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A Non-aqueous Formulation for Efficient Detoxification of Chemical Weapons at Sub-zero Temperatures

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ABSTRACT

An effective decontamination methodology based on nucleophilic non-aqueous decontaminant has been developed against chemical weapons sulfur mustard and soman. This new formulation consists of non-aqueous solution of 2-aminoethanol (60%, w/v), potassium hydroxide (2%, w/v), and N-methyl-2-pyrrolidone (38 %, w/v) and detoxified more than 99 % of sulfur mustard and soman within a period of 30 min at -35 °C. It was found to be operable over a wide range of temperatures starting from -35 °C to +55 °C without losing its fluidity and detoxicant efficiency at sub-zero temperatures promising hassle-free application against chemical weapons. It degrades sulfur mustard to divinyl sulfide and 2-chloroethyl vinyl sulfide and converted soman into O-pinacolyl O'-(2-amino) ethyl methylphosphonate, which are relatively non toxic to humans. This formulation is environmentally benign, relatively non corrosive and has an improved capability to dissolve and decontaminate chemical weapons within 15 minutes at ambient conditions. This approach paves the way for efficient and rapid decontamination platform for chemical weapons and holds considerable promise for field application in near future.

Keywords: Chemical weapons; Non-aqueous detoxicant; Nucleophile; Chemical detoxification; DS-2 solution

1. INTRODUCTION

Rapid and efficient removal of chemical weapons from tainted surfaces is necessitated immediately after chemical attack has taken place. Among a variety of methodologies that have been developed so far for remediation of chemical weapons, chemical detoxification processes are of great interest because of their ability to completely degrade chemical weapons in to non noxious products[1-8]. Current methods for chemical decontamination involve aqueous and non-aqueous chemical formulations. The aqueous chemical formulations suffer drawback such as logistic burden, poor solubility, non operability at sub-zero temperatures, and the inability to neutralise the chemical weapons on painted surfaces[9-10]. Owing to above drawbacks, non-aqueous chemical formulations have attracted the eyes of scientific community for its inherited advantages which circumvent aforementioned shortcomings. Among non-aqueous formulations, DS-2 which consists of diethylenetriamine, sodium hydroxide and 2-methoxyethanol still is being used all over the world for the neutralisation of chemical weapons[11-12]. In order to reduce human health risks, amended formulation of DS-2 was introduced as DS-2P, where 2 methoxyethanol was replaced by propylene glycol monomethyl ether. However, this change does not reduce the toxicity of detoxicants towards test organisms[13]. United States developed an alternative formulation using monoethanolamine, propylene glycol and LiOH which effectively decontaminates chemical weapons. However, complete decontamination takes relatively more time than DS-2 solution and also it is aggressive towards metal surfaces[13-17]. Moreover, Poland military had developed two non-aqueous decontaminants namely ORO and C9 as substitutes to DS-2. ORO and C9 consist of metallic sodium, aminoethanol, ethanol, diethylenetriamine and metallic sodium, aminoethanol, 2-ethoxyethanol, respectively. ORO and C9 are very effective against chemical weapons however; contain components that cause health risk[18]. Recently, researchers have developed an eco-friendly and biodegradable formulation comprised of several aminoalcohols, diethylenetriamine, NaOH which is operational from -30 °C to +49 °C[19-21]. This formulation has replaced DS-2 solution as field decontaminant by many countries. As advancements, GD-5 and GD-6 detoxicants were developed which contain 2-aminoethanol (30-90 %), benzyl alcohol (1-50 %) , propanol (1-50 %), dimethyl sulfoxide (1-50 %), and KOH (1-2 %) which are effective and eco-friendly and do not use components like diethylenetriamine which is not environmentally benign[22-25]. However, it freezes below -20 °C impeding its use below this temperature at high altitude areas, hence there is necessity for development of a non-aqueous detoxicant comprised of environmentally benign components which works at temperatures down to -35 °C, and meeting all the primary military decontamination requirements.

Herein, it was demonstrated an effective and rapid decontamination of chemical weapons sulfur mustard (HD) and soman (GD) based on non-aqueous, environmentally friendly detoxicant. A series of optimisation studies were

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performed such as effect of volume ratio of chemical weapons to detoxicant, reaction temperature, and decontamination time on decontamination efficiency against chemical weapons. Detoxification products were characterised by gas chromatograph (GC) fitted with mass selective detector (GC-MSD). Kinetics at various temperatures was monitored by GC fitted with FID (GC-FID). The present formulation was also tested for corrosion studies and surface decontamination of tainted metal, painted metal, and impermeable NBC suit to assess its field applicability.

2. EXPERIMENTAL

2.1 Materials

2-Aminoethanol (AE), dimethylethanolamine(DMEA), propylene glycol(PG), propylene carbonate(PC), dimethyl sulfoxide(DMSO), benzyl alcohol(BA), dimethyl formamide(DMF), *N*-methyl-2-pyrrolidone(NMP), potassium hydroxide(KOH), isopropanol (IP), and calcium chloride lumps were obtained from E. Merck India Ltd, Mumbai (India). HD and GD of > 99 % of purity were prepared in a facility of our establishment (designated by Organisation for the Prohibition of Chemical Weapons). Chemical detoxification experiments were also conducted in the aforesaid facility. Caution: These agents are toxic, hence to be handled by trained personnel equipped with protective gear only.

2.2 Preparation of Non-aqueous Formulations

Initially, a fixed amount of AE or BA or DMEA was added to round bottom flask fitted with calcium chloride guard tube. Later, 1-2% w/v of KOH was added to above solution and stirred for around 10 h at 60°C. Subsequently, remaining amount of DMEA or PG or PC or DMSO or BA or DMF or NMP was added to above solution to get the decontamination formulations.

2.3 Study of Detoxification Reactions of HD and GD

Chemical detoxification reactions were carried out at different temperature, 27°C (room temperature), +55 °C, and -35 °C by treating 10 µL of either HD or GD with respective volume ratio of detoxicant. Detoxicant was varied from 100 µL – 1000 µL in the case of HD and it was varied from 10-100 µl in the case of GD. After periodic intervals of time, 10 mL of IP was added to the reaction mixture and shaken for 2 minutes to extract the remaining chemical weapon into the solvent to enable it for GC or GC/MSD analysis. Concentrations of the agents remaining in the above solutions were determined by GC-FID fitted with BP-5 GC capillary column. Deep freezer of AR Enterprises, New Delhi make was used for studying detoxification reactions at -35°C and an oven with constant temperature chamber of Narang scientific company, New Delhi was used for studying detoxification reactions at 55 °C.

2.4 GC and GC-MS Conditions used for the Study

GC column had a length of 30 m, internal diameter of 0.5 mm, and a film coating of 0.5 µm thicknesses. Oven temperature was ramped from 50°C to 250° C @ 5°C/min while injection and detection ports were kept at 240 °C and 250 °C. Detoxification reaction products were characterised using GC-MS system of Agilent, USA make. GC-MS oven temperature was ramped from 50 °C to 250 °C @ of 15 °C / min. Temperatures of analyser, source, and interface were maintained at 150 °C, 230 °C, and 280 °C. EI source was used for ionisation of compounds eluting from HP 5MS column (30 m length, 0.25 mm id, and 0.25 µm film thicknesses).

2.5 Decontamination Studies of HD and GD on Various Tainted Surfaces

NBC suit (Impermeable), metal panel, and painted metal panel specimens of 2 cm X 2 cm dimensions were used for studying surface decontamination efficiency against the chemical weapons. Initially, 10 µL of chemical weapons was uniformly distributed over the specimen using micro-syringe and kept at room temperature for 1 h. After that, 1:100 V/V or 1:200 V/V ratio of detoxicant was spread over the tainted specimen and allowed for the occurrence of detoxification reaction for 15 min. Subsequently, the decontaminated specimens were washed with 10 mL IP and the extracted solutions were analysed by GC for monitoring the remaining agents either HD or GD[24].

2.6 Corrosion Studies on Decontamination Formulation

Studies were performed to check the corrosiveness of developed formulation in order to see its field applicability. 5 cm X 5 cm metal panels of SS 316 grade were weighed and immersed in prepared non-aqueous decontamination formulation or DS-2 solution in 500 mL beakers for 72 h at room temperature[25]. After completion, the exposed panels were cleaned thoroughly and dried at room temperature. Weights of dried samples were taken and change in weight was monitored compared to fresh samples. Corrosion rate of SS 316 specimen was deduced using an equation reported in literature[25] and the data was compared against DS-2 solution.

3. RESULTS AND DISCUSSION

3.1 Screening of Ingredients for Making Non-aqueous Formulation for Detoxification of Chemical Weapons

In order to develop an effective formulation for detoxification of chemical weapons HD and GD, several non-aqueous formulations have been prepared based on different combinations of AE, DMEA, KOH, and various protic and aprotic solvents that are eco-friendly in nature[26]. NMP, DMSO, DMF, PG, PC, and BA were used as solvents in the development of decontamination formulations. Initial screening of formulations was based on decontamination efficacy of prepared decontaminant against HD as target chemical weapon. Table 1 presents various decontamination formulations based on different ingredients and compositions for screening the effective detoxicant of chemical weapons.

Each component of the formulation plays an important and additive role in the effective degradation of chemical weapons. AE was selected judicially for the development of formulation as it consists of both amine and alcohol groups and also acts as a good solvent for alkalis. Owing to its self associating properties

Table 1. Non-aqueous formulations for chemical detoxification of chemical weapons

Formulation	No. of formulations	Decon. Efficiency HD %	Note	Active specie
Benzyl alcohol (0.5-20% w/v) Dimethyl ethanol amine (Rest) Benzotriazole (1 % w/v) KOH (2 % w/v) NMP (25% w/v)	10	50-60	Solubility decreases due to increase of benzyl alcohol (BA)	RO^-
Dimethyl ethanol amine (Rest) Benzotriazole (1 % w/v) KOH (2 % w/v), NMP (10-30 % w/v)	12	40-60	Dimethyl ethanol amine forming better Nu^- but not sufficient enough	R_2NRO^-
Dimethyl ethanol amine (17-57 % w/v) 2-Ethanol amine (40-80 w/v) Benzotriazole (1 % w/v) KOH (2 % w/v),	5	56-86%	Ethanol amine & DMEA both forming Nu^- but not sufficient enough as sequestering of K is poor	R_2NRO^- H_2NRO^-
2-Ethanol amine (0-98 % w/v), *N*-methyl-2-pyrrolidone (0-98 % w/v), KOH (2% w/v) (Better than GD-5 /NATO formulation)	5	70-99.9	Ethanol amine forming good Nu^-, NMP showing additive effect, suitable for making formulation.	H_2NRO^-
2-Ethanol amine (60% w/v) *N*-methyl-2-pyrrolidone (38 % w/v), KOH (2% w/v).	1	99.9%		

it makes cages surrounding K^+ ions leading to sequestration of K^+. Moreover, AE is commercially available, economical, less toxic, bio degradable, and have better solvency for chemical weapons. In this formulation, AE acts as nucleophile source as well as sequestering agent for K^+ cation from the alkali. Consequently, liberated hydroxide ion from KOH abstract proton of -OH group of AE and generates aminoalkoxide ion that acts as a nucleophile in this non-aqueous formulation. The nucleophilicity of the $NH_2CH_2CH_2O^-$ is the most important factor for detoxification reactions of chemical weapons. In order to generate the nucleophile, strong base KOH was selected as it has good solubility and easily generates alkoxide ion due to its reaction with AE. Furthermore, K^+ has stronger clatherating effect with amine group of AE, subsequently; it freed alkoxide ion (NH_2RO^-) for nucleophilic attack on the chemical weapons.

In spite of these cited interesting properties, formulation containing solely AE and KOH detoxified only 85 % of HD in 15 min. Rate of detoxification reaction is not sufficient enough to completely degrade HD. However, it is expected to be significantly increased if proper solvent system is added which facilitate the generation of more amount of Nu^- due to possible sequestering effect and the same is investigated in further studies. Solvents like NMP, DMSO, DMF, PG, PC, and BA were selected as they could efficiently dissolve the chemical weapons, components of formulation AE, KOH, and have strong affinity towards K^+ ion [26]. Studies were performed with different solvents and found that formulations with PC, PG, and DMF did not show any significant decontamination efficiency against HD may be due to solvation effect. Formulation with DMEA as solvent showed only 71 % decontamination efficiency against HD in 15 min which is not sufficient for field application. Nevertheless, formulation prepared with DMSO and NMP as solvents completely decontaminated HD in 15 min when used at 1:100 V/V ratio indicating their promising potential for decontaminating chemical weapons. After addition of NMP or DMSO to the formulation composed of AE and KOH, it shows accelerated reactivity against HD. This observation can be attributed to the affinity of NMP or DMSO towards K^+ ion. They sequester the ions and consequently assist easy liberation of anions and increase the amount of nucleophile available for attack on chemical weapon molecules. It might be also possible that NMP or DMSO efficiently solvate Cl^- or F^- with small ionic radius that were formed during the reaction of non-aqueous formulation with HD or GD in addition to K^+ or H^+[27]. Consequently, equilibrium could have been shifted to right side of the reaction and led to completion of the detoxification reaction. After degradation efficiency studies, formulations based on NMP and DMSO were subjected to low temperature -35°C atmosphere and tested for their fluidity. Formulation with DMSO frozen at -35°C making it not suitable for field application, whereas, the one with NMP did not freeze and retained its fluidity at subzero temperatures -35°C promising its field applicability.

The quantity of KOH plays a very important role for the generation of sufficient amount of nucleophile. For this study, various decontamination formulations were prepared by varying the amount of KOH from 1.0 to 2. 5 % w/v with 0.5 % increments in its weight and were tested for their detoxicant activity against HD. Detoxicants with 1.0, 1.5, 2.0, 2.5 % w/v of KOH demonstrated 83, 87, 99.9, 99.9% decontamination efficiency against HD, respectively. Although, 2 .0 and 2.5 % w/v KOH showed same decontamination efficiency for preparation of non-aqueous formulation, 2.0 % w/v KOH was selected as optimal weight in order to decease the corrosiveness and increase the low temperature operability. After optimizing all the active ingredients and keeping operational field requirements in mind, AE, KOH, and NMP were shortlisted for making the formulation. In order to arrive at the best composition for degradation of chemical weapons, AE was varied from 20-80 w/v percent, KOH was varied in between 1-2.5 % w/v, and NMP was varied between 18-78 % w/v and the best results against HD were found for non-aqueous formulation consisted of 60 % w/v of AE, 2 % w/v KOH, and 38 % w/v NMP. Further, AE and NMP were reported to be biodegradable in nature and they displayed 93.6, 95 % removal respectively after 2 weeks which are the components of present formulation. Whereas, diethylene triamine showed 0 % degradation, 2 methoxy ethanol showed 83 % bio-degradation in activated sludge (components of DS-2)[28-31]. Furthermore, subsequent to the application of the decontaminant, i.e., after decontamination, hot water wash is generally given on surfaces which facilitate the conversion of formulation into individual components. Obviously, as per the above reports, after the use and disposal of the decontaminant, the components which are released into the environment are consumed/converted by bacteria into eco friendly benign inorganic compounds like ammonia, etc, hence the above formulation is expected to be environmentally benign unlike in the case of DS-2 solution. These observations are consistent which reported literature as well[19-20].

3.2 Effect of Volume Ratio of Decontaminant and Chemical Weapon on Efficiency of Detoxification

Volume of the decontaminant required for detoxifying HD and GD were optimised by varying volume ratios of chemical weapon and detoxicant. Decontamination efficiency values were determined and the data is incorporated in Fig. 1. As shown in Fig.1, decontamination efficiency increase with increase in ratio of $V_{[detoxicant]}/V_{[Agent]}$. Complete detoxification within 15 min could be accomplished by using $V_{[detoxicant]}/V_{[Agent]}$ ratio of minimum 100 for HD and 2 for GD , respectively.

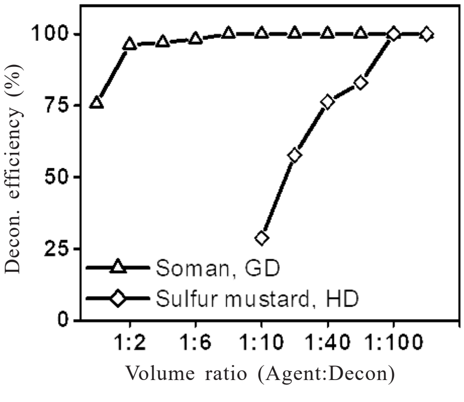

Figure 1. Effect of volume ratio of decontaminant on efficiency of detoxification of sulfur mustard and soman.

3.3 Effect of Reaction Temperature on Detoxification of HD and GD

Detoxification reactions of HD and GD with non-aqueous formulation were studied at 27 °C, 55°C, and -35°C temperatures. Decontamination efficiency data of HD with non-aqueous formulation at above said temperatures is as shown in Fig. 2. Efficiency of decontamination increased with raising temperature. Non-aqueous formulation in ratio of 1:100 V/V of HD and detoxicant completely decontaminated HD in 15 min at room temperature (27 °C) and in 2 min at 55 °C while decontamination efficiency was reduced to 86 % at -35 °C even in 30 min. Nevertheless, when volume ratio increased to 1:300 V/V, HD got completely decontaminated within 30 min at -35°C. Kinetic studies were performed to deduce the mechanism of detoxification of HD. A graph (Fig. 3) was plotted between 1/(conc. change) versus time and found to be linear confirming the second order kinetics [32]. Rate constant values were calculated from slopes and half life values were calculated by using 1/(k.a) (k is rate constant, a is initial concentration) and the data is as presented in Table 2. Rate of detoxification reaction increased from 4×10^{-4} to 0.016 $mL.mg^{-1}.sec^{-1}$ with temperature increase from -35 °C to 55 °C. Energy of activation for the HD detoxification reaction with the non-aqueous formulation was calculated to be 34 kJ/mol as per the Arrhenius equation which is low relative to energy of activation of HD hydrolysis in aqueous solution which was determined to be 84 kJ/mol[25]. It indicates that the Nu^- of non-aqueous formulation is stronger than OH^- in water solutions.

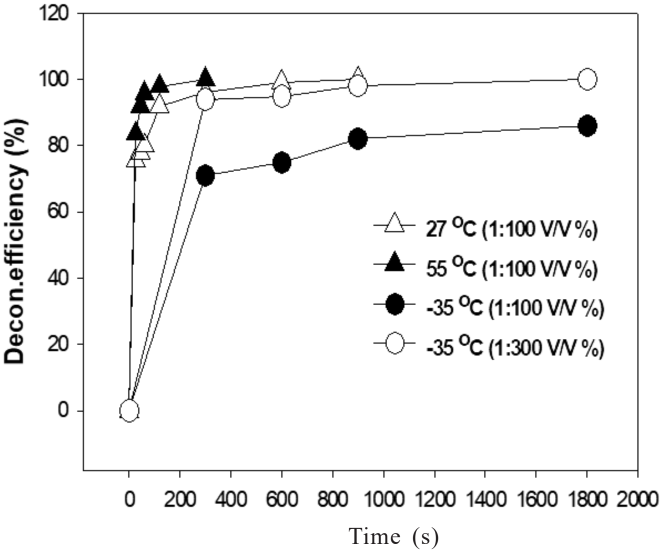

Figure 2. Effect of temperature on detoxification of HD using non-aqueous decontaminant formulation.

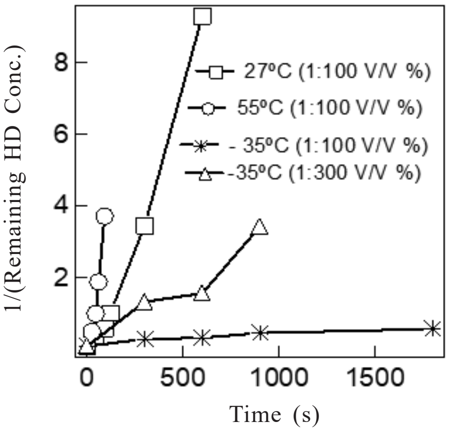

Figure 3. Kinetics of detoxification of HD using non-aqueous decontaminant formulation at various temperatures.

Table 2. Kinetic data of HD detoxification with non-aqueous formulation

Temperature (°C)	Volume ratio of HD: Decontaminant	Rate constant, k ($mL.mg^{-1}.sec^{-1}$)	Half life, $t_{1/2}$ (sec)
27	1:100	0.016	4.9
55	1:100	0.051	1.5
-35	1:100	$4X10^{-4}$	197
-35	1:300	0.004	19.7

Decontamination efficiency data of GD with non-aqueous formulation at above said temperatures is as shown in Fig. 4 as can be seen, decontamination efficiency increased with increased temperature. Non-aqueous formulation completely decontaminated GD in 3 min at room temperature (27 °C) and in 1 min at 55°C when used at a volute ratio of 1:10 V/V of GD and Detoxicant. While using volume ratio of 1:2 V/V of GD and Detoxicant, it got completely decontaminated in 15 minutes at room temperature. However, at -35 °C it took 7 min to completely detoxify GD by using same volume ratio. The detoxification reactions of GD with the non-aqueous formulation followed second order kinetics. Graphs of 1/(conc. change) versus time gave straight lines (Fig. 5) confirming the second order kinetics[32] as per following equation.

rate=k [GD] [DETOXICANT]

Rate constant values were calculated from slopes, half life values were calculated by using 1/k.a and the data is presented in Table 3. Rate of detoxification reaction increased from 0.002 to 0.01 $mL.mg^{-1}.sec^{-1}$ with increased temperature from -35 °C to 55 °C. Energy of activation for the GD detoxification reaction with the non-aqueous formulation was calculated to be 29.2 KJ/mol as per the Arrhenius equation[32].

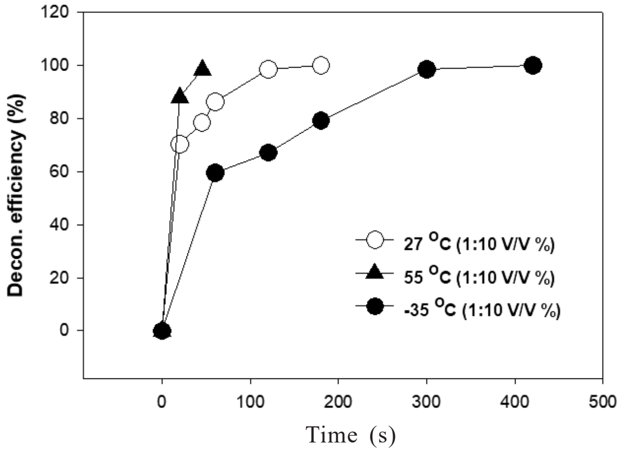

Figure 4. Effect of temperature on detoxification of GD using non-aqueous decontaminant formulation.

Table 3. Kinetic data of GD detoxification with non-aqueous formulation

Temperature (°C)	Volume ratio of GD: Decontaminant	Rate constant, k ($mL.mg^{-1}.sec^{-1}$)	Half life, $t_{1/2}$ (sec)
27	1:10	0.010	9.8
55	1:10	0.027	3.6
-35	1:10	0.002	49

3.4 Detoxification of HD and GD Tainted Metal, Painted Metal, and Impermeable NBC Suit Surfaces

Decontamination efficiency of present formulation was also checked at different field applicable surfaces. Among the different surfaces, metal, painted metal, and impermeable NBC suit specimens are mostly vulnerable and frequently found materials in the battle field. For this study, surfaces were contaminated with HD followed by decontamination using present non-aqueous formulation. This formulation exhibited 98.6, 96, 97 % decontamination efficiencies respectively on metal, painted metal, impermeable suit specimens when decontaminated with 1:100 V/V % agent to detoxicant. However, it exhibited >99.9 % decontamination efficiency on the above surfaces when decontaminated with 1: 200 V/V % agent: detoxicant ratio. GD contaminated specimens were completely decontaminated within 15 min when decontaminated with 1:100 V/V % agent to detoxicant ratio.

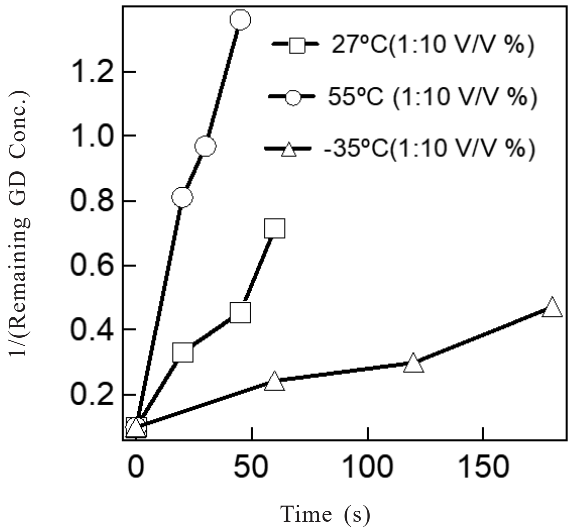

Figure 5. Kinetics of detoxification of GD using non-aqueous decontaminant formulation at various temperatures.

3.5 Mechanisms of Detoxification Reactions of HD and GD with Non-aqueous Formulation

The optimised formulation with sufficiently high amount of Nu^- could have positively influenced the chemical equilibrium, ionisation, solvation processes and abetted the conversion of toxic HD or GD to relatively non hazardous reaction products. Moreover, sufficiently high amount of Nu^- significantly contribute to strong polarisation of P atom of GD and β hydrogen of HD which leads to its detoxification.

GC-MS data (Table 4) indicated the formation of divinyl sulfide and 2-chloro ethyl vinyl sulfide due to the reaction of HD with prepared non-aqueous formulation. The reaction pathway of HD detoxification is as depicted in Fig. 6. It suggests that the detoxification of HD by non-aqueous formulation involves double elimination mechanism. As HD contains β hydrogen's, its detoxification reactions with non-aqueous detoxicant

Table 4. GC-MS data of chemical detoxification of HD and GD by non-aqueous formulation

Reaction product	Retention time (min)	m/z values
Divinyl sulfide	2.353	86,71, 59,45, 27
2 chloroethyl vinyl sulfide	6.89	122, 87, 73, 60, 45, 27
O pinacolyl O aminoethyl methyl phosphonate	12.62	150,123,97,71,58,41

could have taken place by bimolecular E2 process and the same is supported by GC-MS data[33-34].

In the case of GD, GC-MS data indicated the formation of *O*-pinacolyl *O*-(2-amino) ethylmethylphosphate. The reaction pathway of GD detoxification is as depicted in Fig. 6. It suggests that the detoxification of GD by non-aqueous formulation involves cleavage of P-F bond and substitution with Nu^- ($NH_2CH_2CH_2O^-$) and the data is consistent with reported literature[34].

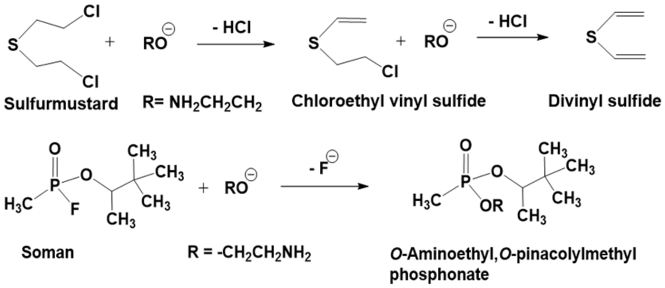

Figure 6. Mechanism of detoxification of HD and GD with non-aqueous decontaminant formulation.

3.6 Corrosion Behaviour of Non-aqueous Formulation

In order to have wider field applicability of present formulation, studies were performed and corrosiveness of the non-aqueous formulation towards SS specimens was tested and the data was compared with DS-2. Results indicated that degree of corrosion in the SS materials when exposed to non-aqueous formulation was lower than that exposed to DS-2 (Table 5) and indicate that prepared non-aqueous decontaminant is better than DS-2 for field applications against chemical weapons.

DS-2 possessed similar reactivity, however, its fluidity vanished/reduced and it got frozen at -35 °C, thereby making it not useful for application in sub-zero temperatures as low as -35 °C. We have not reported the reactivity data of DS-2 as it was already reported.

Table 5. Corrosiveness of non-aqueous formulation and DS-2 towards SS 316 panels

Decontaminant	Corrosion rate (mm/y)	Corrosion degree
Prepared non-aqueous formulation	0.0032	Non corrosive
DS-2	0.0300	Slightly corrosive

4. CONCLUSIONS

It was developed and demonstrated the use of non-aqueous decontamination formulation for effective and rapid degradation of deadly chemical weapons HD and GD while meeting battle field operational requirements. This detoxicant with $V_{[detoxicant]}/V_{[HD/GD]}$ ratio's of 100 or 2 , completely degraded HD or GD within 15 min at room temperature. Detoxification kinetics followed second order and the rate of reaction increased with increased temperature. Detoxification of HD took place *via* elimination mechanism while detoxification of GD took place by nucleophilic substitution reaction as deduced by GC/MSD data. The non-aqueous formulation has been successfully utilised for the decontamination of frequently used material in the battle field like painted metal, metal, and impermeable NBC suit samples contaminated with HD or GD as with an efficiency ranged from 97-99.9%. Additionally this formulation contains biodegradable components hence could be easily disposed off after its application. It showed that the present formulation can be implemented practically for field application and inspire further research in the field of nonaqueous decontaminants for the use against chemical weapons.

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