

REVIEW PAPER

## Decontamination of Chemical Warfare Agents

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### ABSTRACT

Chemical warfare agents (CWA) pose inevitable threat, both to soldiers and civilians. Risk on contact with these deadly agents can be avoided by neutralisation of their toxic effects. A suitable media with essential physico-chemical properties is required for this purpose. Considerable efforts have been made to develop several decontamination media suitable for neutralisation of highly toxic CWAs. This paper reviews history and details of recent technological advancements in the development of versatile, broad spectrum decontamination formulations against CWAs, as also nanosized metal oxides as CWA decontaminants.

**Keywords:** Chemical warfare agents, neutralisation, decontamination, decontamination media

### 1. INTRODUCTION

Contamination of the environment by chemical warfare agents (CWA) can cause serious health hazards. Of CWA, vesicants act as blistering agents and attack skin and mucous membranes. Nerve agents attack central nervous system by reacting with enzyme acetylcholinesterase to cause respiratory collapse, convulsions, and death. Blood and choking agents create symptoms like choking of breath, vomiting blood, etc.. These health hazards can be avoided by decontamination of CWA<sup>1-5</sup>. Literature classifies decontamination by mechanical, physical, and chemical methods. Covering CWA under soil when no option is available during war-like situation, come under mechanical decontamination methods. Physical methods like dilution, washing operations, adsorption procedures, evaporation, reverse-osmosis and ultra-filtration come under physical decontamination methods. Chemical decontamination includes reactive compounds which take part in either hydrolysis or elimination or oxidation reactions with enhanced rates to neutralise these completely into non-toxic products<sup>6</sup>.

Bleaching powder, i.e., calcium hypochlorite or sodium hypochlorite were the first decontaminants that were employed against CWA. Other category of bleaches is N-chloro compounds. Although, these were found to be promising, lack of stability hindered their widespread application<sup>6</sup>. Decontamination solution (DS2) is another general purpose formulation found useful against a variety of agents such as sulphur mustard (HD), isopropyl methyl phosphono fluoridate (GB), 3,3-dimethyl-2-butyl methyl phosphonofluoridate (GD), O-ethyl N,N-dimethyl phosphoramido cyanidate (GA), and O-ethyl S-2-(di-isopropylamino) ethyl methyl phosphonothioate. However, it causes corrosion to metal surfaces after prolonged

contact and softens, removes paint. Owing to this reason, a need exists for developing a versatile CWA decontamination solution<sup>7</sup> which is non-corrosive, non-toxic, non-flammable, and environmentally safe. Freeze-dried nerve agent-hydrolysing enzyme preparations have been shown to be effective in decontaminating gaseous nerve agents<sup>8</sup>. In previous years, a large number of research studies have been published on this subject<sup>9-13</sup> and one of the most promising carrier systems for active decontaminants is microemulsions<sup>14-20</sup>.

Aqueous foam, a broad spectrum formulation<sup>21</sup> with enhanced physical stability has already been developed. It is based on a surfactant system to solubilise sparingly soluble CWA and to increase rates of reaction with nucleophilic reagents. Swager<sup>24</sup> developed a sensitive, fluorescent chemosensor for the detection of nerve agents<sup>22-24</sup>. He showed that upon intramolecular cyclisation reaction of nerve agents, he could transform a flexible chromophore into a rigid delocalised system causing "off-on" response in the micromolar concentration range. This detection, when integrated with decontamination, can be confidence boosting and user-friendly. Additionally there have been many other methods developed for the detection of these species, including colourimetry<sup>24</sup>, surface acoustic wave devices (SAW)<sup>25-26</sup>, enzymatic assays<sup>27-28</sup>, and interferometry<sup>29-30</sup>, however, presently these are not suitable for integration with the decontamination systems<sup>31</sup>. Besides this, nanosized particles of  $MgO$ ,  $Al_2O_3$  and  $CaO$  are promising reactive sorbent materials that have been used as advanced decontaminant materials. Owing to their high surface area, strong adsorbability, potential reactivity towards chemical warfare agents, these nanosized particles remove the agent rapidly from the contaminated surfaces and degrade it *in-situ* and render the agent non-toxic<sup>32-38</sup>.

In this review, focus is on the CWA that pose the greatest threat, several conventional and advanced formulations that are available till date to mitigate their toxic effects to humans.

## 2. HISTORY OF CHEMICAL WEAPONS

A German scientist named Gerhard Schrader accidentally discovered the first nerve agent, Tabun, in the late 1930s. By the mid-1950's, a group of more stable nerve agents had been developed, known as the V-agents in the American nomenclature. These are approximately ten-fold more poisonous than sarin and are thus among the most toxic substances ever synthesised<sup>39</sup>.

The first use of nerve agent in war was by Afghanistan in 1979-80 followed by Iraq-Iran war from 1984-1987. Iraq was accused and found guilty of violating the 1925 Geneva Protocol that prohibited the use of chemical or biological warfare agents<sup>40-45</sup>. The resulting Iraq-Iran chemical warfare was estimated to be responsible for about 10,000 casualties. Immediately after the war, research was mainly concentrated on studies of the mechanisms of the nerve agents to discover more effective forms of protection against these new CWA. The results of these efforts led, however, not only to better forms of protection but also to new types of agents closely related to the earlier ones.

Types of Chemical Weapons are

- GA–Tabun
- GB–Sarin
- GD–Soman

- GF–Cyclosarin
- VX–Methylphosphonothioic acid
- HD–Sulfur mustard (Yperite)
- HN–Nitrogen mustard
- L–Lewisite
- CX–Phosgene oximine
- CG–Phosgene
- DP–Diphosgene
- Cl–Chlorine
- PS–Chloropicrin
- AC–Hydrogen cyanide
- CK–Cyanogen chloride
- PFIB–Perfluoroisobutylene
- Tear gases
- Vomiting agents
- Sneezing agent like o-dianisidine sulphate
- Psychotropic agents like LSD & BZ
- Defoliants–Herbicides, etc.

## 3. CHEMICAL STRUCTURE OF CWA

Certain CWA share chemical characteristics that present an opportunity for the development of countermeasures. The chemical agents– sarin, soman, and tabun (G-agents) are all examples of phosphorus-containing compound which, when altered chemically at –P–X (X=F or CN) bond, can lose their toxicity. Mustard, which is an example of the H-agents, and VX, which is an example of the V-agents, can also be altered chemically and rendered harmless (Table 1) by oxidising at S atom. Certain types of organophosphorus compounds

**Table 1(a). Use of chemical warfare agents in various wars**

War	Year	Agents used
World War I	1914-18	Chlorine, tear gas, sneezing powder, and Mustard gas
Abyssinia	1936-37	Mustard gas and tear gas
World War II	1939-45	Tabun–Nerve gas and S.M.
Yemen	1963-67	Mustard gas
Vietnam	1965-74	Defoliant, herbicides
Laos	1976	Herbicides
Cambodia	1979	Mustard
Afganistan	1979-80	Nerve gas
Kurdish town of Halabja	1988	Sulphur mastard

**Table 1(b). Structures of persistent CWAs**

Family	Agent	Acronym	Formula
Vesicants	Sulfur Mustard	HD	$ClCH_2CH_2SCH_2CH_2Cl$
-	Nitrogen Mustard	HN-1	$(CH_2CH_2Cl)_2NC_2H_5$
-	Nitrogen Mustard	HN-2	$(CH_2CH_2Cl)_2NCH_3$
-	Nitrogen Mustard	HN-3	$N(CH_2CH_2Cl)_3$
-	Lewisite	L	$ClCH=CHAsCl_2$
G	Tabun	GA	$C_5H_{11}N_2O_2P$
-	Sarin	GB	$C_4H_{10}FO_2P$
-	Soman	GD	$C_7H_{16}FO_2P$
V	-	VX	$C_{11}H_{24}PO_2SN$

are commonly used as insecticides even though they display extreme toxicity to human.

These compounds and their structural variants also have the potential to be very effective weapons of chemical warfare. The general chemical structure of this type of deadly organophosphorus compounds consist of a tetra substituted phosphorus (V) centre, an oxygen or sulphur atom double-bonded to the phosphorus, a leaving group, and two substituents that vary widely depending on the sub class<sup>41</sup>. Molecularly, nerve agents are characterised as alkylphosphonic acid esters that contain at least one carbon-phosphorus bond. These deadly compounds can be further divided into two subclasses, G and V (Figs 1 & 2) based on additional functionalities that contribute to the unique properties of each individual member including persistence on surfaces, resistance to hydrolysis, solubility, and stability.

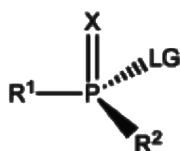


Figure 1. The general chemical structure of deadly organophosphorus compounds (X = O or S; LG = leaving group; R<sup>1</sup> and R<sup>2</sup> = alkyl, O-alkyl, or OH).

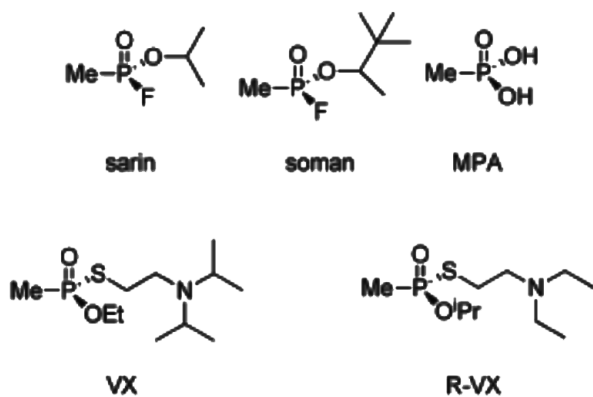


Figure 2. Chemical structure of sarine, soman, VX, R-VX, and the degradation product common to all nerve agents, methylphosphonic acid (MPA).

### 3.1 Physical and Chemical Properties of Chemical Warfare Agents

The 'G' agents and 'V' agents are persistent. Some 'G' agents may be thickened with various substances to increase their persistence, and therefore, the total amount that penetrates the intact skin. At room temperature, GB is a comparatively volatile liquid. GD is also significantly volatile, as is GA though to a lesser extent. VX is a relatively non-volatile liquid, and therefore, persistent. It is regarded as presenting little vapour hazard to people exposed to it. In the pure state, nerve agents are colourless liquids. In an impure state, nerve agents may be encountered as yellowish to brown liquids. Some nerve agents have a faint fruity odour. GB and VX doses, which are potentially life-threatening, may be only slightly larger than those producing least effects. Death usually occurs within 15 min after absorption of a fatal VX dosage. Although only about half as toxic as GB by inhalation, GA in low concentrations is more irritating to the eyes than GB. Symptoms appear much more slowly from a skin-absorbed dosage than from a respiratory-absorbed dosage. Although skin absorption is more, death may be delayed for 1 h to 2 h. Respiratory lethal dosages kill in 1 min to 10 min, and liquid in the eye kills almost as rapidly. In general, nerve agents are moderately soluble in water with slow hydrolysis, highly soluble in lipids, rapidly inactivated by strong alkalis and chlorinating compounds (Table 2).

### 4. DECONTAMINATION OF CWAS

Decontamination can be defined, as a method essentially involving the conversion of toxic chemicals into harmless products by degradation. Decontamination is based on one or more of the following principles:

- To destroy CWAs by chemically modifying these (destruction),
- To physically remove CWAs by absorption, washing or evaporation,
- To physically screen-off the CWAs so that these cause no damage.

Most CWA, can be destroyed by means of suitable

Table 2(a). Physico-chemical properties of mustards, blood agents, choking agents<sup>81</sup>

Physical property	Tabun	Sarin	Soman	VX
Appearance	Colourless to brown liquid giving off colourless vapours	Colourless to brown liquid giving off colourless vapours	Colourless to brown liquid giving off colourless vapours	Amber coloured liquid
Molecular formula	$C_5H_{11}PO_2N$	$C_4H_{10}PO_2F$	$C_7H_{16}PO_2F$	$C_{11}H_{24}PO_2SN$
Molecular weight	162.12	140.10	182.20	267.40
Liquid density (gm/ml)	1.07	1.09	1.02	1.01
Freezing point(°C)	-50	-57	-42	-51
Boiling point @ (760 mm Hg)	(220 °C to 246 °C)	(158 °C)	(167 °C to 200 °C)	(298 °C)
Vapour density	5.63	4.86	6.33	9.20
Vapour pressure mm Hg at 25° C	0.07	2.90	0.40	0.007
Volatility mg/m <sup>3</sup> @ 25°C	61.0	22.0	3.90	10.5

**Table 2(b). Physico-chemical properties of mustards, blood agents, choking agents**

Property	Sulphur Mustard	HN-1	HN-2	HN-3	HCN	CNCl	COCl <sub>2</sub>
Appearance	Pale yellow to dark brown oily liquid with garlic odour	Dark oily liquid	Colourless liquid when pure	Oily dark liquid colourless when pure	Colorless gas, pale blue highly volatile liquid	Colourless gas with pepperish odour like tear gas	Colorless gas
Molecular formula	$C_4H_8Cl_2S$	$C_6H_{13}Cl_2N$	$C_5H_{11}Cl_2N$	$C_6H_{12}Cl_3N$	HCN	CNCl	COCl <sub>2</sub>
Molecular weight	159.07	170.08	156.05	204.53	27.03	61.471	98.92
Liquid density (gm./ml) @ 25 °C	1.2685	1.086 C	1.118	1.2352	0.686	1.18	1.360
Freezing point (°C)	14.45	-34.2	-70	-3.74	-13.4	-6.9	-128
Boiling point (°C)	218	192	177 Extrapolated	257 Extrapolated	26.0	12.8	7.8
Vapour density	5.5 (Calculated)	5.9 (Calculated)	5.4 (Calculated)	7.1 (Calculated)	0.94	2.1 (Air=1)	3.4
Vapour pressure mm Hg (Torr) × 10 <sup>3</sup> @ 25 °C	0.11	0.25	0.427	0.011	620	1000	1.40
Volatility mg/m <sup>3</sup> @ 25 °C	9.20	22.9	3.6	0.12	-	613.20	-

chemicals. However, such chemicals may be unsuitable for use in certain conditions since these corrode, etch or erode the surface. Sodium hydroxide dissolved in organic solvent breaks down most of the substances but should not be used in decontaminating skin other than in extreme emergencies when alternative means are not available. Ideally, a decontamination formulation should be broad-spectrum in nature, and must have the following requirements<sup>46-47</sup>

- It should be compatible with, and non-corrosive to, equipment used in its application as well as to the equipment to be decontaminated.
- It should not soften nor damage paints, coatings, polymeric seals or gaskets or transparencies such as windscreens.
- It should not interfere with in-service monitoring equipment used to verify the effectiveness of the decontamination or to locate residual contamination.
- It should be easy to prepare, easy to apply and remove, and remain stable for a reasonable length of time after preparation.
- It is highly desirable that it adhere to and coat vertical surfaces for sufficient periods of time for agent desorption from the surface and detoxification, yet be easy to remove by evaporation or by rinsing. If used in combination with a surfactant, the decontamination formulation should not compromise the integrity of the foam.
- It should be of low toxicity, be non-flammable and have a low impact on the environment in order that

training can be realistically and frequently performed.

For example, in Sandia National Laboratory, USA (SNL) foam formulation, positively charged micelles were present, which solubilise the CWA and attract the negatively charged nucleophiles. In the aqueous environment, the CWA is located (solubilised) within the micelle comprising of an aggregate of surfactant molecules with hydrophobic tails forming the interior core of the micelle, and hydrophilic heads concentrating at the surface of micelle. These positively charged hydrophilic heads attract the negatively charged nucleophiles, greatly enhancing the reaction rates with the CWA within the micelle.

The currently fielded chemical decontamination methods use the chemical reactions like alkaline hydrolysis or oxidation by hypochlorite ion, based on non-aqueous decontamination solution, i.e., DS2 or aqueous bleach. Both are found to be quite effective in decontaminating CWA. Another modern decontaminant is the German emulsion which consists of calcium hypochlorite, tetrachlorethylene, emulsifier (“phase transfer” catalyst) and water. Instead of tetrachlorethylene, the more environmentally harmless xylene is sometimes used<sup>6</sup>.

#### 4.1 Methods for Decontamination of chemical warfare agents

Decontamination is a complex process and can be considered in different ways. From methodological point of view, there are three basic methods of decontamination: (i) mechanical decontamination (ii) physical decontamination, and (iii) chemical decontamination.

#### 4.1.1 Mechanical Decontamination

Simplest method for ground decontamination is to remove or cover the contaminated surface. For both removal and covering several technologies have been developed for combat situations. Scraping with a wooden stick, i.e., a tongue depressor or Popsicle stick, can remove bulk agent.

#### 4.1.2 Physical Decontamination

Physical method is cheapest and easiest of the possibilities for CWA decontamination. It is not as effective as chemical decontamination, but the main advantage is that physical procedures act universally and they do not depend on the chemical nature of CWA to be destroyed. The main physical procedures are:

- Dilution and washing operations
- Adsorption procedures
- Evaporation
- Reverse osmosis and ultra-filtration

Several types of physical methods are potentially suitable for decontaminating equipment and material. Flushing or flooding contaminated skin or material with water or aqueous solutions can remove or dilute significant amounts of agent, however, there exist chances that the agent can spread and cause more damage to surface like skin. For the decontamination of clothing only, adsorbents like Fullers earth and containment materials (to be used on outer garments before their removal and disposal) have been considered.

### 5. INDIVIDUAL DECONTAMINATION

Personal decontamination is decontamination of self and casualty decontamination refers to decontamination of casualties. The steps involved in individual decontamination are:

- Mopping up liquid droplets with adsorbents (Fullers earth), cloth or tissue paper.
- Washing with water/soap/detergent.
- Use of active ingredients like chloramines.
- Specific antidote if available.

Personal decontaminants containing chlorinated lime have, however, an irritating effect on the skin. Consequently, comprehensive use should be followed by a bath or shower within a few hours. Sodium phenolate or sodium cresolate in alcohol solution have been used for individual decontamination of nerve agents in some countries. Chloramines in alcohol solution, possibly with additional substances, are commonly used against, e.g., mustard agent. Instead of liquid individual decontaminants, it is possible to use solution of potassium permanganate which gives effective decontamination of CWA on the surface of the skin and also a certain penetrating effect.

#### 5.1 Personal Decontamination Kit of DRDE, Gwalior

This kit consists of two components: PDK-I, PDK-II which contained Fuller's earth. These are used for decontamination of body surface and equipment. The principle is based on adsorption. The adsorbent should be disposed of carefully after decontamination is over.

#### 5.2 Decontamination Solid Sorbent System M258 and M291 Kit

M258 kit consists of two packets: Packet I contain a towelette pretreated with phenol (10 %), ethanol (72 %), sodium hydroxide (5%), ammonia (0.2 %), and water (12%). Packet II contains a towelette impregnated with chloramine-B and a sealed glass ampoule filled with zinc chloride solution. The ampoule in packet II is broken and the towelette is wetted with the solution immediately prior to use. The presence of zinc chloride maintains the pH of the chloramine-B in water between 5 and 6 which would otherwise rise to 9.5. The M291 kit is a solid sorbent system. The kit is used to wipe bulk liquid agent from the skin and is composed of non-woven fiber pads filled with a resin mixture. The resin is made of sorptive material based on styrene/divinylbenzene and a high surface area carbonised macroreticular styrene/divinylbenzene resin, cation-exchange sites (sulfonic acid groups), and anion-exchange sites (tetraalkylammonium hydroxide groups). The sorptive resin can absorb liquid agents and the reactive resins are intended to promote hydrolysis of the reactions. GD slowly hydrolysed with a half-life of about 30 hour prompting further research in this area<sup>6</sup>.

#### 5.3 Active Ingredients for Decontamination Formulations for Personal Decontamination

Sodium dichloroisocyanurate, other chloroisocyanuric acids, their alkali metal salts were also found to be suitable for use as the active ingredient. Where, lithium hypochlorite was used to augment the active hypochlorite content of the solution over a short term, thus providing a higher level of active species in the initial stages after the addition of water<sup>6</sup>. Alternatively, Super Tropical Bleach (STB) or High Test Hypochlorite (HTH) were also used as active ingredients<sup>48-49</sup>.

In addition to the above, it is also observed that the "N,N-Dichloro-4-methylbenzenesulphonamide (Dichloramine-T), reacts with 2,2'-dihalodiethyl sulphide (mustards) vigorously and decontaminate them almost instantaneously, even at sub-zero temperature, especially in a scenario where use of aqueous medium is undesirable. This high reactivity of dichloramine-T is due to positive chlorine compound in a homogeneous phase since both the toxic sulphides and dichloramine-T are soluble in the organic medium used<sup>50</sup>.

Another formulation is *N, N<sub>2</sub>-dichloro bis(2,4,6-trichlorophenyl)urea (CC-2)* which effectively decontaminated CWA. The chlorine content of CC-2 (Fig. 3) was checked by standard iodometric titration and was found to be 14.51 per cent (theoretical value 14.54%). Structure<sup>51</sup> of CC-2 is given in Fig. 3.

### 6. CHEMICAL METHODS FOR DECONTAMINATION OF CHEMICAL WARFARE AGENTS

Depending upon chemical nature of the CWAs, a large number of compounds and formulations are available presently and which can easily be employed for the

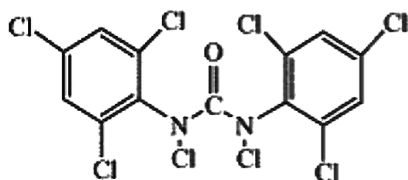


Figure 3. *N,N'*-dichloro bis(2,4,6-trichlorophenyl) urea.

decontamination of CWAs. One of the great advantages of chemical decontamination is that it converts the toxic CWA into innocuous products which can be handled safely, while in the physical process, the CWA are temporarily removed from the site. The general chemical reactions, that can be applied as chemical decontamination procedures include:

- Nucleophilic and elimination reactions
- Electrophilic reactions (oxidations)
- Thermal destruction
- Photochemical and radiochemical reactions

Based on chemical reactions of CWAs with various reagents, formulations have been developed for their effective decontamination. For example, in the case of DS2 solution, the active ingredient is  $CH_3OCH_2CH_2O^-$  which works as nucleophile and reacts with CWA. This formulation decontaminates HD by elimination reaction and the scheme is given in Fig. 4. and it reacts with nerve agents through nucleophilic reaction and converts them to non toxic products (Fig. 5).

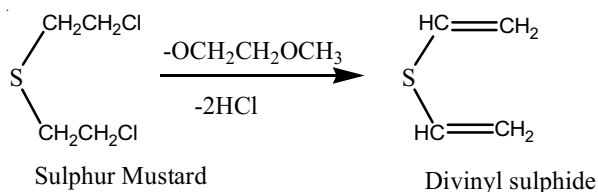
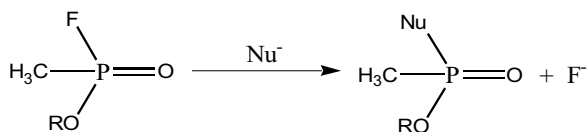


Figure 4. Decontamination of HD by elimination reaction.



R =  $i\text{-C}_3\text{H}_7$  Sarin (GB)  
 R =  $(\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2$  Soman (GD)  
 $\text{Nu}^- = ^-\text{OCH}_2\text{CH}_2\text{OCH}_3$

Figure 5. Decontamination of G agent by nucleophilic substitution.

### 6.1.1 Surfactants-based Formulations

Since decontamination of hydrophobic CWAs is hampered by their low solubility in the aqueous medium; formulations have been developed with surfactants (detergents) which not only enhance solubility of agents in aqueous medium, but also contribute to catalyse their detoxification. The main ingredients of such formulations are surfactants like:

- Sodium dodecylsulphate or cetyltrimethylammonium halide
- Nuclei like hydroperoxides or hypochlorite

Active ingredients like hypochlorite decontaminate the CWA by means of oxidation reactions. For example HD reacts with hypochlorite ion to get oxidised to sulphur mustard sulphoxide and sulphone which are relatively non-toxic as given in Fig. 6. With G agent alkaline  $^-OCl$  reacts by nucleophilic substitution reaction and the mechanism is given in Fig. 7. Whereas, oxidising agents like hydroperoxides or hypochlorites or *m* chloroperoxybenzoic acid or oxone ( $\text{KHSO}_5$ ) reacts with VX to give the non-toxic<sup>52</sup> products (Fig. 8).

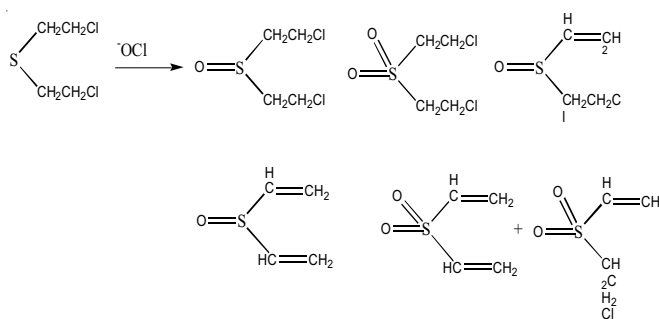
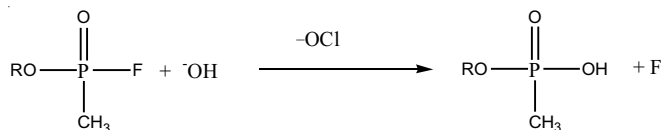


Figure 6. HD reaction with hypochlorite ion.



R =  $i\text{-C}_3\text{H}_7$  Sarin (GB)  
 R =  $(\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2$  Soman (GD)

Figure 7. Reaction of G agent with hypochlorite ion.

### 6.1.2 Variables Effecting Decontamination

The variables which determine the effectiveness of decontamination are contamination time, temperature, contamination density, decontamination medium, nature of agent and nature of decontaminants. Surface of the object, on which contamination is present, i.e., the target for decontamination, surface-agent interactions, surface-decontaminant interactions also play a major role in decontamination along with the preparedness of the individuals wearing the protective gear<sup>53</sup>.

## 7. DECONTAMINATION SYSTEMS AVAILABLE

### 7.1 Super Tropical Bleach

It is a mixture of 93 per cent calcium hypochlorite and 7 per cent sodium hydroxide and is more stable than bleach in long-term storage and easier to spread. Mustard gas reacts with bleach by oxidation of the sulphide to sulphoxide and sulphone and by dehydrochlorination to form compounds such as  $\text{O}_2\text{S}(\text{CHCH}_2)_2$ . The G agents are converted by hydrolysis to the corresponding phosphonic acids with the hypochlorite anion acting as a catalyst<sup>4</sup>. In acidic

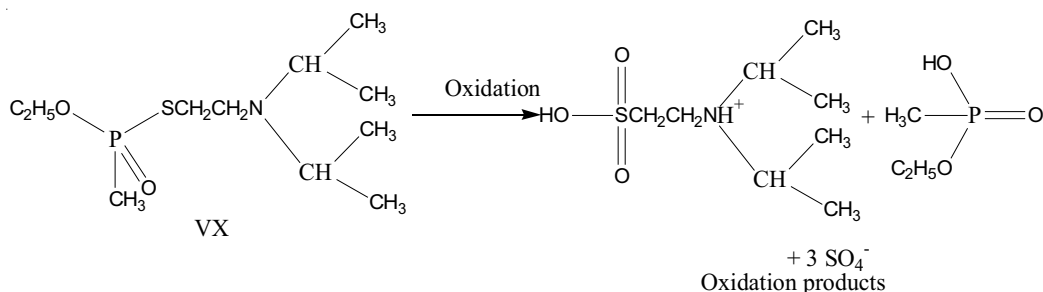


Figure 8. Oxidative decontamination of VX.

solutions, VX is oxidised rapidly by bleach at the sulfur atom and dissolves by protonation at the nitrogen<sup>6</sup>.

### 7.2 Activated Vapour Treatment for Decontamination of CWAs

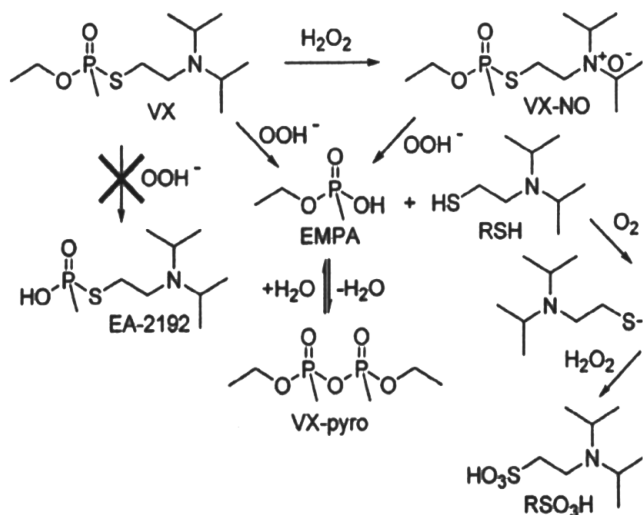
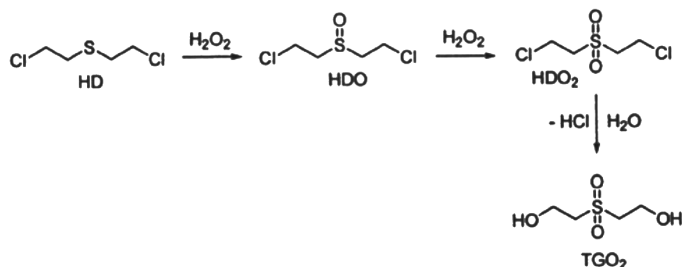
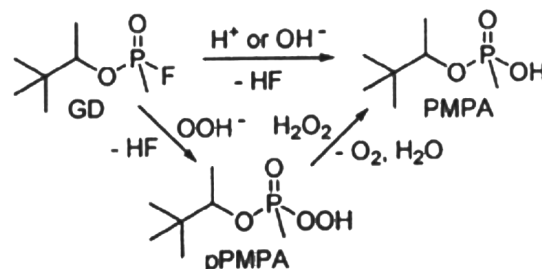
Activated hydrogen peroxide vapours are effective against blistering agents and nerve agents, such as VX, which exhibit selective oxidation and selective perhydrolysis. By the addition of ammonia to the vapour stream, the hydrolysis-based deactivation of GD is also effected. Ratio between hydrogen peroxide and ammonia gas is maintained with in a 1:1 and 1:0.0001<sup>54</sup>. Reaction schemes for VX, HD, GB with  $H_2O_2$  are given in Fig. 9-11.

### 7.3 Activated Aluminium Oxide-based Decontaminant

By spraying activated aluminum oxide on contaminated surfaces, the contamination is absorbed and decontaminated subsequently<sup>44</sup>. The sorbent materials may also include a blend of the activated aluminum oxide and magnesium monoperoxyphthalate (MMPP). In this, the MMPP can be present from about 1 per cent to about 50 per cent by weight.

### 7.4 Microemulsion-based System in Decontamination of CWAs

This formulation includes a microemulsion composition for decontaminating chemical and biological warfare agents.

Figure 9. Decontamination reaction of VX with  $H_2O_2$ .Figure 10. Decontamination reaction of HD with  $H_2O_2$ .Figure 11. Decontamination reaction of G agent with  $H_2O_2$ .

The microemulsion preferably comprises 5 Wt per cent to 60 Wt per cent water, 5 Wt per cent to 60 Wt per cent hydrocarbon compound and 5 Wt per cent to 60 Wt per cent surfactant. An exemplary microemulsion composition includes approximately 42.4 Wt per cent water, 17.2 Wt per cent decane and 24.6 Wt per cent surfactants (neat). Buffers, and other known microemulsion additives may be added, as desired<sup>55</sup>.

### 7.5 Decontamination Solution 2

Decontamination Solution 2 (DS2) is a wide-spectrum, ready-to-use, chemically reactive nucleophilic decontaminant, having long-term stability over an extended range of temperature of 26 ° C to 52 ° C. This polar, non-aqueous liquid consists, by weight, of 70 per cent diethylenetriamine, 28 per cent ethylene glycol monomethyl ether, and 2 per cent sodium hydroxide. At ambient temperature, it reacts with any of the HD, VX, GA or GB agents within a few seconds<sup>6</sup>. The reaction mechanism is similar to as given in Figs 4 and 5.

### 7.6 German Emulsion (C8)

This system consists, by weight, of 76 per cent water, 15 per cent perchloroethylene, 1 per cent anionic surfactant, and 8 per cent high-test-hypochlorite (HTH). Many of the benefits of this system are attributed to the perchloroethylene continuous phase. C8 is of low corrosivity despite the high *pH* of the aqueous phase<sup>6</sup>. It is effective in dissolving thickeners and can easily penetrate into paint surfaces and react with the embedded agents, without damaging the paint. It is viscous enough to provide a thin and coherent film on the surface to allow sufficient time for reaction with the agents. C8 has several drawbacks. It must be mixed an hour prior to use to generate the emulsion. The reaction mechanism is similar to as given in Figs 6 and 7.

### 7.7 Surfactant-based CWAs Decontamination Formulation

The formulation contains sodium dichloroisocyanurate, other chloroisocyanuric acids, their alkali metal salts. The formulation contains about 1 per cent to 15 per cent hydrated dichloroisocyanuric acid salt. The formulation may additionally comprise 1 per cent to 9 per cent lithium hypochlorite to enhance the activity of the dichloroisocyanuric acid salt. It also contains a co-solvent 1 per cent to 10 per cent by volume propylene glycol. In addition, it also contains 1 per cent to 15 per cent by volume of a surfactant. The surfactant is soluble in an aqueous medium, and when aerated, creates a foam. The amount of surfactant used varies with the amount of co-solvent, active ingredient and buffer present. Finally, it also contains a buffer and maintains an initial *pH* in the range of 10 to 11, sufficient to enable hydrolysis of G-agents and mustards and favour oxidation of the V-agents so as to produce non-toxic products<sup>56</sup>. The reaction mechanism is similar to as given in Figs 6 and 7.

### 7.8 Surfactant and Diol-based Formulation

The formulation containing benzyltrimethylammonium chloride (55 g) and benzyltriethylammonium chloride (15 g), along with sodium perborate tetrahydrate (2 g), propylene glycol (68 g) and 2-amino-2-methyl-1-propanol (12 g) has been found to decontaminate CWAs effectively. The propylene glycol, 2-amino-2-methyl-1-propanol solution was heated to ease the dissolution of the sodium perborate tetrahydrate (sodium perborate tetrahydrate decomposes at about 60°C). The final mixture was stirred until the solid components have substantially dissolved. When no more solid was dissolved, the solution was decanted, and then stored in a sealed container<sup>57</sup>.

### 7.9 Water-based Decontaminant Formulation

Benzyltrimethylammonium chloride (90 g), benzyltriethylammonium chloride (25 g), 2-amino-2-methyl-1-propanol (185 g) and water (20 g) along with sodium perborate tetrahydrate (2 g) was used as CWA decontamination formulation-based on aqueous system. The *pH* of the

decanted solution was adjusted to about 10.6 (about 20 g water was added)<sup>57</sup>.

### 7.10 Plasma-based Decontamination of CWAs

A "plasma decon chamber" has been developed at Los Alamos National Laboratory (LANL), Albuquerque, NM, to study the decontamination of chemical and biological warfare agents. This technology is targeted at sensitive electronic equipment for which there is currently no acceptable, nondestructive means of decontamination. Chemical reactivity is provided by a downstream flux of reactive radicals such as atomic oxygen and atomic hydrogen, produced in a capacitatively coupled plasma. In addition, the decon chamber provides an environment that accelerates the evaporation of chemical agents from contaminated surfaces by vacuum, heat, and forced convection. Once evaporated, agents and agent byproducts are recirculated directly through the plasma, where they undergo further chemical breakdown<sup>58</sup>.

### 7.11 Enhanced Formulation for Neutralisation of Chemical, Biological Toxicants

The formulation includes at least one solubilising agent, a reactive compound, a bleaching activator and water<sup>51</sup>. It contains 5.3 per cent of cationic surfactant, 2.8 per cent adogen 477 (cationic hydrotrope) 0.65 per cent 1-dodecanol (fatty alcohol) 0.6 per cent isobutanol (short chain alcohol) 0.1 per cent jaguar 8000 (cationic polymer) 1.35 per cent diethylene glycol monobutyl ether (solvent) 4 per cent potassium bicarbonate (buffer and peroxide activator) 4 per cent hydrogen peroxide (oxidant) 81 per cent water. This formulation can be adjusted to a *pH* value of 8 for optimal decontamination of Mustard gas and Anthrax spores; and can be to a *pH* value of 10 for optimal decontamination of VX. Also, it can be adjusted to a *pH* of 9.2 for less than optimal decontamination of all agents<sup>59</sup>. The reaction mechanism is similar to as given in Figs 6 and 7.

### 7.12 Chemical Warfare Agent Decontamination Foaming Composition and Method

This foam-based CWA decontaminating composition contains a quaternary ammonium complex component, a corrosion inhibitor, an oxidiser component, and a foam component, with an adjusted *pH* of at least 8. It contains 13 per cent by weight of benzyl-trimethylammonium chloride, 20 per cent by weight of isobutanolamine, 27 per cent by weight of toluenesulfonic acid, 20 per cent by weight of hydrogen peroxide, and 20 per cent by weight of water<sup>60</sup>. The reaction mechanism is similar to as given in Figs. 8 to 11.

### 7.13 Activated Peroxide Solution with Improved Stability for the Decontamination of Chemical Warfare Agents

In this Potassium citrate monohydrate, potassium bicarbonate, potassium molybdate, propylene glycol, propylene carbonate, TRITON X-100, and 35 per cent by weight



water were added. Microemulsions were mixed by first dissolving the solid ingredients (e.g., potassium citrate monohydrate,  $KHCO_3$  and  $K_2MoO_4$ ) in water. To this, a mixture of propylene glycol, TRITON X-100 and propylene carbonate was added. Finally 35 per cent  $H_2O$  was added. The vessel holding the components was capped and vigorously shaken to thoroughly mix the components. Composition contains 10 vol per cent propylene carbonate, 20 vol per cent propylene glycol, 10 vol per cent TRITON X-100, 30 vol per cent hydrogen peroxide (35 per cent aqueous solution used), and 30 vol per cent of an aqueous solution of potassium citrate monohydrate, potassium bicarbonate and potassium molybdate such that the final concentrations of these activators in the decontaminating solution were 0.25 M, 0.5 M, and 0.02 M, respectively. The amount of agent (HD, VX AND GD initially present) to decontaminant was 1:50 or 2 vol. per cent<sup>61</sup>. The reaction mechanism is similar to Figs 8 to 11.

#### 7.14 Chemical and Biological Warfare Decontaminating Solution using Bleach Activators

This microemulsion-based decontaminating solution contained 296 mg of 76 per cent didecyl methylamine oxide, 499 mg of 30 per cent decyldimethylamine oxide, 394 mg decane, 224 mg of water, 110 mg of a bleach activator (nonanoyloxybenzene sulfonate, and 37 mg of sodium carbonate (buffer). 96 mg of 30 per cent hydrogen peroxide was then added and a peroxycarboxylic acid of pernonanoic acid was generated *in-situ*<sup>62</sup>. The reaction mechanism is similar to that given in the Figs. 6 and 7.

#### 7.15 Microemulsions Containing Sulpholanes

This formulation contained 3-methylsulpholane together with a cationic surfactant such as cetyl trimethylammonium bromide or a non-ionic surfactant such as polyoxyethylene octylphenol ether. In another aspect, seawater may be substituted for the aqueous phase. This novel microemulsion is useful for the detoxification of pesticides and chemical warfare agents by enabling their better removal and/or destruction through one or more of the processes of solubilisation, oxidation or hydrolysis. It contained microemulsion 20 per cent w/w to 92 per cent w/w of water, 4 per cent to 40 per cent w/w of cetyl trimethylammonium bromide as a cationic surfactant and 4 per cent w/w to 40 per cent w/w of sulfolane as a cosurfactant (3-methylsulfolane) and 2 to 10 per cent oxidising compound<sup>63</sup>.

#### 7.16 Granulated Decontamination Formulations

It contained 40 g of variquat 80MC (cationic surfactant), 55 g potassium carbonate (carbonate salt), 20 g polyethylene glycol 8000 (water-soluble polymer), 20 g amorphous silica sorbent additive, 40 g glycerol diacetate or propylene glycol diacetate (bleaching activator) and 135 g urea hydrogen peroxide (reactive compound). These were mixed with 700-1000 g water and then granulated to obtain the decontamination formulation<sup>64</sup>. The reaction mechanism is similar to that given in Figs 8-11.

#### 7.17 Ozone-containing Fluid System for Chemical and/or Biological Warfare Agents

This method utilises ozone-containing solution. The ozone-containing solution is produced by combining ozone-containing gas with an ozone vehicle, such as an organic solution. The ozone-vehicle prolongs the shelf life of the ozone to allow for extended periods of storage. A storage container is used to store the ozone-containing solution and facilitate its transportation to an environment contaminated by the biological and/or chemical warfare agents, or near a potential site for biological or chemical attack. The ozone-containing solution is drawn out of the storage container to spread it to a contaminated environment<sup>65</sup>.

#### 7.18 Cleaning Composition for Neutralising Biological and Chemical Weapons Removal Agents

This composition is used for treating and removing stains from an object and for removing residue following a clean-up after a chemical or biological weapons attack. It contains 35 per cent–45 per cent by volume of ethanol, 1.5 per cent–2.5 per cent by volume of isopropyl alcohol, 0.05 per cent–0.5 per cent by volume of ethylene glycol *n*-hexylether, 3 per cent–4 per cent by volume of each myristyltrimethylammonium and benzethonium chloride, 0.2 per cent– per cent by volume of the tetrasodium salt of ethylenediamine tetraacetic acid, and 0.1 per cent–0.50 per cent by volume of polyvinyl alcohol<sup>66</sup>.

#### 7.19 Neutralisation of Vesicants Related Compounds

Blister-type chemical agents such as lewisite and mustards, as well as G or V class nerve agents and phosphorus-containing pesticides, react with above solution of a persulphate, preferably potassium peroxymonosulphate, and a peroxide, preferably hydrogen peroxide, at temperatures ranging from ambient to boiling for a time sufficient to reduce the residual agent concentration to levels acceptable for disposal in a routine manner. It contains 22 per cent solution of oxone and 15 per cent solution of hydrogen peroxide<sup>67</sup>. The reaction mechanism is similar to as given in Figs 8 to 11.

#### 7.20 Decontamination of Chemical Warfare Agents using a Reactive Sorbent

It was prepared by mixing 148 g sodium methoxide solution (25 per cent Wt by sodium methoxide in methanol) to 38.6 g diethylenetriamine. The resulting solution was stirred for one hour and then it was impregnated on carbon of surface area 1800 m<sup>2</sup>/g and dried to get the reactive sorbent. This reactive sorbent was used efficiently to decontaminate CWA<sup>68</sup>. The reaction mechanism is similar to as given in Figs. 4 and 5.

#### 7.21 Oxidiser Gels for Detoxification of Chemical and Biological Warfare Agents

Composition contains oxidising agents and thickening or gelling agents and is used to detoxify chemical and biological warfare agents by application directly to a

contaminated area. The gelling agent is a colloidal material, such as silica, alumina, or alumino-silicate clays, which forms a viscous gel that does not flow when applied to tilted or contoured surfaces. Aqueous or organic solutions of oxidising agents can be readily gelled with less than about 30 per cent colloidal material. Gel preparation is simple and suitable for field implementation, as the gels can be prepared at the site of decontamination and applied quickly and uniformly over an area by a sprayer. After decontamination, the residue can be washed away or vacuumed up for disposal.

A 13.5 per cent fumed silica (EH-5) gel made with 5.5 per cent sodium hypochlorite in water, 14.5 per cent fumed silica (EH-5) gel of 0.3N-ammonium persulphate and 16.4 per cent fumed silica (EH-5) gel of 30 per cent hydrogen peroxide were found to be effective against CWA<sup>69</sup>. The reaction mechanism is similar to as given in Figs 8 to 11.

### 7.22 Universal Decontaminating Solution for Chemical Warfare Agents

This decontaminating composition contains a carbonate component, peroxide component, and alcohol component effective to degrade a chemical warfare agents. It comprised of 30 Wt per cent hydrogen peroxide and 50 Wt per cent urea hydrogen peroxide addition compound and the remaining 20-40 % polypropylene glycol and 1-10 per cent  $\text{NaHCO}_3$  in the aqueous  $\text{H}_2\text{O}_2$ <sup>70</sup>. The reaction mechanism is similar to as given in Figs 8 to 11.

### 7.23 Metal Phenoxide/Polyethylene Glycols Chemical Decontaminant System

A barrier cream consisting essentially of at least one active ingredient chosen from the alkali metal salts of phenols, dispersed in a substantially anhydrous state in a base medium comprising a polyethylene glycol, which has been at least partially etherified to reduce the free hydroxyl group content thereof. These creams are simple to prepare, effective for a reasonable period of time, and do not produce adverse skin reaction, and are simple, both to apply and to remove. These afford protection against chemical warfare agents of both the V and G types, and against mustard gas (H or HD). This cream contains 0.625M potassium phenoxide in polyethylene glycol 750 monomethyl ether<sup>71-72</sup>. The reaction mechanism is similar to as given in Figs 4 and 5.

### 7.24 Detoxification of Organophosphate Nerve Agents by Bacterial Phosphotriesterase

Bacterial enzymes capable of hydrolysing the lethal organophosphate nerve agents are of special interest. Phosphotriesterase (PTE)<sup>65</sup> isolated from the soil bacteria *Pseudomonas diminuta* displays a significant rate enhancement and substrate promiscuity for the hydrolysis of organophosphate triesters. Directed evolution and rational redesign of the active site of PTE have led to the identification of new variants with enhanced catalytic efficiency and stereo selectivity towards the hydrolysis of organophosphate

neurotoxins. PTE has been utilised to protect against organophosphate poisoning *in vivo*. Biotechnological applications of PTE for the detection and decontamination of insecticides and chemical warfare agents are developing into useful tools. In this review, the catalytic properties and potential applications of this remarkable enzyme are discussed by Eman & Raushel<sup>73</sup>.

### 7.25 Molybdate/Peroxide Microemulsions useful for Decontamination of Chemical Warfare Agents

A formulation composed of molybdate and peroxide was designed for the decontamination of CWAs. It decontaminates HD by oxidation to its corresponding sulphoxide and nerve agents VX and GD by perhydrolysis to their non-toxic phosphonic acids using environmentally safe reactants, specifically a peroxomolybdate compound having a dominant tetraperoxomolybdate species and peroxy anion (Fig. 12). Composition contained  $\text{K}_2\text{MoO}_4$  (0.001 M to about 1.0 M), *n*-BuOH (20 vol per cent),  $\text{CH}_2\text{Cl}_2$  (10 Vol per cent), sodium dodecyl sulphate (SDS) or triton X-100 (10 vol per cent), *i*-PrOH, hexane, 50 per cent aqueous  $\text{H}_2\text{O}_2$  and (1 to 30 vol per cent) and water (30 Vol per cent). Microemulsions (MEs) were mixed by first adding the solid, followed by co-surfactant, surfactant, organic solvent, and finally, 50 per cent  $\text{H}_2\text{O}_2$ <sup>74</sup>.

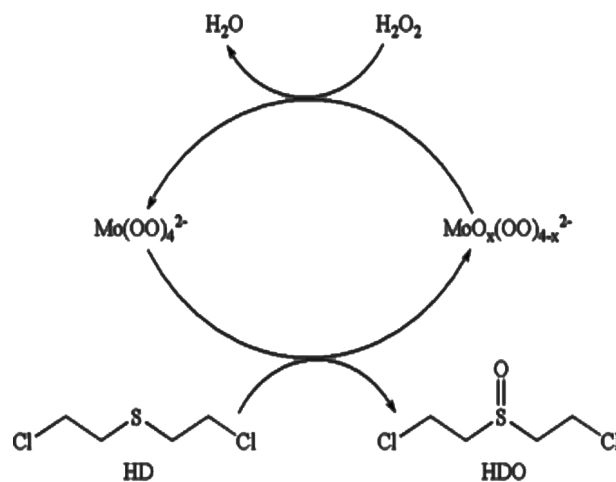


Figure 12. Oxidative decontamination of HD in molybdate/peroxide microemulsions.

### 7.26 Peroxybicarbonate-based Formulations

Peroxides are desirable reactants for CWA decontamination because they are non-toxic and non-corrosive, as compared to hypochlorite-based processes which are toxic and environmentally harmful. Additionally, peroxides are preferable because of their extremely low freezing points. However, while it is desirable to decontaminate chemical warfare agents by oxidation in a peroxide system, presently known systems are inefficient. However, hydrogen carbonate activator is efficient at generating peroxy anion<sup>31</sup> ( $\text{OOH}$ ) for VX and GD perhydrolysis<sup>75</sup>. The reaction mechanism is similar to as given in Figs 8 to 11.

## 7.27 Nanosized Metal Oxides as CWA

### Decontaminants

Recently, nanosized particles of  $MgO$ ,  $Al_2O_3$  and  $CaO$  have been found to be the potential reactive sorbent materials owing to their high surface area, strong adsorbability, potential reactivity towards chemical warfare agents, and these remove the agent rapidly from the contaminated surfaces and degrade them *in situ* and render the hazardous agents non-toxic<sup>32-38</sup>. In addition, titania nanotubes, manganese oxide nanotubes were also found to be having promising CWA decontamination properties<sup>76-80</sup>.

## 8. FUTURE TRENDS

Recent trends in the world alarm research and development departments of chemical defence all over the globe to continue search for alternative advanced technologies for CWA decontamination applications. Reasons are the problems associated with existing decontamination systems. Corrosion, user friendliness, leaving bulk amount of organic residues after decontamination, lack of suitability to all weather and environmental conditions, lack of eco-friendliness, etc are some of the problems. In the near-future, researchers have options to look into bio-degradable formulations for CWA decontamination which can be user-friendly, eco-friendly, and having negligible corrosive properties and contain highly stable active ingredients. Nanotechnology could also offer several formulations with enhanced advantages like high surface area, high reactivity, high surface-to-volume ratio towards CWA. Nanoporous materials, nanosised metal oxide aerogels also could be used due to above promising properties. Advanced oxidation technologies using gaseous oxidants like ozone, aerosolised hydrogen peroxide and photolytic and photocatalytic technologies also offer several future CWA decontamination-related applications.

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