# Investigating Possibilities and Recent Trends for the Development of Novel Decontamination Technologies

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Despite international prohibition of chemical warfare agents (CWAs), defined in Chemical Weapons Convention, recent events during military conflict in Syria and isolated events in Salisbury (UK) and Kuala Lumpur (Malesya) airport prove that these agents still pose a major threat for civil society. In parallel with the development of CWAs and systems for their dissemination, various materials and accompanying technologies for their neutralization and decontamination were developed. However, to this date, no universal decontamination agent and technology has been developed that meets all quality requirements. In this article, we briefly reviewed all commercially available decontamination products, discussed their effectiveness in various scenarios, and considered their potential comparative advantages and drawbacks. Along with this, we reviewed novel materials and technologies, from common oxidizing and hydrolysing chemicals to metal-organic frameworks and nanotechnologies that show potential for the industrial development.

*Key words*: chemical warfare agents, nerve agents, blister agents, decontamination technologies, hydrolysis, oxidation, nanotechnologies.

## Introduction

DESPITE international prohibition of chemical warfare agents (CWAs), as stated in Chemical Weapons Convention, recent events during military conflict in Syria and isolated events in Salisbury (UK) and Kuala Lumpur (Malesya) airport prove that these agents still pose a major threat for civil society [1-3]. Chemical weapons convention defines chemical warfare agents under Schedule 1A, which describes the three broad categories of substances including: (a) nerve agents of G-class (i.e. O-alkyl N,N-dialkylphosphoroamidocyanidates and O-alkyl alkylphosphonofluoridates), the most common of which are tabun (GA), sarin (GB) and soman (GD); (b) nerve agents of V-class (O-alkyl S-2-dialkylaminoethyl alkylphosphonothiolates), the most common of which are VX and the Russian VX; (c) blistering agents which comprise three subcategories of substances that include halogenated aliphatic thioethers such as sulphur mustard or S-yperite (HD), halogenated aliphatic amines such as nitrogen mustard (HN3) and halogenated aliphatic arsines such as lewisite. Along with the development of CWAs and systems for their dissemination, various materials and accompanying technologies for their neutralization and decontamination were developed. In this review paper we will briefly summarize the most commonly used decontaminants and commercially available decontaminant formulations, and subsequently give an brief overview of the most relevant emerging technologies regarding decontamination formulations including various types of gels, foams, nanostructured materials and metal-organic frameworks (MOFs).

## Commercially available decontamination mixtures and formulations

Decontamination is the process of making any person, object, or area safe by removing - absorbing, destroying, neutralizing and rendering harmless of chemical agents [4]. In practice, complete decontamination is impossible – the efficiency of the process will always be less than 100%. This is because the process depends on many variables: temperature, humidity, resistance of particular agent toward degradation, and a type of material to be decontaminated regarding the nature of the surface which may be hardly accessible or hidden, absorption capacity and porosity of particular material – for instance, smooth nonporous surfaces such as glass or stainless steel are exceedingly easier to decontaminate than porous surfaces such as concrete, rubber or wood. The waste disposal options should also be taken into account when planning decontamination procedures. Remaining contamination is called residual contamination, which is unavoidable and must be considered when planning decontamination procedures and processes and maintaining decontamination equipment. Decontaminants and their formulations are substances used to remove, completely destroy CWAs or reduce their content to the acceptable level, transforming the contaminant into nontoxic chemicals, taking into account both human health and the environment. There are numerous quality requirements which any decontaminant should satisfy [5]:

1. It should be a broad spectrum decontaminant, capable of destroying all possible CWAs.

2. It should be easy to prepare, apply and remove from the equipment and objects that are decontaminated. Ideally, it should be in the formulation that assures easy adherence to the both hidden and vertical surfaces for a sufficient amount of time. It should be able to penetrate into porous materials.

3. It should be stable upon storage for at least two years, in

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the temperature range from -20 to +40 ℃.

4. It should not be destructive or corrosive for equipment used for its application, nor for the objects and equipment that are being decontaminated. Moreover, it should not damage the paints, coatings or polymeric seals of the equipment that is being decontaminated.

5. It should not influence the chemical detectors used to verify the presence of contamination, and effectiveness of decontamination.

6. It should be nontoxic or at least of low toxicity, eco-friendly or even biodegradable and non-flammable.

The oldest means of chemical decontaminants are those that hydrolyse CWAs and those are strong bases, such as sodium and potassium hydroxide in aqueous environment. Indeed, this is the most efficient way to destruct G-class nerve agents. For instance, the half time of the hydrolysis of GB and GD at pH 10 is 3-5 minutes. The reaction products are nontoxic sodium methylphosphonate, sodium fluoride and a corresponding alcohol. However, hydrolysis in the basic conditions is not the best possible route for decontamination of V-agents and blister agents, particularly for sulphur mustard. The cleavage of P-S bond is critical for VX decontamination; however the ethoxy-group is easier to remove hydrolytically from the molecule, yielding the EA2192 product that is even more toxic than VX [6]. These reactions are competing, so depending on a pH, around 12% of EA2192 remains in decontamination mixture. Moreover, VX has reduced solubility in basic conditions. Regarding sulphur mustard, thiodiglycol is the main product of hydrolysis in aqueous basic solutions, but due to the limited solubility of the HD, often polymeric products occur, organized in micelles which in their core contain the intact sulphur mustard, Figure 1 [7].
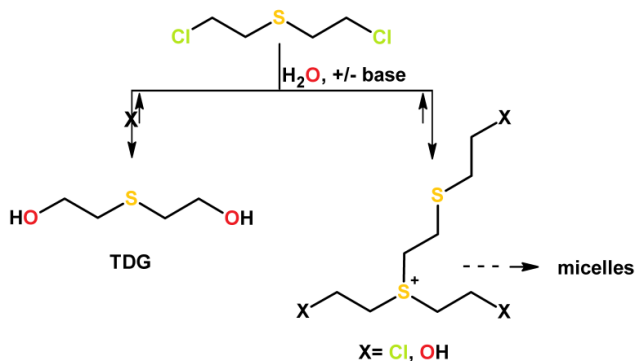


**Figure 1.** Hydrolytic reactions of HD

Because of all the above stated, oxidation routes are better choices for decontamination of HD and VX. For that purpose, the most common agents used are bleach or sodium hypochlorite and calcium hypochlorite. They are all effective in decontamination of G-agents, VX and HD. In acidic environment, approximately 3 mols of $Ca(OCl)_2$ per 1 mol of VX is sufficient for detoxification, but in basic media, due to the limited solubility of VX, even 9 mols of hypochlorite is needed for complete detoxification. The mechanism of the reaction in basic aqueous media is not completely understood, nor have all reaction products been determined so far. Similarly, for complete decontamination of 1 mol of HD, around 9 mols of $Ca(OCl)_2$ is needed for complete destruction. It is important that oxidation of HD proceeds to completeness, since during this process, the bis(2-chloroethyl)sulfone as an intermediate product with blistering activity occurence, Figure 2.
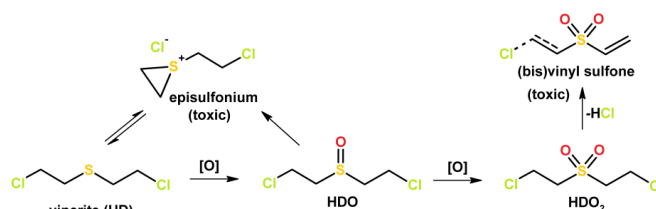


**Figure 2.** Oxidation products of sulphur mustard

So far, several commercially available decontamination mixtures based on hypochlorite have been developed and used in the past decades. The examples are supertropical bleach (STB) and German microemulsion C8 [5]. Supertropical bleach is a combination of $Ca(OCl)_2$ and a strong base, calcium oxide, CaO. It has strong oxidizing action due to hypochlorite anions formed by dissolution in water, and strong hydrolytic action due to high concentration of hydroxide ions that originate from CaO. STB is effective for decontamination of all CWAs. Microemulsion C8 is designed for better dissolution of HD and VX, since it contains detergents, and it also sticks to surfaces by forming a thin film. It also penetrates through paints and is able to decontaminate the CWAs that are embedded inside it. It contains by weight 15% tetrachloroethylene, 76% of water, 1% of anionic detergent and 8% of $Ca(OCl)_2$. Although very effective for destruction of majority of CWAs, hypochlorite based decontaminants are highly corrosive for different kinds of surfaces, irritable for skin, not eco-friendly, they leave residues behind, and should always be used freshly prepared since concentration of active chlorine species gradually decreases over time.

Due to the drawbacks of hypochlorite, dichloroisocyanurate salts have been proposed as another source of active chlorine species, able to destruct CWAs. Sodium dichloroisocyanurate (NaDCC) upon dissolution in water releases hypochlorous acid, Figure 3. Therefore, reactions of CWAs with NaDCC are similar to those described with $Ca(OCl)_2$. Yet, NaDCC is less corrosive and more stable in aqueous environment comparing to $Ca(OCl)_2$. Moreover, significantly smaller amount of NaDCC is needed for the detoxification of VX comparing to $Ca(OCl)_2$ (Figure 4).

Several decontamination mixtures are developed based on NaDCC. The most representative products are BX-24 and CASCAD. The BX-24 was developed by Cristanini, Inc (Verona, Italy) and it is used by NATO countries. This formulation is in powder form and it contains NaDCC, detergents, foaming agents, buffers and thickeners. It is prepared before use as 10-15% aqueous solution.
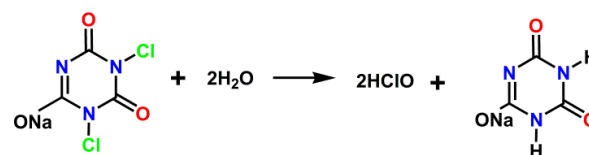


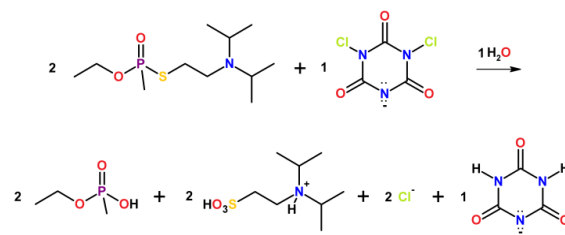**Figure 3.** Reaction of sodium-dichloroisocyanurate with water



**Figure 4.** Reaction of sodium-dichloroisocyanurate with VX

Efficacy of decontamination by BX-24 is between 91-99% depending on the surface. It is also biodegradable as it decomposes to ammonia and carbon-dioxide, thus avoiding bioaccumulation, and is not harmful to skin and respiratory tract. CASCAD is decontaminant developed by Allen-Vanguard manufacturer (Ottawa, Canada) and contains several surface active components in mixture with NaDCC. It has two components, the solid and liquid one, which upon mixing produce foam that easily sticks to all kinds of surfaces. It is highly efficient for decontamination of majority of CWAs.

Another very important active component with oxidative action for decontamination of CWAs is hydrogen-peroxide. It is highly desirable as an active component since it degrades to oxygen and water, and allows design of more "green" and eco-friendly versions of decontamination formulations. The VX readily react with perhydroxyl ion, in a selective manner, to form non-toxic EMPA, thus avoiding formation of EA2192 [8], Figure 5. The only drawback of $H_2O_2$ is its poor dissociation and therefore lower effectiveness in oxidation of HD. However, it has been found that $H_2O_2$ activated with bicarbonate to produce monoperoxocarbonate was very effective for the selective oxidation of HD to the non-vesicant sulfone.

The two main formulations which use $H_2O_2$ as an active ingredient are DeconGreen and Sandia Foam DF200. The early formulation of Decon Green contained three simple components: baking soda, $H_2O_2$ and alcohol co-solvent used to dissolve HD. However, in the current version of the decontaminant, carbonate is replaced with potassium-molibdate $K_2MoO_4$, which forms tetraperoxomolybdate with $H_2O_2$, which is more effective than monoperoxocarbonate for the oxidation of HD [9, 10]. In catalytic amounts, potassium-molibdate is non-toxic and even used as a food supplement. Another benefit of utilizing molybdate as the oxidation catalyst is that the tetraperoxomolybdate species is red-coloured, so activity of Decon Green is self-indicating: as the $H_2O_2$ degrades the concentration of $Mo(OO)_2^{4-}$ species decrease and, hence, the red colour diminishes, when $H_2O_2$ is depleted in the decontaminant.
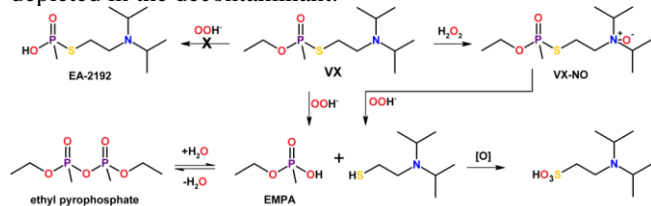


**Figure 5.** Peroxide-based decontamination of VX

Decon Green also contains co-solvents and surfactants which are required for fast dissolution particularly of HD. They provide adequate surface wetting and penetration to quickly dissolve agent during decontamination operations. Therefore, surfactant (Triton X-100) and co-solvents (propylene carbonate and propylene glycol) are also included in the Decon Green formulation for this purpose. All ingredients in Decon Green are either food additives (propylene glycol, potassium citrate, potassium bicarbonate, potassium molybdate) or materials approved for topical (propylene carbonate, 3% $H_2O_2$) or oral (1.5% $H_2O_2$) use.
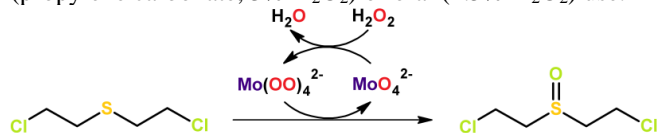


**Figure 6.** Oxidative decontamination of sulphur mustard with peroxide/molybdate decontaminant (Decon green)

Another example of decontaminant formulation based on $H_2O_2$ is Sandia Foam designated as DF200 (or EasyDecon). This formulation is developed by Sandia National Laboratories (Albuquerque, NM, USA) with the aim to obtain less toxic and less corrosive decontaminant for counter terrorism and military applications. The specific ingredients have not been revealed yet, but formulation contains surfactants, mild solvents, buffering substances, peroxide solution, with the final peroxide concentration being 3,6%, and a novel activator for $H_2O_2$ [11].

The L-gel is also decontaminant which uses peroxo-compounds as effective agents for decontamination. Decontaminants in the form of gel represent a good choice for decontamination of vertical surfaces as they adhere to them. The other advantage is that they may be strippable and easily removable, which facilitates secondary waste management and their disposal. The L-gel was developed by Raber et al. at Lawrence Livermore National Laboratories. It contains Oxone™, with a potassium peroxomonosulfate as an active ingredient, an oxidant developed by DuPont company, which proved to be the most active among all other oxidants tested ($H_2O_2$, $KMnO_4$, Fenton's reagent, cupric chloride, peroxy-disulfate, Virkon S™ and Snoop™) [12]. The experiments for the selection of gelling agent showed that organic based components do not have long-term compatibility with oxidizing agents. Because of that, fumed silicon-dioxide colloidal particles were chosen as the gelling agent. They are inert, commercially available (Cab-O-SIL®EH5) and do not require special preparation. Authors claimed that the final formulation was non-corrosive (with a pH value of 4,8), non-expensive and it clings well to walls and ceilings, and its preparation was simple and is expected to have a long shelf life (more than a year). The resulting formulation of L-Gel was tested both in the laboratory and in field conditions, on various types of surfaces (materials). It was found that L-gel was better than $Ca(OCl)_2$ in decontamination of asphalt and concrete contaminated with GD and VX. In tests using VX, GD and HD for contamination of painted oak, acrylic painted steel and carpet materials, all agents used were completely destroyed by L-Gel, except for GD on acrylic painted surfaces. In this case GD was destructed in the range of 80-96%, due to its penetration into the paint. The L-Gel was less effective in decontamination of materials with thickened GD and HD. Therefore, further improvements for this formulation are necessary.

It is evident from the described studies that decontamination efficiency is highly dependent upon method employed, i.e. the procedure for its evaluation, but also upon materials which are decontaminated. Therefore, studies which examine decontamination efficiency of various decontamination formulations and procedures under the same conditions and in comparative fashion are highly valuable. One such study was performed by Love et al. [13]. They used bench scale testing for the evaluation of the four commercially available decontamination formulations: 0.5% bleach solution with trisodium phosphate, Allen Vanguard Surface Decontamination Foam (SDFTM), U.S. military Decon GreenTM, and Modec Inc. and EnviroFoam Technologies Sandia Decontamination Foam (DF-200). For the challenge GB, HD and VX were used, and various representative indoor materials were contaminated, including stainless steel, vinyl floor tile, latex painted dry wall, concrete coupons and glass. All decontamination formulations, except for the bleach solution, performed well on nonporous and non-permeable glass and stainless-steel surfaces. However, chemical agent residual contamination typically remained on

porous and permeable surfaces, especially for the more persistent agents, HD and VX. Solvent-based Decon GreenTM performed better than aqueous-based bleach or foams on polymeric surfaces, possibly because the solvent is able to penetrate the polymer matrix. Bleach and foams out-performed Decon Green for penetrating the highly polar concrete surface. Authors concluded that different characteristics needed for an ideal and universal decontamination technology may be hard or impossible to achieve in a single formulation and a strategy for decontaminating a complex facility will require a range of technologies and different formulations.

## Emerging technologies

In the past decade, several novel formulations for broad decontamination of all CWA's or specific decontamination of particular CWA's have been made on laboratory scale. Majority of these used various gel formulations. Voss et al. [14] made decontamination barrier coating in gel form, specific for HD, based on the three components: (1) ionic liquid 1-hexyl-3-methylimid-azolium bis(trifluoro-methyl-sulfonimide), a melted organic salt at ambient conditions, (2) low molecular weight organic chelator based on aspartame and (3) organic amine tetraethylenetetramine. Ionic liquid in formulation serves to provide a stable fluid medium that can envelop the contamination area, extract out the CWA via solubilisation, and depress the vapour pressure of any CWA underneath or dissolved in the gel. The role of the gelling agent is to form a soft solid with lower vapour diffusivity while retaining spreadability. The formation of a spreadable gel also helps the applied coating adhere onto angled or vertical surfaces and prevents runoff. Amine serves to react and decontaminate HD. The formulation has been tested on various surfaces including glass, wood, rubber and painted steel. As a challenge agent, the 2-CEES was used. The results have shown that the reactive gel coating is able to extract/react away >98% of the CEES originally applied on the surface of nonadsorbing substrates (e.g., glass) and 70−90% of the original liquid CEES soaked into adsorbing substrates (e.g., wood, rubber, and cured paint) after 24 h of contact at ambient temperature.
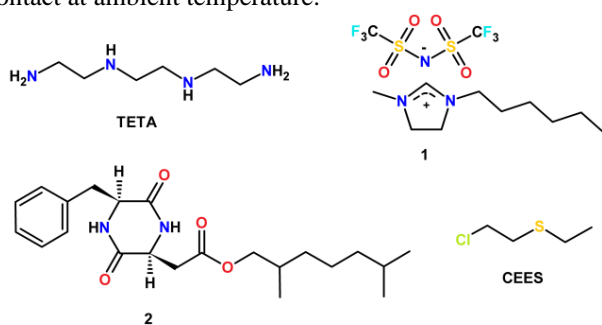


**Figure 7.** Components of the decontamination gel, developed by Voss et al [14]

Elias et al. [15] investigated polysaccharide thickened solutions of potassium-fluoride (KF) for the degradation of VX. Polysaccharides represent a good choice for decontaminant gelling since they are environmentally friendly, natural and inexpensive. Oxidizing agents cannot be thickened with polysaccharides since the later one are sensitive to hypochlorite anion, $H_2O_2$ and other peroxides, so the KF was chosen as a hydrolysing agent. Among all formulations tested, the one with 1,5 wt% of guar-gum and 4 wt% of KF proved to be the most suitable. The reaction rates were monitored using NMR technique. The half-times of

degradation in the pH range from 7-9,5 were approximately 4-5 min, with the EMPA as the only product. Although specifically designed for the degradation of organophosphorous nerve agents, this formulation showed promising properties for implementation as a spray decontaminant for common and sensitive environmental surfaces.

The same group of authors also prepared hydrogels for decontamination of both blister and nerve agents that are based on polyvinyl alcohol (PVA), borax and sodium perborate [16]. PVA polymers were chosen since they are nontoxic, hydrophilic, biocompatible and biodegradable. Hydrogels were made by mixing of PVA and borax in aqueous environment. In water, borax is hydrolysed to boric acid and tetrahydroxyborate anion which assures the pH of environment around 9. The borate anion further cross-links PVA to afford hydrogel. As a solid generator of hydrogen peroxide, sodium-perborate, $NaBO_3$, was chosen, that has better storage stability, longer shelf-life and easier handling than $H_2O_2$. It is also commercially available, a frequent component of household laundry detergents and even used as a tooth bleaching agent. To further increase gel's decontamination efficiency, a low amount of tatraacetylethylenediamine (TAED) was added, which accelerates the release of $H_2O_2$ from sodium-perborate. Because of low solubility of HD and VX in basic aqueous media, a detergent sodium-dodecylbenzene sulfonate (SDBS) was added in the formulation. The final formulation with the best performance was mixture of the two components A (10 wt% of PVA and 0,1 wt% TAED) and B (4 wt% of borax, 2,5 wt% of $NaBO_3$ and 0,5 wt% of SDBS). It is interesting to note that this formulation contains almost 90% of water, and is composed of common nontoxic readily available agents. Decontamination kinetics of VX, GB and HD was determined in test tubes, using 31P and 13C NMR spectroscopy. The half-times of GB, VX and HD degradation of were 3, 30 and 260 min, respectively. Low decontamination efficiency in case of HD was ascribed to its low solubility, so the ethylene-glycol was added into the final mixture, which improved decontamination both for HD and VX with half-times of degradation being 1.8 and 0.7 hours. The gel possessed also good rheological properties. Authors concluded that the universal decontamination abilities of this mild hydrogel, as well as its facile application and removal processes suggest that it holds high potential for future development as a new CWA decontamination tool.

In recent years there have been attempts to introduce novel small molecules as active ingredients into various decontaminant formulations. For instance, Karton-Lifshin et al. [17] investigated the novel small molecule N-methyl-1,4-diazabicyclo[2.2.2]octane fluoride (Me-DABCOF) to act as a bifunctional agent able to detoxify both HD and VX, Figure 8. This compound has low basicity which decreases its corrosive properties, but high nucleophillicity, and therefore reactivity toward HD and VX. It combines the two different nucleophillic centers, the non-basic free amine and an ammonium fluoride moiety in one small molecule. In experiments with HD in aqueous solutions, results showed that using 8 equivalents of Me-DABCOF results in formation of 56% of bihydrolised product and 44% of monohydrolised product (Figure 8). When 8 eq of Me-DABCOF reacted with VX in aqueous solution, a pretty fast total decomposition of VX was achieved, with an EMPA as the only product of hydrolysis. Authors also investigated the application of Me/DABCOF in formulation with $Al_2O_3$ powder and hydrogel which should serve as decontaminants for delicate

equipment and vertical surfaces, respectively. The 20wt% Me-DABCOF/Al$_2$O$_3$ formulation was effective for

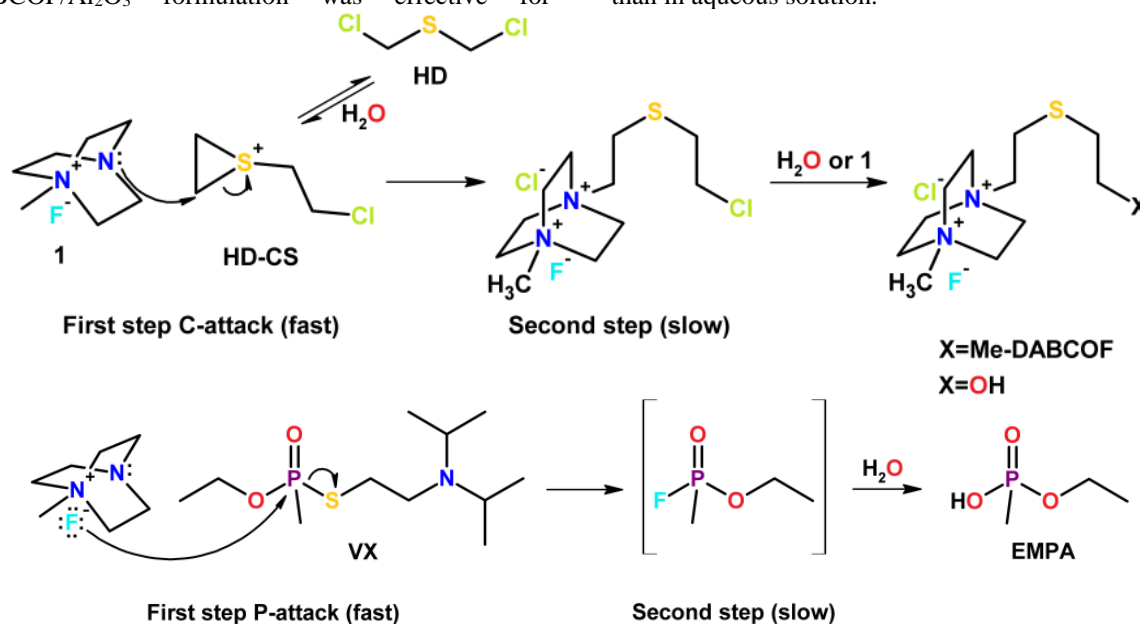degradation of HD and VX, but with slower reaction rates than in aqueous solution.



**Figure 8.** Mechanisms of VX and HD decontamination by Me/DABCOF

The hydrogel formulation made of 2,5 wt% of sodium-carboxymethylcellulose and 6 wt% of Me-DABCOF showed degradation rates of HD and VX to be essentially the same as in aqueous solutions. Therefore, Me-DABCOF is the promising novel agent to be used as an active ingredient in various types of decontaminant formulations. The same group of authors also proposed N-iodosuccinimide (NIS) for degradation of both HD and VX. The fast degradation of HD (t1/2= 3 min) in organic solvents (acetonitrile or propylene carbonate) in access of NIS resulting in formation of non-vesicant sulfoxide product. The similar results were obtained with VX in DMSO as a solvent.

In recent years, series of many different chemically active nanoparticles were designed and tested for chemical and biological decontamination: titanium-dioxide, silver nanoparticles, magnesium-oxide and calcium oxide aerogels, zirconium-hydroxide and cerium-oxide. Titanium-dioxide is photoactive material which is under UV irradiation capable of destruction of any organic material, including both CWA's and other toxic chemicals. The UV light induces the charge separation in the TiO$_2$ material, with electrons migrating to the conduction band while positively charged holes remain in the valence band. The generated charge carriers react with molecules adsorbed on the surface of the catalyst and subsequently cause their degradation. The water may be also the third partner in the degradation process, since its presence leads to the formation of hydroxide and superoxide anion radicals which subsequently react with CWA causing its degradation by free-radical reactions. The processes described occur in the crystal lattice defect sites, so the more defects are present in the bulk material, the higher is its photocatalytic activity. The number of defect sites depends of the surface area of the material. This is why photocatalytic activity of nano- TiO$_2$ strongly depends on particle size of the material. Beyond that, TiO$_2$is relatively cheap and readily available as well as also nontoxic. Numerous studies investigated both simulants and the real CWA decomposition on nano- TiO$_2$. For instance Tanaka et al. investigated the VX photocatalytic

decomposition in aqueous suspensions of P25 nano- TiO$_2$ [18]. They found that degradation reaction increases with increase in pH, with the half-time of degradation being 6,93 min at pH 7 and 1,38 min at pH 10. Below the pH 6, the rate of degradation reaction is very slow. The authors also found that there is an optimal ratio of VX and TiO$_2$quantity in aqueous environment, with increasing in reaction rate with increasing concentrations of both reactants but only to the certain concentration point, where reaction rate starts to decrease due to inner filter and adsorption effects. The reaction products were determined by LC/MS-MS, and they found that the major products were diisopropylamine and ethyl methylphosphonic acid, and several oxygenated VX species, while EA2192 product was not found, confirming that photocatalytic VX degradation primarily occurs via P-S bond cleavage. Another highly relevant study was published by Ramacharyulu et al. [19] which investigated decontamination of sulphur mustard (HD) on the surface of nano- TiO$_2$ of various average particle sizes (as determined by TEM), including 11, 16, 35, 70, 200 and 1000 nm. The experiments were conducted in the stream of clean air, without light or in the presence of sunlight or UV-light. In all experiments, irrelevant to the irradiation procedure, the degree of HD decomposition was consistently inversely proportional with the particle size and surface area. The presence of the sunlight or UV-light significantly increased decomposition rate; for instance, in the absence of irradiation only 25% of the HD was degraded while in the presence of sunlight irradiation, the 100% of degradation was achieved. It was interesting to note that sunlight irradiation showed slightly higher reaction rate comparing the UV irradiation. Also, without irradiation, only hydrolysis products of decomposition were found (that is, thiodiglycol mainly) while with irradiation, acetaldehyde, CO$_2$ and 15 other, both hydrolytic and oxidation products were found, which might be taken as an evidence of inherently different decomposition reaction mechanisms in the absence and in the presence of sunlight or UV-light.

The major drawback of the TiO2 is the necessity of using UV light for its activity, however there are other examples of metal-oxide nanoparticles which do not need sunlight for their catalytic activity. Another type of nano-sized materials, for the destruction of CWA are so-called aerogels of CaO and MgO. These materials do not need a UV-light for the degradation of CWA, since their reactivity and high efficiency originates from a large number of hydroxyl groups and crystal lattice defect sites on the surface of the nanoparticles, since they possess high surface area and high porosity. The aerogel nanoparticles of MgO and CaO are usually prepared by hydrolysis of metoxide precursor by addition of small amounts of water in an organic solvent, usually toluene [20]. Subsequently, the gel formed is dried supercritically under pressure of an inert gas. Nanosized $Mg(OH)_2$ or $Ca(OH)_2$ thus obtained are then dried in vacuum in the temperature range 200-500 °C. The last treatment causes partial condensation of hydroxyl groups and formation of M-O-M bonds. The ability of these oxide aerogels to decompose CWA's, including GD, VX and HD were investigated by Wagner et al. [21] using the $^{13}C$ and $^{31}P$ NMR spectroscopy. The GD exhibited the fastest decomposition reaction with the half-time of 28 min, followed HD decomposition with $t_{1/2}$=17,8 h and VX with $t_{1/2}$= 68 h. The main products of decomposition of GD and VX were corresponding alkyl methylphosphonic acids and methylphosphonic acid, without formation of toxic EA2192 compound. HD decomposition included both hydrolytic and elimination reaction path with the final decomposition products being thiodiglycol and divinylthoether in and approximate ratio of 50:50. Since the decomposition reactions took place on the dry aerogels, without solvent, authors showed that decomposition reaction rate are correlated with surface tension and viscosity of the reaction influence liquid agent spreading through porous aerogel structure, but also with vapour pressure and vapour diffusion coefficient of the agent which influences the rate of liquid agent evaporation and subsequent spreading of the agent vapours through aerogel structure.

A very thorough study by Wagner et al. investigated GD, HD and VX decomposition on amorphous, commercially available zirconium-hydroxide (obtained from Magnesium Electron, Inc.)[22]. The reactions took place in closed vials, without any solvent and were followed by MAS NMR spectroscopy. The half-times of the reaction for GD was 8,7 min, for HD 2,3 h and interestingly, near instantaneous decomposition of VX was observed, with a half-time of less than a minute which is comparable to classical liquid decontaminants. It was proposed that adsorbed water molecules, as well as coordinated ones along with the bridging and terminal hydroxyl groups, acidic in nature, play a crucial role in VX decomposition reaction. The acidic nature of $Zr(OH)_4$ facilitates the protonation of VX nitrogen atom, subsequently increasing its solubility and spreading in the multilayers of adsorbed water present in the material. A mechanism of decomposition was proposed in which bridging hydroxyl groups protonate the VX nitrogen atom, with phosphorous coordinated to the Zr ions, yielding and zwitter-ionic trigonal-bipyramidal reaction intermediate (Figure 9). The importance of both water and hydroxyl groups was further confirmed by investigation of VX decomposition on the calcined samples at temperatures 150, 300, 500 and 900 °C. The changes in the materials structure and chemical properties were investigated by TGA, DSC and TEM techniques. It was shown that below 70 °C desorption of loosely bound water occurs and in the temperature range from 70-400 °C dehydroxylation reactions occur and subsequently

above 400 °C a phase transition from amorphous to crystalline material occurs. Undoubtedly the loss of –OH groups leads to loss of decomposition ability of the material with sample calcined at 900 °C had a half-time of decomposition rate of 42h. Therefore, amorphous $Zr(OH)_4$ is highly promising material for the decontamination of both G- and V-agents decontamination.
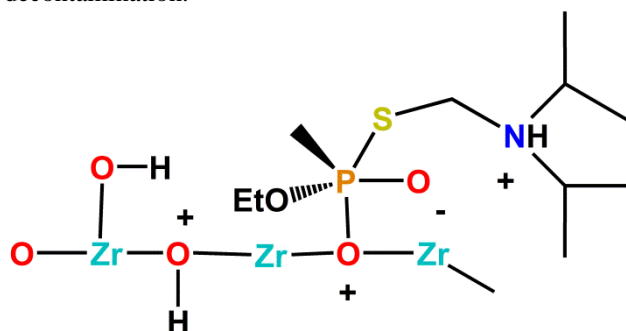


**Figure 9.** Tetrahedral zwitterionic reaction intermediate during VX hydrolysis on $Zr(OH)_4$

More recently, metal organic frameworks (MOF's) have been proposed as agents for decontamination and incorporation in the CWA protective materials [23]. MOF's constitute remarkably broad and rapidly growing class of crystalline materials. They consist of the so-called secondary binding units (SBU) which are usually metal cations or metal coordination complexes, which are mutually linked by ditopic or polytopic organic linkers in geometrically ordered fashion. They usually possess exceptionally large surface areas, between 1000-10000 m2/g and consequently high and intrinsic hierarchical porosity, thermal stability with more or less acceptable chemical stability. By careful selection of SBU's and organic linkers, taking into account isoreticular principle, as well as numerous possible post-synthetic modifications allow the design of MOF's in a numerous ways to fit a particular purpose. The zirconium based MOF's of several series were found promising for adsorption and destruction of CWA's: UiO (University of Oslo) series UiO-66 [24], Ui-O-66-NH2 [25], UiO-67 [26], NU-1000 [27], MOF-808 [28], all with Zr6 nodes, and different carboxylate linkers (Figure 10). To be a good candidate for CWA catalytic degradation, certain MOF needs to fulfil the three basic demands: (a) good thermal and chemical stability, (b) topologic organisation which provides intrinsic hierarchical porosity, providing a high specific surface area and good accessibility of catalytic sites, i.e. metal cation nodes and (c) optimal local or partial hydrophobicity. The later basically means that material should adsorb water only at high partial pressures, since the water is the necessary third partner in the CWA catalytic decomposition reaction. On contrary, MOF's with high hydrophilicity will adsorb water even at the low partial pressures which results in blockage of catalytic reactive sites with water molecules before CWA's succeed to reach them.

De Koning at al. [29] investigated degradation of paraoxon (POX) GA, VX and GD in pure water (pH 2.8-4.4) and 0.4 M N-ethylmorpholine buffer (pH 10) in the presence of following MOF's: UiO-66-NH2, MOF-808, NU-1000, PCN-777 by 31P NMR spectroscopy. The concentrations of MOF's and CWA's were 0,83 mM and 5 mM respectively, i.e. a molar ratio of 1:6 was used for investigation. In basic buffered media, majority of agents were decomposed within less than a minute by all investigated MOF's, with paraoxon being the most resistant toward decomposition. On contrary, in pure water, POX and GD were independently of investigated MOF, almost resistant toward degradation, while

decomposition of VX was satisfactory with half-time of the reaction being in the range of 5-17.3 minutes, depending on the particular MOF. The decomposition of GD was also noticeable, but at much lower rate, with the half-times being in the range 30-100 minutes, approximately.

Ryu et al. [30] investigated decomposition reactions of GD and VX on the solid phase of following materials: $Zr(OH)_4$, UiO-66, UiO-66-NH2 and MOF-808. Two distinct reaction conditions were investigated: (a) on the neat samples of $Zr(OH)_4$ and MOF's, pre-treated in relative humidity of 0, 60 and 80%, (b) and in non-buffered aqueous media. All MOF's proved to possess excellent catalytic activity in all humidity conditions, with 90% of both agents decomposed in less than a 10 minutes. MOF-808 proved to be superior comparing to the other two, reaching an almost complete degradation of both CWA's. On contrary, $Zr(OH)_4$ exhibited excellent activity in dry conditions, satisfactory at 60% humidity, but at 80% of relative humidity its decomposition ability drastically decreased with less than a 10% of conversion. Similar results were obtained in aqueous solution with three MOF's show excellent catalytic activity while $Zr(OH)_4$ being almost ineffective. The sharp decrease of $Zr(OH)_4$ decomposition rates in the presence of humidity and in aqueous solutions authors explained by the high hydrophillicity of the material, so water molecules block the reaction catalytic centres for the interaction with CWA's even at low partial pressures.

In the study performed by Wang et al. [31] it was assumed that actually adsorption and not decomposition on solid phase of MOF's takes place. That is why they applied method of digestion to investigate both these effects. They incubated dimethyl 4-nitrophenylphosphate (DMNP), GD and VX (5 µL) with 5 mg of chosen MOF, including UiO-66, UiO-66-NH2 and NU-1000. After specified time, they added digestion medium into these mixtures (1.8 M in DMSO-d6), with the main role to decompose MOF's and to release firmly adsorbed organophosphate agents. The remaining agents, as well as degradation products were determined by $^1H$ and $^{32}P$ NMR spectroscopy. Hydrolysis rates of DMNP on all three tested MOF's were very slow, with half-lives measuring in even more than 10 days, with UiO-66-NH2 being the most, and NU-1000 being the least effective. All the three tested MOF's were more effective in hydrolysis of GD and VX, with half-times of approximately several hours, with NU-1000 being the least active.



**Figure 10.** Linkers for various MOF's
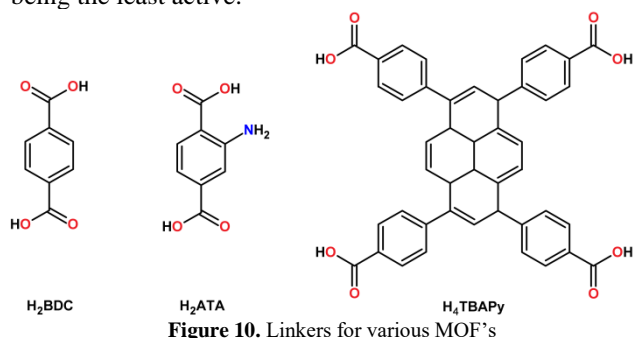
## Conclusion

From all that was discussed above, it is clear that recent trends in the development of novel decontaminant formulations and technologies would involve preferably residue free active ingredients with broad reactivity such as hydrogen-peroxide or maybe other mild non-corrosive agents with both nucleophilic and hydrolytic activity combined with an oxidative action. Also, other auxiliary ingredients such as thickening, gelling or foaming agents should be non-toxic, cheap, eco-friendly and readily available. Special emphasis should be given to decontamination of highly porous surfaces. Also, novel molecular entities, such as zirconium-based MOF's show promise in application in the future decontaminants' formulations, although their precise mechanism of action whether is tight adsorption and/or hydrolytic decomposition remains to be further examined. However, broad range, highly active decontaminant for various types of surfaces would be almost impossible to achieve in a single formulation.

## Literature

[1] JOHN, H., van der SCHANS, M. J., KOLLER, M., SPRUIT, H. E. T., WOREK, F., THIERMANN, H., NOORT, D.: Fatal Sarin Poisoning in Syria 2013: Forensic Verification within an International Laboratory Network, Forensic Toxicology, 2018, Vol. 36, pp. 61−71.

[2] CHAI, P. R., BOYER, E. W., Al-NAHHAS, H., ERICKSON, T. B.: Toxic Chemical Weapons of Assassination and Warfare: Nerve Agents VX and Sarin, Toxicology Communications, 2017, Vol. 1, pp. 21−23.

[3] CHAI, P. R., HAYES, B. D., ERICKSON, T. B., BOYER, E. W.: Novichok agents: a historical, current, and toxicological perspective. Toxicology Communications, 2018, Vol. 2, pp. 45−48.

[4] YANG, Y.C., BAKER, J.A., WARD, J.R.: Decontamination of Chemical Warfare Agents, Chemical Reviews, 1992, Vol. 92, pp. 1729–1743.

[5] SINGH, B., PRASAD, G.K., PANDEY, K.S., DANIKHEL, R.K. and VIJAYARAGHAVAN R.: Decontamination of Chemical Warfare Agents, Defence Science Journal, 2010, Vol. 60(4), pp. 428-441.

[6] YANG, Y.C.: Chemical Detoxification of Nerve Agent VX. Accounts of Chemical Research 1999, Vol. 32(2), pp. 109–115.

[7] BREVETT, C. A. S., SUMTER, K. B. and NICKOL, R. G.: Kinetics of the degradation of sulfur mustard on ambient and moist concrete, Journal of Hazardous Materials, 2009, Vol.162, pp. 281–291.

[8] YANG, Y.C., BERG, F.J., SZAFRANIEC, L.L., BEAUDRY, W.T., BUNTON, C.A., KUMAR, A.: Peroxy Hydrolysis of Nerve Agent VX and Model Compounds and Related Nucleophilic Reactions. Journal of the Chemical Society-Perkin Transactions 1997, Vol. 2(3), pp. 607–613.

[9] WAGNER, G. W.: Hydrogen peroxide-based decontamination of chemical warfare agents, Main Group Chemistry 2010, Vol.9, pp. 257–263.

[10] WAGNER, G.W., PROCELL, L. R., SORRICK, D. C., LAWSON, G. E., WELLS C. M., REYNOLDS, C. M., RINGELBERG, D. B., FOLEY K. L., LUMETTA, G. J., and BLANCHARD, D. L.: All-weather hydrogen peroxide -based decontamination of CBRN contaminants, Industrial & Engineering Chemical Research, 2010, Vol. 49(7), pp. 3099–3105.

[11] Australian Government, Department of Defence, DSTO-GD-0662, Review of the MDF-LSA 100 Spray Decontamination System, Unclassified report.

[12] RABER, E., McGUIRE, R.: Oxidative decontamination of chemical and biological warfare agents using L-Gel, Journal of Hazardous Materials, 2002, Vol.B93, p. 339.

[13] LOVE, A., BAILEY, C. G, HANNA, M. L., HOK, S., VU, A. K., REUTTER, D. J., RABER, E.: Efficacy of liquid and foam decontamination technologies for chemical warfare agents on indoor surfaces, Journal of Hazardous Materials 2011, Vol. 196, pp. 115–122.

[14] VOSS, B. A., NOBLE, R. D., GIN, D. L.,: Ionic Liquid Gel-Based Containment and Decontamination Coating for Blister Agent-Contacted Substrates, Chemistry of Materials, 2012, Vol.24, pp. 1174−1180.

[15] ELIAS, S., SAPHIER, S., COLUMBUS, I., ZAFRANI, Y.:

Polysaccharide-Thickened Aqueous Fluoride Solutions for Rapid Destruction of the Nerve Agent VX. Introducing the Opportunity for Extensive Decontamination Scenarios, Environmental Science and Technology, 2014, Vol. 48, pp. 2893−2900.

[16] EISAR, O. R., NAHUM, V., YEHEZKEL, L., MARCOVITCH, I., COLUMBUS, I., FRIDKIN, G., CHEN, R.: Active and Strippable PVA/Borax/NaBO3 Hydrogel for Effective Containment and Decontamination of Chemical Warfare Agents, ACS Omega 2021, Vol. 6, pp. 5359−5367.

[17] KARTON-LIFSHIN, N., KATALAN, S., COLUMBUS, I., CHEN, R., YEHEZKEL, L., MADMON, M., DAGAN, S., ELIAS, S., FRIDKIN, G., ZAFRANI, Y.: Effective neutralization of chemical warfare agents (HD, VX) by Me-DABCOF: a small molecule with dual action, Chemcal Communications, 2019, Vol. 55, p. 12471.

[18] KOMANO, A., HIRAKAWA, T., SATO, K., KISHI S., NISHIMOTO C. K., MERA, N., KUGISHIMA, M., SANO, T., NEGISHI, N., ICHINOSE, H., SETO, Y., TAKEUCHI, K.: Titanium dioxide photocatalytic decomposition of ethyl-S-dimethylaminoethyl methylphosphonothiolate (VX) in aqueous phase, Applied Catalysis B: Environmental, 2013, Vol. 135, pp. 19–25.

[19] RAMACHARYULU, P.V.R.K., PRASAD, G.K., GANESAN K., SINGH B.: Photocatalytic decontamination of sulfur mustard using titania nanomaterials, Journal of Molecular Catalysis A: Chemical, 2012, Vol. 353–354, pp. 132–137.

[20] UTANPANAYA, S., KLABUNDE, K. J., SCHLUP, J. R., Nanoscale metal oxide particle/clusters as chemical reagents. Synthesis and properties of ultrahigh surface area magnesium hydroxide and magnesium oxide, Chemistry of Materials, 1991, Vol. 3, pp. 175-181.

[21] WAGNER, G. W., BARTRAM, P. W., KOPER, O., KLABUNDE, K. J., Reactions of VX, GD, and HD with Nanosize MgO, Journal of Physical Chemistry B, 1999, Vol. 103, pp. 3225-3228.

[22] BANDOSZ, T. J., LASKOSKI, M., MAHLE, J., MOGILEVSKY, G., PETERSON, G. W., ROSSIN, J. A., and WAGNER G. W., Reactions of VX, GD, and HD with Zr(OH)4: Near Instantaneous Decontamination of VX, Journal of Physical Chemistry C, 2012, Vol. 116, pp. 11606−11614

[23] GRISSOM, T. G. and FRENKEL A. I.: Metal-Organic Framework- and Polyoxometalate-Based Sorbents for the Uptake and Destruction of Chemical Warfare Agents, Brookhaven National Laboratory Report, BNL-215981-2020.

[24] WINARTA, J., SHAN, B., MCINTYRE, S. M., YE L., WANG, C., LIU, J., MU, B., A Decade of UiO-66 Research: A Historic Review of Dynamic Structure, Synthesis mechanisms, and Characterization Techniques of an Archetypal Metal–Organic Framework, Crystal Growth and Design, 2020, Vol. 20 (20) pp. 1347–1362.

[25] TAMBAT, S. N., SANE, P. K., SURESH, S., VARADAN, O. N., PANDIT, A. B., SONTAKKE, S. M., Hydrothermal synthesis of NH 2-UiO-66 and its application for adsorptive removal of dye, Advanced Powder Technology, 2018, Vol. 29(11) pp. 2626-2632.

[26] VAHABI, A. H., NOROUZI, F., SHEIBANI, E., RAHIMI-NASRABADI, M., Functionalized Zr-UiO-67 metal-organic frameworks: Structural landscape and application, Coordination Chemistry Reviews, 2021, Vol. 445, pp. 214050.

[27] WANG, T. C., VERMULEN, N. A., KIM, I. S., MARTINSON, A. B. F., STODDART, J. F., HUPP, J. T., FARHA, O. K., Scalable synthesis and post-modification of a mesoporous metal-organic framework called NU-1000, Nature Protocols, 2016, Vol. 11, pp. 149–162.

[28] KEVAT, S., LAD, V. N., Green synthesis of zirconium-based MOF-808 by utilizing sustainable synthesis approaches, Journal of Organometallic Chemistry, 2023, Vol. 999(15), p. 122832.

[29] deKONING, M.C., VAN GROL, M., BEIAERT, T., Degradation of Paraoxon and the Chemical Warfare Agents VX, Tabun, and Soman by the Metal−Organic Frameworks UiO-66-NH2, MOF-808, NU-1000, and PCN-777, Inorganic Chemistry 2017, Vol. 56, pp. 11804-11809.

[30] Ryu, S. G., Kim, M.-K., Park, M., Jang, S. O., Kim, S. H., Jung, H., Availability of Zr-Based MOFs for the degradation of nerve agents in all humidity conditions, Microporous and Mesoporous Materials 2019, Vol. 274, pp. 9–16.

[31] WANG, H., MAHLE, J. J., TOVAR, T. M., PETERSON, G. W., HALL, M. G., DeCOSTE, J. B., BUCHANAN, J. H., KARWACKI, C. J., Solid-Phase Detoxification of Chemical Warfare Agents using Zirconium-Based Metal Organic Frameworks and the Moisture Effects: Analyze via Digestion, ACS Applied Materials and Interfaces, 2019, Vol. 11, pp. 21109-21116.

# Istraživanje savremenih trendova i mogućnosti za razvoj novih dekontaminacionih tehnologija

Uprkos međunarodnoj zabrani upotrebe bojnih otrova određenoj Konvencijom o hemijskom oružju, nedavni događaji tokom vojnih konflikata u Siriji, kao i oni u Salisberiju (Ujedinnjeno kraljevstvo) i na aerodromu u Kuala Lumpuru (Malezija) dokazuju da ovi agensi još uvek predstavljaju ogromnu pretnju za civilno društvo. Paralelno sa razvojem bojnih otrova kao i sistema za njihovu diseminaciju, razvjali su se i različiti materijali i prateće tehnologije za njihovu neutralizaciju i dekontaminaciju. Medutim, do danas nije razvijeno ni jedno univerzalno dekontaminaciono sredstvo koje zadovoljava sve postavljene zahteve kvaliteta. U ovom radu je dat kratak pregled savremenih komercijalno dostupnih proizvoda za hemijsku dekontaminaciju, razmatrana je njihova efikasnost u različitim scenarijima primene, kao i njihove komparativne prednosti i pojedini nedostaci. Takođe, dat je i pregled novih materijala i tehnologija od uobičajenih oksidujućih i hidrolizujućih hemijskih smeša pa do metalo-organskih umreženih okvira i nanotehnologija koje pokazuju potencijal za industrijsku primenu.

*Ključne reči:* bojni otrovi, tehnologije za dekontaminaciju, hidroliza, oksidacija, nanaotehnologije.