, when used as an adsorbent in respiratory protection gears against HD vapour, it is able to provide full day protection.

On the other hand, UiO-66 adsorption capacity starts to fall short with its HD concentration detected at the highest among the three test specimens. At the concentration of 1.1 mg/m^3 of HD in the filtered air, it is higher than the IDLH exposure guideline limit of 0.7 mg/m^3 and therefore, cannot be used for full day protection. One probable explanation could be due to UiO-66 having only micropores, it can get saturated easily, as compare to activated carbon which has a mixture of micro, meso and macropores. However, further studies have to be done to validate this hypothesis.

For MOF to replaced or work in tandem with activated carbon as an adsorbent in protective gears, the stability of these MOFs is one of the essential considerations. In this study, ageing was performed for HKUST-1 and UiO-6 by storing them in a 20 ml vial under S.T.P room conditions for a period of six months. These storage vials were not purged with nitrogen nor sealed under vacuum. This was followed by a series of characterization studies were performed to study the effect of ageing on these MOFs. From the results, the MOFs were indeed stable by having their structural integrity intact as shown by the PXRD spectrums. This was despite that both TGA graph and FTIR spectrum indicated the presence of moisture picked up from the environment during storage. This study has therefore demonstrated the stability of HKUST-1 and UiO-66.

Last but not least, this study has for the first time demonstrated that MOFs, specifically HKUST-1 and UiO-66 ability in adsorbing actual CWA vapour which has been lacking in the literature^[3]. Most of the studies performed on MOFs against vapours were using either the chemical warfare agent simulants or TICs. Therefore, this study has achieved the aim of designing a setup to challenge MOFs with actual CWAs vapour which laid the groundwork for more dynamic studies in the future.

The results obtained from the comparison study to understand the performance of the aged MOFs against activated carbon in the same HD vapour generation setup was promising. HKUST-1 outperformed activated carbon for having a more extended first breakthrough volume. As discussed above, both HKUST-1 and UiO-66 has higher BET surface area, and therefore was expected to have higher average adsorption capacities than activated carbon as shown in Table 4. This study has consequently demonstrated the superiority of MOFs against activated carbon in the adsorption of HD vapour.

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Chapter 4: Future Work and Conclusion

4.1 Future Work

This work showed the adsorptive capability of HKUST-1 and UiO-66 for HD vapour, which makes them a potential activated carbon alternative in the mitigation efforts against CWAs vapour. However, to make MOFs be widely adopted materials, further studies and tests have to be done.

Firstly, is the extension of similar work done in this research to other classes of agents such as nerve agents to demonstrate MOFs ability to cover a broad spectrum of chemical agents and threats. Although numerous literature has demonstrated its effectiveness ability in a solvent medium, it will be imperative for a vapour challenge study to be conducted if MOFs are to be deployed against chemical vapour threats.

Secondly, is to conduct studies that look into the neutralisation capability of MOFs on CWAs vapour after adsorption. With the defect sides or the addition of basic functional groups, HD should undergo degradation through hydrolysis in the presence of moisture^[1].

Figure 26: The hydrolysis of HD^[1]

To facilitate this study, the ability to introduce moisture into the CWAs vapour generation line must first be established. Research study has to include a firm understanding chemical agent's stability and its fate under a moist environment, which in turn adds complexity in the generation and the vapour challenge. One possible challenge for this study is the capability to generate and maintain a constant concentration stream of CWAs at the stipulated temperature and relative humidity.

Thirdly, for a stretch target is to explore the expansion of the use of MOFs from being an adsorbent with decontaminating properties, to other application like in sensing the presence of CWAs with good sensitivity and low detection limit. One potential application will be to incorporate it into the adsorbent layer of the chemical PPE suit that first responder don in their mission. The benefit is that on top of providing protection, it would be ideal if the MOF is able to provide early warning to the first responder. This is in-line with suit maker of envisioning the idea of having a smart suit, which comprises a multi-functional chemical PPE suit with the integration of smart sensors and materials.

Lastly, is to explore the discovery and synthesise of novel MOFs. The need to have new suitable materials to have high adsorption capacity coupled with functionalities and stability will never be quenched. With reticular chemistry, new MOFs can be specifically designed to suit the needs of an application. Organic linkers can be modified before reaction to include useful functional groups. Another possibility is to perform post-synthetic modification can be performed to alter MOF structure after it has been synthesised. Taking UiO-66 as an example, post-modification can be performed to introduce acidic, basic and missing linkers defect sites to enhance its degradation reactivity against CWAs.

Figure 27: Post synthesis modifications on UiO-66 ^[2]

4.2 Conclusion

This study has successfully tested two MOFs namely, HKUST-1 and UiO-66 against a constant stream of HD vapour in a vapour generation system based on permeation tube technology. The MOFs were aged for six months by storing in a 20ml vial under standard room temperature and pressure before they were challenged with HD vapour. Post-ageing characterisation studies were done, and both the MOF samples showed that their structural integrity remained intact. Their stabilities were further supported by their excellent performance over activated carbon in having a higher adsorption capacity before their first breakthrough hours were reached. Among the two MOFs, HKUST-1 outperformed all the three test specimens as the only adsorbent able to provide protection up to 24 hours with HD vapour concentration detected to be below IDLH levels.

This study has therefore demonstrated the possibility of substituting activated carbon as an adsorbent in protective gears such in respiratory mask canisters and chemical protective suits. However, future works such as the need to test the MOFs with other classes of CWAs, and to demonstrate their ability in detoxifying these toxic chemicals have to be explored. Nonetheless, as of till to date of this thesis was written, few studies were reported to test MOFs against toxic chemicals in their gaseous phase and none with CWAs vapours in the literature. Hence, the work performed in this study has established the groundwork for more dynamic research in this area for the near future.

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