Review

Catalysis and decontamination: a versatile tool in the safe and sustainable degradation of chemical warfare agents

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Abstract Decontamination is a critical and enabling capability to mitigate and, in the best cases, neutralize the threat of chemical warfare agents (CWAs) to human health and the environment. Well-established conventional decontamination methods will be described and compared to more recent approaches based on catalytic degradation, in the presence of nanostructured catalysts or enzymatic systems, photochemical and photocatalytic abatement and active adsorption on high-performance innovative porous solid materials.

1 Introduction

The current unstable international geopolitical context and global risk reports draw attention to the evolving landscape of conventional and unconventional threats, both natural, accidental and deliberate in scope. In this context, the risks associated with incidents involving hazardous chemical, biological, radiological, nuclear and explosive (CBRNe) agents, in both civilian and military scenarios, are undeniably real and could lead to potentially devastating consequences [1]. Today, we are facing new dimensions of the CBRNe threat, associated with the potential use of weapons of mass destruction by states or, more likely, by terrorist groups. Additionally, incidents involving CBRNe materials can arise from releases of toxic and hazardous industrial materials, caused by bad practices or natural disasters [2]. This emerging reality places civilian populations, infrastructures and the environment as the primary targets of such incidents or attacks [3]. The interest in such agents to build non-conventional CBRNe weapons (*e.g.* chemical warfare agents, biotoxins, "dirty bombs" or radioactive material trafficking) by rogue states, non-state armed groups, terrorists or criminals, for illicit purposes, is on the rise [4, 5].

Experts and policymakers attribute part of this increase to the growth in the global spread of technology and materials, as well as dual-use knowledge, within scientific research and related chemical, biological (*i.e.* life sciences, biotechnology and pharmaceuticals), radiological and nuclear industries [6, 7]. Therefore, the rapid diffusion of technology and knowledge will make CBRNe materials more easily accessible to a wider range of groups and individuals, including those who will use them with malicious intent. CBRNe incidents have further emphasized the need for increased international collaboration to mitigate these risks. Non-proliferation and disarmament operations, implemented at state level through treaties and conventions, in particular the Chemical Weapons Convention, CWC [8], have made a significant contribution by limiting the access of both state and non-state actors to CBRNe agents, but this may not be sufficient. There is a need for a comprehensive and multidisciplinary approach to CBRN risks mitigation, involving scientific research, policymakers, military forces and industry as key players, in order to promptly respond to new threats [1, 9].

2 Decontamination: an enabling capability

Despite the existence of supra-national agreements on the synthesis, development, production and proliferation of CBRNe weapons, the potential use of these kind of weapons or hazardous substances cannot be excluded [10]. Unluckily, an ever-growing urbanization and global industrialization enhance the possibility of accidental releases or deliberate misuse of hazardous industrial materials. Assuring prevention and protection against incidents where hazardous materials can make harm to population, properties and, in particular, strategic governmental institutions, is vital for first response agencies [11].

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In the framework of a civil scenario, the typical response to a CBRNe emergency is based on three 'pillars': detection, protection and decontamination. These three actions represent the tools for dealing with a threat from CBRNe agents, with the aim of mitigating the risks associated with these events in which they are involved. In the present text, special attention will be paid to the last response action, decontamination, that is a crucial step for the complete recovery of an area where a release of hazardous CBRNe agents occurred. In particular, the huge variety of highly hazardous chemicals that should be taken into account as potential contaminants makes this activity particularly challenging and still widely debated [12].

Decontamination is a fundamental activity aiming at removing or, at least, mitigating CBRNe agents, so that they are no longer harmful to humans and to the environment. It represents the process of securing a person, object or area by absorbing, destroying, neutralizing or removing chemical or biological agents or radioactive material on or around them. Along with prevention and protection, decontamination is an essential part of CBRNe defence. On victims and operators with no protective equipment, the most effective decontamination treatment is performed within the first minutes after exposure [13]. So, robust operational decontamination procedures and an adequate training of the professionals on the scene can save lives. Decontamination plays an essential role in the defence against CBRNe agents. Hazardous chemicals, pathogenic microorganisms or radioactive materials must be removed by applying countermeasures as quickly as possible to avoid casualties and restore normal activities.

Decontamination methods can be divided into four basic processes: physical, thermal/energetic, chemical and enzymatic approaches. Physical methods aim to mechanically remove and displace contaminants from contaminated surfaces without destroying or neutralizing them. Conversely, chemical, enzymatic and thermal/energetic ones aim to modify the physico-chemical structure of contaminants to reduce, neutralize or eliminate their hazardous properties. For hazardous chemicals, it involves a change in the chemical structure of the active molecule, while for biological agents, decontamination aims at the destruction and degradation of pathogenic cells or hazardous microorganisms. For radioactive substance, on the contrary, only physical decontamination can be envisaged, since, clearly, the radioactive nature of atoms cannot be quenched or degraded by any physical or chemical method. Moreover, the effectiveness of decontamination relies on various factors, not only the characteristics of the hazardous material, but also the location (indoor, outdoor site), the meteo-climatical conditions, under which decontamination is carried out, the extension and morphology of the affected area and the nature and type of contaminated surface and/or material [1].

3 Conventional decontamination methods of highly hazardous chemicals

When contamination is due to the presence of chemical warfare agents, CWAs, during decontamination procedures higher safety and security standards must be put in place, considering the extremely hazardous nature of the agents (on average, orders of magnitudes more toxic than common hazardous industrial chemicals), which were specifically designed to make maximum harm to humans and the environment [5].
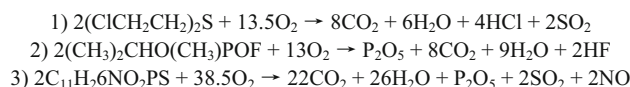
Decontamination of CWAs is required not only at an incident site, but also in chemical agent stockpiles, research laboratories, destruction sites as well as on personnel. Site-specific factors have to be taken into account when selecting the most suitable decontamination approach [14]. In detail:

- The amount of the agent;
- The physical state (*e.g.* gas, vapour, aerosol, liquid droplets) of released CWAs;
- Meteo-climatic conditions (temperature, humidity, wind, etc.);
- Substrates and analytical matrices to be decontaminated (*e.g.* nonporous or porous surfaces, soil, metallic surfaces, human skin, electronic components [15, 16]);
- Size and complexity of the area to be treated;
- Future uses of the premises after decontamination;
- Availability of resource.

A timely evaluation of this site-specific information, integrated by general data about the chemical-physical properties of the CWAs, their rate of environmental degradation and the specific decontamination technology to be adopted (pro's *vs.* con's), is conducive to a more rapid and effective response. A further factor worth considering is whether natural attenuation (self-decontamination with time and weathering) might be the most viable and prudent strategy.

Conventional decontamination and degradation processes of CWAs, well known and adopted since decades, are essentially based on physical, thermal or energetic and chemical methods. These methods rely on techniques such as dissolution with solvents, adsorption on porous solids, removal, thermal decomposition and over-stoichiometric chemical degradation of the toxic agents, by means of oxidation, hydrolysis or combustion processes.

Physical decontamination is the cheapest and easiest among the possibilities for CWAs decontamination [17], relying in the use of different equipment ranging from simple brush to more complex blasting machines [18]. It is not as effective as chemical decontamination, but the main advantage is that physical procedures act generally and do not depend on the chemical nature of the CWA to be destroyed. As mentioned above, it consists primarily in removing or encapsulating hazardous agents. In most cases, no destruction, degradation or detoxification is attained and therefore the contamination is simply relocated elsewhere (in liquid or solid phase). A next treatment step of the relocated agent is then always needed to attain a complete decontamination. For these reasons,

1) $2(ClCH_2CH_2)_2S + 13.5O_2 \rightarrow 8CO_2 + 6H_2O + 4HCl + 2SO_2$

2) $2(CH_3)_2CHO(CH_3)POF + 13O_2 \rightarrow P_2O_5 + 8CO_2 + 9H_2O + 2HF$

3) $2C_{11}H_{26}NO_2PS + 38.5O_2 \rightarrow 22CO_2 + 26H_2O + P_2O_5 + 2SO_2 + 2NO$

Scheme 1 Total (and ideal) combustion reactions for selected CWAs: **1** sulphur mustard, **2** sarin, **3** nerve agent VX

physical decontamination is to be considered as a partial method, even if a thorough removal of contaminants has the advantage of limiting the spread of contamination (also cross-contamination) and reducing any further exposure of victims to CWAs [18]. A combination of physical and chemical/thermal methods is generally necessary to attain full decontamination. Without any form of active decontamination, chemical agents may also fade over time through evaporation or spontaneous degradation due to the action of the sun and exposure to air. In the case, for example, of soil contamination with aggressive chemicals, a simple and inexpensive method is to isolate the soil.

Widely adopted and established examples of physical decontamination are:

- Intense washing with water, organic solvents, liquid formulations and surfactants [16]. Typically, this method consists of rinsing contaminated surfaces with water to remove contaminants. Not only does it remove contaminants, but it can also provide a slow detoxification of chemical agents, via gradual hydrolysis of most labile species. The efficiency of rinsing methods depends on several factors: pressure of the rinsing liquid, solubility of the agents in the rinse fluid and degree of agent adsorption into contaminated surfaces. Techniques to enhance physical removal efficiency include the use of brushes or abrasive material, special additives to augment solubility or to enhance cleaning power (*e.g.* detergents, surfactants, organic solvents, chelating agents) by lowering the surface tension to optimize the extraction of absorbed agents;
- Adsorption, absorption and removal with solid sorbents (*e.g.* clays, zeolites, silica gels, porous metal organic frameworks). Solid decontaminants with adsorption capabilities are very useful in the removal of aggressive chemicals from contaminated surfaces: activated carbon, some polymeric ion exchangers and diatomaceous earths, such as the "fuller's earth" (a mixture of clays, among which montmorillonite, attapulgite and kaolinite), are typical examples of solids that adsorb toxic agents and retain them, allowing their safe removal, collection and disposal. Clays, zeolites and oxidic sorbents can be in principle regenerated by thermal treatments at high temperature under air or oxygen; nevertheless, special attention has to be paid to the type of toxic compound adsorbed and the conditions to be used for regeneration. Moreover, in some decontamination applications, mineral oxidic sorbents are often used as disposable materials. Spent solids are therefore used to gather the dispersed hazardous agent and then sent to a proper controlled disposal. The usefulness of these solids can be limited when they must be applied over large surface areas;
- Accelerated evaporation by heating (sometimes combined with vacuum techniques). Thermal desorption of aggressive chemicals can be achieved using heated air that causes evaporation of the contaminant. This method can be used in the decontamination of clothing or other objects with uneven surface;
- Burying or sealing contamination;
- Vacuum cleaning.

Among the traditional methods of decontamination and removal of CWAs, thermal treatments lead to the chemical degradation or destruction of the hazardous agent. In the past, combustion and incineration were common methods of disposal of toxic substances that accounted for the highest percentage of all approaches to destroy dangerous substances [19]. Combustion at high temperatures is considered an environmentally safe procedure for disposing of toxic substances, including hazardous substances and chemical weapons. From 1969 to 1976, a US programme applied this method to destroy almost 3000 tonnes of sulphur mustard at the Tooele Army Ammunition Plant, together with 19,000 missiles and 14,000 rockets loaded with paralytic or convulsive agents at the Johnston Atoll Chemical Agent Disposal System [20, 21]. The thermal degradation process requires a lot of energy to maintain high temperatures, often more than 1400 °C [20]. The products of complete (and ideal) combustion of organic agents containing carbon, oxygen and hydrogen atoms are carbon dioxide and water vapour. If compounds also contain chlorine, fluorine, nitrogen, phosphorus and/or sulphur, other products of combustion are obtained: typically, HF from sarin, P_2O_5 from sarin, tabun and VX, NO_2 from tabun and VX agents and SO_2 and HCl in the case of HD agent. Moreover, for certain chemical agents such as lewisite, combustion can lead to the release of poisonous organo-arsenic by-products into the atmosphere.

The overall combustion reactions for selected toxic agents are summarized in Scheme 1.

In a typical industrial plant, CWAs in the liquid form undergo a two-stage combustion process, where the resulting gases from the treatment at temperature above 1400 °C are sent to an afterburner maintained at more than 1000 °C: herein, hazardous substances are degraded in combination with natural gases (*e.g.* propane, gaseous diesel) to eliminate the risk of combustion intermediates or dangerous chemical weapon residues, thus ensuring an overall reduction in the pollution in (and around) the combustion installation and the final safe disposal of CWAs [20–22].

Currently, research is ongoing to improve the combustion method for CWAs. As an example, the decomposition kinetics of dimethyl methyl phosphonate, DMMP, was studied using a hydrogen–oxygen flame-assisted thermal process. The system included a low-pressure combustion chamber, a sampling system and an ion-mobility spectrometer, in combination with a flat stainless steel burner surrounded by a shield through which argon flowed. The combustion of DMMP in this system resulted in a range of fragment products such as H_2CO_3, $CH_3\bullet$, CH_3OH, CH_3O, HOPO, $HOPO_2$ [20, 23].

Fig. 1 Reactions of **1** HD and **2** G-agent with hypochlorite ion; adapted from [23]
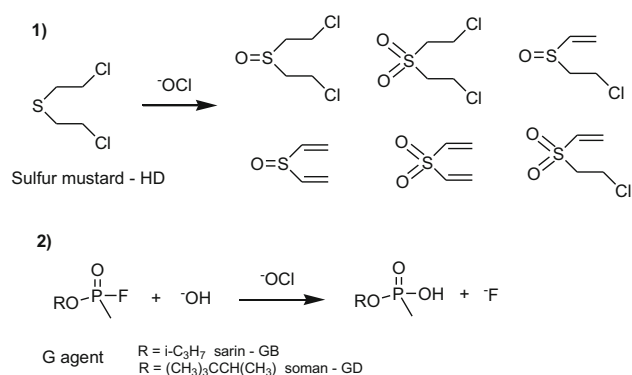
A further thermal method is pyrolysis, a high-temperature thermolysis carried out in the absence of oxygen or other oxidants [20]. The pyrolytic decomposition of sulphur mustard, phosgene, diphosgene and chloropicrin led to a promising degradation under reduced pressure. Particularly, the pyrolysis of HD conducted under N_2 (at 13.33 kPa) and air (at 16.67 kPa) at 450 °C led to a conversion of 99% of the hazardous substrate. The main reaction products were ethylene and vinyl chloride, alongside methane, ethane, acetylene and tiny amounts of propane. At lower pressure, lower sulphur mustard conversion levels were recorded, together with the co-production of other decomposition side products, such as CS_2, 1,2-dichloroethane, thiophene and methylthiophene. Although these thermal methods are attractive destruction techniques, growing public concern about the possible dangers arising from emissions from incineration plants, as well as the high energy costs, has led to the examination of alternative technologies to waste destruction [24]. Combustion methods, in all of its forms, tend to require specific heavy equipment on dedicate sites for the safe disposal of the toxic chemicals treated under the necessary harsh conditions.

Chemical degradation methods rely on chemical reactions, transforming hazardous molecules into non-toxic (or less toxic) compounds [17]. These reactions might be promoted by suitable reactants, but also by high-energy irradiation with UV light or the use of plasma. Since early times of chemical warfare, hydrolysis and oxidation are the fundamental approaches to efficient decontamination. For instance, blister H- and nerve V-type CWAs (classification according to NATO codes) have a sulphur atom which is prone to oxidation, whereas both nerve G- and V-type ones can undergo hydrolysis at the phosphorus atom.

Chemical decontamination approaches mainly rely onto either electrophilic or nucleophilic transformations, such as: oxidation [25–27], chlorination [28], hydrolysis [29, 30] or plasma-induced radical reactions [31].

In particular, oxidation reactions are based on chlorine- and peroxide-containing decontaminants, nucleophilic substitutions rely on alkaline hydrolysis, and alternative chemical approaches exploit hydrolysis catalysed by metal ions, reactive adsorbent materials or highly active nanoparticles. The requirement for chemical agent decontamination dates back to World War I, prior to that time, the poisonous chemicals used on the battlefield, such as chlorine or phosgene, were non-persistent gases/vapours and required no decontamination. The first decontaminants used, especially on sulphur mustard agent HD (Fig. 1), were chlorine-based decontamination materials, such as $Ca(OCl)_2$ bleaching powders, NaOCl solution, and, to a lesser extent, $KMnO_4$.

For instance, the sulphide moiety of HD is oxidized by hypochlorite leading to sulphur mustard sulphoxide, sulphone and further by-products. With nerve G-agents, OCl^- under alkaline conditions reacts by nucleophilic substitution reaction (Fig. 1) [32]. So far, among all strategies for the degradation of organophosphorus nerve agents, hydrolysis is the most effective in decreasing their toxicity. In these reactions (Fig. 2), water (or OH^-), as a nucleophile, attacks the central phosphorus atom of the nerve agent, cleaves the P–X bond (where X is –Cl, –F, –OR, etc.) and –X is replaced by a hydroxyl group. The hydrolysis of organophosphorus nerve agents of the G-series led to the substitution of –CN or –F leaving groups with one –OH function (at least), thus neutralizing the toxicity of the contaminant (Fig. 2). However, this route is less effective on V-series nerve agents that were designed to resist hydrolysis with the introduction of a thioamino moiety [33]. On the other hand, mustard agents, such as HD, are generally poorly soluble in water and react very slowly in this medium: due to this, the expected thiodiglycol is not normally produced, but the toxic substrate can undergo partial hydrolysis and/or oligomerization, rearranging into micelles with non-negligible amounts of undegraded HD agent in their core [33]. Therefore, this direct pathway is seldom applied to mustard agents.

Hydrolysis reactions may be promoted either by an acid or a base. Acid hydrolysis is of less importance in field decontamination because of the limited reaction rate and the lack of efficient catalysts for these reactions. However, they may be an option for decontamination procedures that are not constricted by operational timeframes (*e.g.* in clearance decontamination). Base hydrolysis is efficient in caustic environments (pH > 10), in the presence of certain catalysts (*e.g.* TiO_2 and ZnO) and at high temperatures [34, 35] or also in the presence of light irradiation at room temperature.

Based on these principles, the most widely used decontamination techniques in the last decades have been based on over-stoichiometric oxidation in the presence of active chlorine-based oxidants (*e.g.* commercial chlorinated lime, hypochlorite solutions, sodium dichloroisocyanurate $(NCO)_3Cl_2Na$ and chloramine-B hypochlorite C_6H_5-SO_2ClNNa) [36] and hydrolysis (basic solutions mainly with NaOH or KOH) reactions and are still partially in use today. Additional oxidizing decontaminants may rely on the action of ClO_2, chloride-amines, peroxides and ozone. So-called super-tropical bleach, STB, is a mixture of 93% calcium hypochlorite
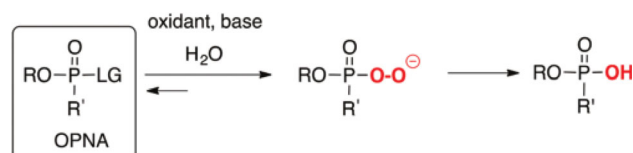
Fig. 2 Hydrolysis pathway of
common nerve agents involving
P-X moieties, organophosphorus
nerve agents, OPNA and yperite,
HD; adapted from [33]
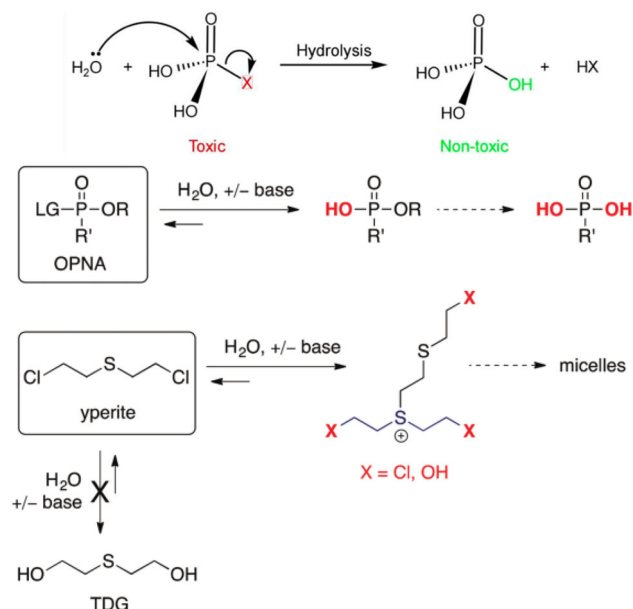
Fig. 3 Reaction of VX with HOCl
(**1**) and hydrolysis of sarin, GB,
with aqueous NaOH (**2**); adapted
from Ref. [35]
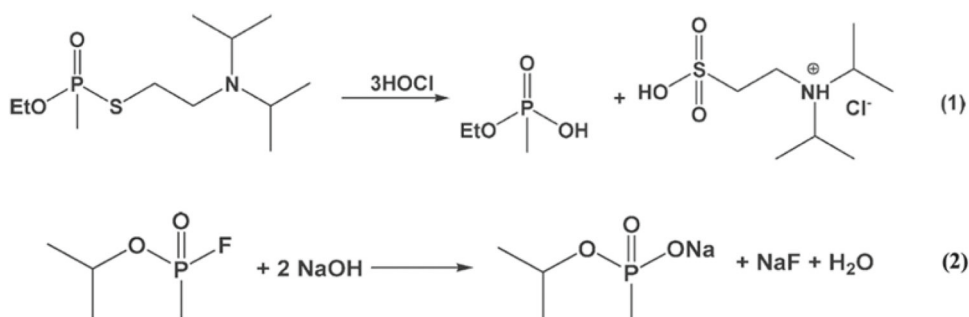
Fig. 4 Oxidation neutralization
path for organophosphorus nerve
agents, OPNA, substances;
adapted from Ref. [33]

and 7% sodium hydroxide which releases hydroxyl moieties in solution. STB is effective in detoxifying H-series, G-series agents and nerve VX, provided it does not solidify at low temperatures [32]. The use of a dilute aqueous solution of hypochlorite has been shown to be effective in degrading VX, or neutralization with aqueous NaOH allows for the destruction of sarin [35] (Fig. 3).

Chloramines are effective against blister HD and V-series nerve agents, but are ineffective towards G-series ones. NaOH solution, on the other hand, renders G-agents harmless, but as far as V-agents are concerned, it generates a product that is as toxic as the original substance [37]. Peroxides (R–O–O–R′) are strong oxidants which, with a limited impact on the environment, offer an alternative to toxic and corrosive chlorine-based decontaminants. Decontamination methods using the nucleophilic character of hydroperoxyl anion, OOH⁻, have been known for decades [38]. This anion is a much stronger nucleophile than H_2O itself or HO^- ion and, for example, it is able to degrade organophosphorus nerve agents, by perhydrolysis more effectively than by conventional hydrolysis (Fig. 4) [33].

Nerve agents react very rapidly with peroxide anions in basic solutions to give rise to non-toxic alkyl methyl acids. The efficacy is higher when free hydroxyl radicals are present: for instance, undissociated H_2O_2 is not completely effective in degrading VX, as the bonds that contribute to the dangerousness of that nerve agent are not cleaved by the peroxide species alone. However, hydroxyl radicals are very effective in detoxifying VX and other CWAs, so H_2O_2 is often mixed with other reagents to enhance its effectiveness and activity [29].

Historically, a long series of ready-to-use chemical decontamination formulations have been designed, since the 1960s. The DS-2 decontaminant solution, used by NATO armed forces until the 1990s, is a broad-spectrum, chemically reactive nucleophilic decontaminant. This polar, non-aqueous liquid consists of diethylenetriamine (70 wt%), ethylene glycol monomethyl ether (28 wt%) and NaOH (wt2%). DS-2 is used on equipment contaminated with liquid vesicant or nerve agents to reduce their hazard in few
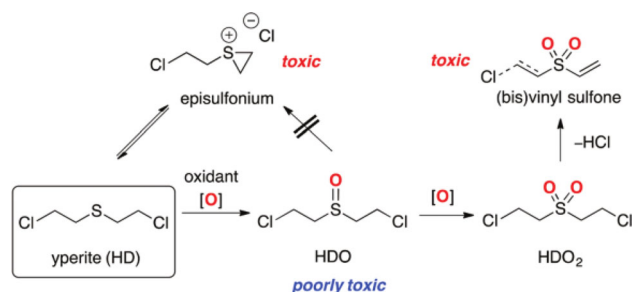
Fig. 5 Dehydrochlorination of HD in the presence of the decontamination solution DS-2; adapted from ref. [32]
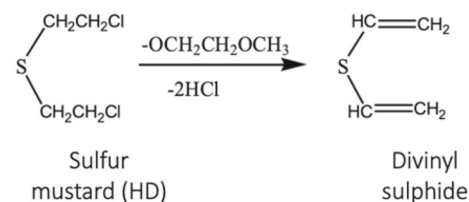
Fig. 6 Reaction of VX, GB, and GD with decontamination solution DS-2; adapted from [35]

1 VX R = Et, X = SCH$_2$CH$_2$N(^{i}Pr)$_2$
2 GB R = ^{i}Pr, X = F
3 GD R = CH(CH$_3$)C(CH$_3$)$_3$, X = F
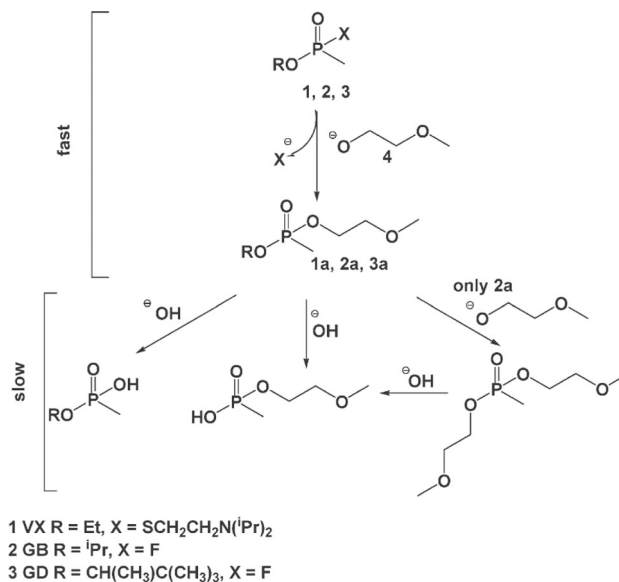
Fig. 7 Typical oxidative neutralization path for yperite; adapted from [33]

minutes. DS-2 readily detoxifies HD via elimination of the Cl atoms (Fig. 5) [32] or G- and V-type nerve agents, by nucleophilic substitution, to give diesters as the major products (Fig. 6) [35]. These diesters decompose further to give other products, but these reactions are slower.

The toxicity of mustard agents is associated with the highly electrophilic character of the sulphur atom in its activated form of episulphonium ion. Sulphur mustards are thus effectively detoxified by oxidation at sulphur with various oxidants to give rise to the corresponding sulphoxide, HDO (Fig. 7) [33]. However, the selectivity of the reaction plays an essential role as overoxidation leads to the formation of the sulphone, which via rapid HCl elimination gives a bis(vinyl)sulphone, which is as toxic as the pristine episulphonium species (Fig. 7). In addition, water-soluble oxidants, such as H$_2$O$_2$ and KOCl, are scarcely active on yperite, because of its lipophilic character, while microemulsions can be a suitable medium for the oxidative degradation of this kind of CWAs. In the last two decades, supported catalytic systems were applied for a more effective and selectively oxidation of the yperite and its simulant 2-chloroethyl ethyl sulphide, CEES, into the non-noxious sulphoxide in organic media [33].

Other formulations are skin decontamination kits (*e.g.* the M258, M258A1 or M280 kits), developed by the US Army and containing a wipe soaked with a solution of phenols (10%), ethanol (72%), H$_2$O (12%), NaOH (5%) and NH$_4$OH (0.2%). These kits were used on blister or nerve agents to thwart their toxic character in short times. Then, in many formulations, surfactants play an important role, since the decontamination of hydrophobic chemical agents is hindered by their poor solubility in the aqueous medium. Therefore, the main ingredients of such formulations include sodium dodecyl sulphate or cetyltrimethylammonium halides.

Such conventional decontamination methods, even though they proved to be often safe and effective for users, present some disadvantages. Adsorption on solids, dissolution, thermal decomposition or (over)-stoichiometric chemical degradation (*e.g.* hydrolysis, oxidation, combustion) are methods that require remarkable amounts of reactants, solvents and/or energy [20]. All this poses several

problems in terms of safety, efficiency, environmental and economical sustainability, selectivity, reliability and easy disposal of the degraded by-products. Furthermore, these techniques often pose additional problems in terms of corrosion onto the surfaces they are applied, scarce user friendliness, leaving bulk amounts of organic residues after decontamination, and lack of suitability to all-weather and environmental conditions.

4 Innovative high-performance decontamination methods

To circumvent the problems of conventional decontamination methods, the attention of academic and industrial research moved, in last times, from stoichiometric to catalytic chemical decontamination, through the design and development of more active reliable and cheap reactive sorbent materials, able to transform highly toxic compounds into non-toxic, or far less toxic, degradation products under mild conditions (ideally, under ambient conditions). Moreover, thanks to the recent advances in the field of nanostructured materials, systems, such as nanosized inorganic, organic or composite materials, metal oxides, metal nanoparticles or metal–organic frameworks, are particularly suitable for these applications. They indeed feature very high specific surface areas, high reactivity and a remarkable number of reactive and easily accessible active sites, enhanced by their tailored size at nanometric scale (1–100 nm) [39]. Nanosystems indeed show chemical, electronic, mechanical, optical, magnetic or catalytic properties that are significantly different not only from the ones of single molecules, but also from the ones of macroscopic objects. Thanks to this, nanostructured materials can be promising candidates as catalysts for the chemical decontamination of CWAs. In addition, the use of catalytic amounts of decontaminating materials is undoubtedly advisable in outdoor on-field decontamination of large surfaces and terrains, where a total-loss use of decontaminating solids is necessary [40, 41].

Nevertheless, in some specific cases, the use of nanostructured systems for decontamination is not necessarily the best option. In some academic papers, the high costs and the technical difficulty to prepare and obtain efficient catalytically active nanomaterials have been underrated and this is a major weak point when a large-scale production and use of these systems are required. In other works, nanoparticles containing non-negligible amounts of precious metals (typically, Au or Pd) are essential to carry out the catalytic degradation of the toxic agents [42]. Clearly, the lack of a sound transdisciplinary research approach may lead to preliminary results that then can hardly find practical application. Furthermore, some recent concerns about possible negative consequences on human health induced by nanosized materials must stimulate a careful evaluation of the toxicological and pathogenic impact of these materials, especially in total-loss applications [43]. So, risks and advantages in the use of nanosystems as methods for decontamination and depollution from highly hazardous agents must be carefully balanced [44].

Ideally, an efficient catalytic system for the decontamination of CWAs should be:

- Active, since decontamination has to be as rapid as possible;
- Selective, to avoid the generation of side products which might be even more hazardous than the pristine CWA;
- Cheap, for an economically viable scale-up production;
- Safe, sustainable and non-toxic, for users and the environment;
- Versatile, to be applied against a broad range of aggressive agents;
- Able to be active under mild (preferably, ambient) conditions;
- Reliable and robust, in terms of stability under real-case conditions and in all practical on-field scenarios.

To date, a very wide variety of metal nanoparticles, inorganic metal oxides, magnetic nanoparticles, porous materials, layered solids, polyoxometalates, POM, supported transition metal (*e.g.* V, Mo and Fe) complexes, metal-containing silica and zeolite-based nanosized solids, modified activated carbons and graphenes, metal organic frameworks, MOFs, and, in some cases, their combination, as catalysts for efficient CWAs decontamination and/or abatement, have been reported in the literature [33, 36, 45, 46]. Of particular interest are also biochemical methods based on enzymatic catalysis [17] or the application of nanometric photocatalysts [47, 48].

4.1 Nanosized metal particles and nanostructured inorganic oxides for decontamination of CWAs

Supported metal nanoparticles (size in the range 1–20 nm) are an important class of nanostructured materials for the decontamination and the abatement of CWAs [42, 45]. They find application in filters for air purification, in high-performance textiles or active sorbent materials. One of the main drawbacks in their use for CWAs decontamination is that the sites at the metal surface must be able to efficiently cleave P–O, P–C, S–C and P–S bonds, but, at the same time, to minimize the co-production of by-products difficult to be removed (fouling organic species containing P and S atom), which eventually poison the metal surface, leading to a gradual deactivation of the catalyst itself [49, 50]. Garcia et al. showed that Au/TiO$_2$ systems containing 2–5-nm-large metal nanoparticles (with different loadings, from 0.4 to 1.5 wt%) can decompose HD, soman and VX under visible light at room temperature [51]. At the end of the reaction, harmless products are formed only and minimal amounts of strongly absorbed organic materials can be found on the solid. No information is given on the recoverability and reusability of the material, even though this kind of catalysts is designed for a total-loss use.

Blister sulphur mustard, soman and nerve VX can be hydrolysed over the surface of TiO$_2$-based nanotubes [33]. The decomposition of VX is particularly rapid after their adsorption on nanotubes, with a half-time reaction of 30 min, approaching similar conversions

normally achieved with conventional decontamination liquids. Soman and yperite are effectively hydrolysed as well under the same conditions, thanks to the presence of catalytic Ti(IV) species in the materials: in these two cases, the reaction led to formation of titanophosphonate species and sulphonium ion (a dimer of thiodiglycol), respectively.

For decontamination purposes, inorganic oxides (either pure or mixed oxides) are generally at nanometric scale in two forms: nanopowders and nanoporous materials. Nanopowders (with average particle size < 100 nm) typically feature a neat phase homogeneity and lower densification temperature. On the other hand, nanoporous materials are porous solids with pores in the range from 1 to 100 nm. Nanopowders and nanoporous solids find application in CWAs decontamination, since they show very high specific surface areas (from 400 up to 1800 m^2 g^{-1} or more) and a remarkable fraction of defective sites with enhanced adsorption and catalytic properties [52]. Oxides from metals, like Mg, Al, Ti, Zr, Fe, Mn, Zn or Cu, therefore with marked oxidizing and/or acid character are typically the most interesting and studied systems. The simulant of sulphur mustard, (2-chloroethyl)phenylsulphide, CEPS, was successfully decontaminated, with total conversion and good selectivity to non-noxious by-products, using nanocrystals of mixed metal oxides (Al_2O_3-Fe_2O_3, Al_2O_3-V_2O_5 or Al_2O_3-CuO) obtained through aerogel synthesis process [53]. Ceramic nanofibers of zinc titanate (especially, ZnO-TiO_2 40–60%) were proposed as active filters for personal protective equipment and displayed a good decontamination performance for the organophosphorus pesticide paraoxon and the sulphur mustard simulant 2-(chloroethyl)ethylsulphide, CEES [54]. It is worth noting that the use of heterogeneous solid catalysts allows the simultaneous presence of active species, at the surface of the material, which typically cannot be compatible with one another. On solid materials, for instance, acid and basic sites can be accommodated and stabilized together on the same support. Nanosized magnesium oxide shows, in fact, a good number of Lewis acid centres (Mg^{2+} in the lattice of MgO) and Lewis basic ones (O^{2-}) in close proximity, without any mutual neutralization. Furthermore, nanostructured porous materials with a high specific surface area are optimal supports to insert or deposit catalytically active sites with redox properties (typically, oxidizing centres). The use of metal oxides in CWAs decontamination is the subject of numerous research articles and patents [55]. For instance, the commercial product Fast-Act®, mainly made up of nanostructured MgO and TiO_2 has been developed in order to degrade CWAs such as HD, soman, and VX agents [56, 57]. Likewise, Wagner et al. [58] studied hydrolysis of nerve VX, GD, and blister HD on TiO_2 materials for the development of self-decontaminating paints that can be used to protect military vehicles.

With regard to polyoxometalates, the polyoxomolybdate species $K_2H[(H_2O)_4$ M$][AsMo_6O_{21}(Ala)(PHBA)_2]$-$nH_2O$ (POM-1) was found to be efficient in the hydrolysis of diethyl cyanophosphonate, DCNP, a simulant of tabun, achieving a complete conversion within 10 min at only 0.1 wt% loading of the catalyst. This result is far superior than the ones on polyoxoniobates $[C_nH_{2n+1}N(CH_3)_3]_7HNb_6O_{19}$ (POM-2) materials. Additionally, POM-1 can be more easily recovered using a simple filtration and reused with full retention catalytic activity. The 1-D polymeric polyniobate with the structure $K_{12}[Ti_2O_2][GeNb_{12}O_{40}]-19H_2O$ (KGeNb) led to a complete hydrolysis of the same substrate in a reasonable time (*ca.* 30 min). This polyoxometalate was found to be efficient in the decomposition of HD agent [59, 60]. POM-1 and POM-2 were also found to be very versatile in the fast oxidative decontamination of CWAs (within 5–20 min) in the presence of H_2O_2. POM-3 instead, combining a polyoxoniobate and a polyoxovanadate, was able to complete oxidize CEESO species with 3% H_2O_2 in just 3 min, but with the side effect of producing dehydrochlorinated VESO species of unknown toxicity [61].

Besides polyoxometalates, several studies in the literature also address the use of zeolites or zeolite-derived solids for the decomposition of different real and CWA simulants, owning to their interesting properties such as good adsorption capabilities, high ion-exchange capacity, surface acidity and surface area and excellent thermal stability [62]. For example, Meenu et al. [63] evaluated the decontamination performance of zeolite-a and its derived metal oxide composites (with Cr and Ag) against the CWA simulants 2-chloroethyl ethyl sulphide, CEES, and dimethyl methyl phosphonate, DMMP. These nanocrystalline solids proved to powerful adsorbents, demonstrating a significant decontamination potential on these CWAs. Particularly, Cr-O-a and Ag-O-a materials showed promising results, achieving an average of 93–98% CWA decontamination among all other synthesized metal oxide composites in the study. Reactive organic suspensions combining ZnO, TiO_2 and zeolite nanosized adsorbents were examined for the decontamination performances against tow real CWAs, soman and sulphur mustard. The authors of the study observed a good decontamination efficiency into harmless degradation products for the HD agent with just a 1 wt% of nanoparticles concentration (*i.e.* with ZnO nanoparticle suspensions) [64]. The positive influence on the enhancement of the degradation performance was also more noticeable for GD nerve agent. In comparison with blister HD, which required from 5 to 24 h for a complete degradation, only approx. 60 min was found to be necessary in the case of GD. Besides, the TiO_2 and zeolite mixed suspension led to better HD decontamination than ZnO, whereas on GD both systems behaved in a similar manner. Sadeghi et al. [65] prepared NiO NPs/Ag-clinoptilolite zeolite composite adsorbents for the conversion of CEES and DMMP simulants to non-harmful products. These materials demonstrated high catalytic performance in the decontamination of the aforementioned agents, showing a degradation of 86% and 89% of CEES and DMMP on their solid surface in *n*-hexane solvent after 8 and 12 h at room temperature, respectively.

Phyllosilicate clays, in particular, Fe-bentonite and synthetic smectite saponites, have been used successfully in the decontamination of hazardous CWAs (Fig. 8), thanks to their high robustness, broad chemical versatility, good adsorption capabilities and very modest production costs. The montmorillonite-rich bentonite from the natural origin was modified by introducing iron species and acid sites in the interlayer space, aiming to obtain a sorbent with strong catalytic oxidizing and hydrolytic properties. The catalytic performance of these materials was first evaluated in the oxidative abatement of the simulant compound CEES, in the presence of aqueous H_2O_2 as an oxidant. Then, tests carried out on the blistering warfare agent, sulphur mustard HD, showed that, because of the synergistic presence of the iron-containing clay together with a solid oxidant component, sodium perborate, up to 80%
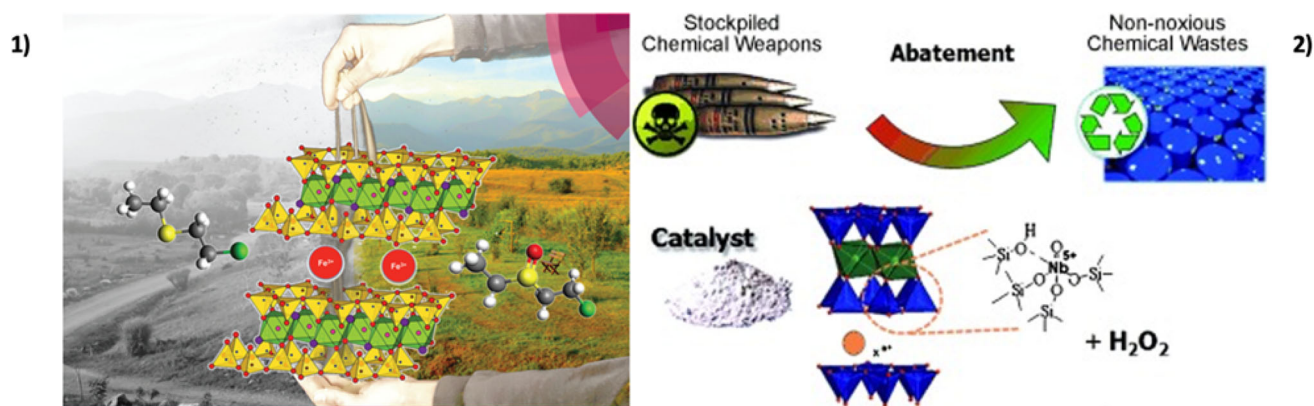
Fig. 8 Iron-montmorillonite clays as active sorbents for the decontamination of hazardous CWAs; adapted from [66] (**1**); bifunctional Nb(V)-containing saponite clay designed for the selective oxidative abatement of CEES; adapted from [67] (**2**)
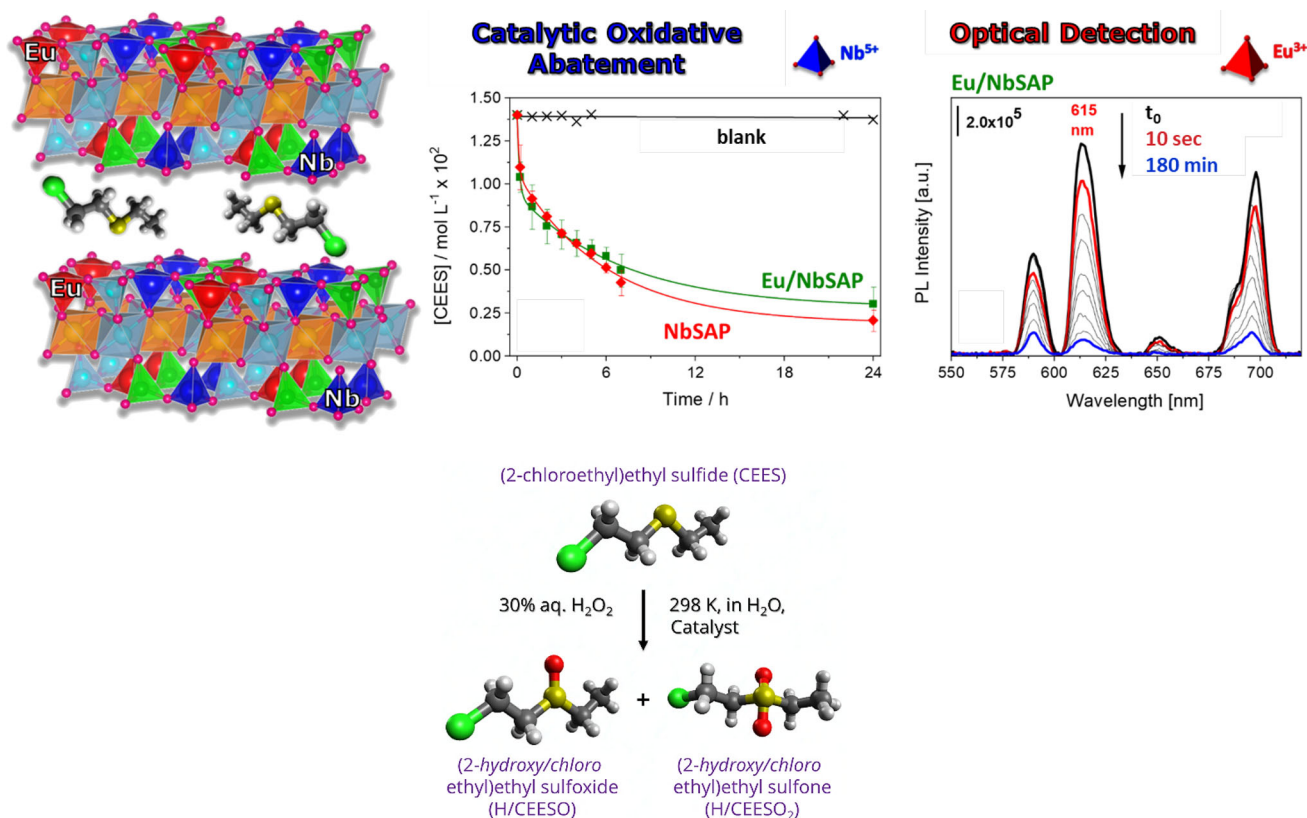
Fig. 9 Eu(III)-containing Nb(V)-saponite clays used in the catalytic oxidative decomposition and optical detection of CEES under very mild experimental conditions in water medium; adapted from [68]

decontamination of the test surface, could be achieved under mild ambient conditions, in 24 h [66]. Saponite clays with relatively high Brønsted surface acidity, featuring in-framework catalytically active Nb(V) sites, were effectively employed in the selective oxidation of > 90% of CEES into non-noxious sulphoxide under mild conditions too, in organic solvents with diluted aqueous H_2O_2 (used as oxidant) within 6 h [67]. More recently, the co-presence of luminescent Eu(III) and catalytic Nb(V) metal sites in the saponite structure has been exploited for the simultaneous optical detection and oxidative catalytic degradation of the blister agent simulant CEES. The two metal centres were introduced into structural positions of the clay, particularly in the interlamellar space and/or within the inorganic structure, following two different synthetic preparation techniques. These functionalized saponites were able to detect the presence of CEES after a few seconds of contact time in water, and more than 80% of the substrate was catalytically decomposed after 24 h in the presence of diluted aqueous hydrogen peroxide, thanks to synergistic effects of Nb(V) sites and the surface acidity of the clay. Moreover, in aqueous phase the two solids tested led to the hydrolysis of the chloroethyl moiety, with the formation of non-noxious hydroxy-organosulphur by-products (Fig. 9) [68].

Fig. 10 Hydrolysis of paraoxon catalysed by phosphotriesterase, PTE
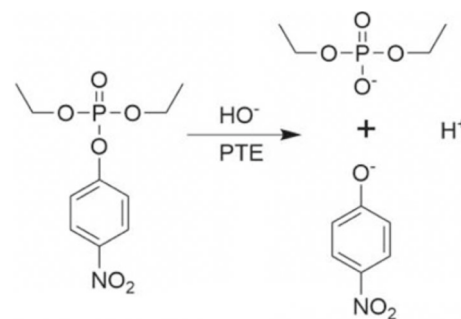
4.2 Biochemical decontamination

An alternative to conventional decontaminants with more environmentally friendly substances has been found in the use of enzymatic catalysis. Biochemical decontamination is based on agent-scavengers or on enzymes able to promote tailored detoxification reactions. As main advantage, enzymes are highly selective and exhibit remarkable catalytic turnover numbers, whereas purely stoichiometric reactants are consumed during each reaction. In general, enzymatic processes are very susceptible to temperature, pH and reaction environment in which they are carried out. Hydrolytic enzymes promote the hydrolysis of nerve agents, but, as a drawback, the pH of the reaction medium rapidly decreases, because of the concurrent in situ generation of phosphoric and phosphonic acids and hence to the increased acidic conditions. To avoid this problem, buffers are typically added to keep a neutral pH. Enzymes can act directly on agents, but also on the products of neutralization reactions, enhancing the total reaction rate by continuously removing these products. Enzymatic methods are largely promising and a complete detoxification of CWAs can be achieved very quickly, generally giving rise to non-toxic products and fulfilling the principles of green chemistry. Hereafter are some examples of enzymes effective in the degradation of CWAs.

Among the best enzymes studied in the decomposition of CWAs are phosphotriesterase, PTE, organophosphorus acid anhydrolase, OPAA, organophosphorus hydrolase, OPH and di-isopropylfluorophosphatase, DFPase. These hydrolyse several nerve agents to their stable methylphosphonate alkyl ester derivative [46]. Enzyme phosphotriesterase, PTE (EC 3.1.8.1), for example, possesses a marked catalytic activity against many organophosphorus compounds and the highest catalytic capacity was recorded on the pesticide paraoxon (Fig. 10) [69]. PTE is one of the enzymes that is able to catalyse the cleavage of P-S bond, which is present in CWAs such as second-generation nerve agents.

A further enzyme capable to catalyse the hydrolysis of organophosphorus anticholinergic agents is paraoxonase 1, PON1 (EC 3.1.8.1) [70], an enzyme that is present in the human body. Organophosphorus acid anhydrase, OPAA (EC 3.1.8.2), does not promote the hydrolysis of VX, but enhances at a great extent the breakdown of P-F and P-CN bonds in nerve G-type agents [71]. In this case too, the poor solubility in H_2O of sulphur mustard hinders its hydrolytic decomposition. The enzyme that can accelerate the hydrolysis of sulphur mustard HD is haloalkane dehalogenase (EC 3.8.1.5), which promotes the hydrolysis of carbon–halogen bonds [72].

The immobilization of enzymes on specific solid supports typically improves the overall enzyme performance, due to the enhancement substrate specificity and the reduction in the effect of inhibitors [46]. The success of enzyme immobilization largely depends on the properties of the supports. Biocatalysts based on encapsulated enzyme carriers frequently use polyethylene glycol-coated liposomes, nano-emulsions, nanosized dendrimers (from 10 to 100 nm) and dendritic polymers, thanks to their inertness to temperature, solvent and pH conditions, and relatively good biocompatibility and/or biodegradability.

Organophosphorus-hydrolysing enzymes also show great promise as catalytic bioscavengers for use as safe medical countermeasures against nerve agent poisoning, for in vivo decontamination [73]. Indeed, if an effective bioscavenger is present in the blood prior exposure to nerve agents, the reduction in the concentration of the toxic chemicals to a toxicologically irrelevant level will be very rapid. Candidate enzymes include paraoxonase (PON1), mutants of butyrylcholinesterase (BChE) and acetylcholinesterase, bacterial and eukaryotic OPH, OPAA and DFPase.

4.3 Photochemical decontamination

Photocatalysis is widely used in the degradation of CWAs and one of the most studied systems are based on TiO_2 nanoparticles [74]. In particular, an interesting approach is based on nanostructured photocatalysts as decontaminating systems. They can be sprayed on contaminated surfaces to aid decontamination by adsorptive removal of CWAs. After adsorption, they promote photocatalytic reactions under light radiation. For instance, photocatalytic decontamination of blister HD was studied using titania particles of different sizes, under visible sunlight or UV-A irradiation. HD was completely decontaminated, into relatively non-toxic products, by TiO_2 within 6 h under sunlight [20] (Fig. 11).

Some authors have shown that dispersed aerosols of nerve agent sarin and blister HD can be successfully degraded under UV irradiation generated by germicidal lamps, through photolytic and photocatalytic pathways. The CWAs can thus polymerize under

Fig. 11 Photocatalytic decontamination of sulphur mustard HD with nano-TiO$_2$ under sunlight; adapted from [20]
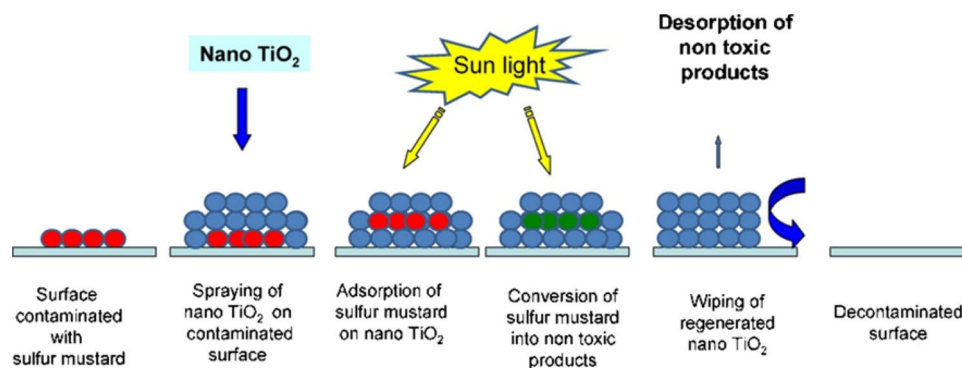
these irradiation conditions. A photodegradation process takes place at the surface of TiO$_2$, leading to the formation of innocuous inorganic compounds. Thanks to systems like these, photolysis or photocatalysis can be used to clean indoor air, in large spaces contaminated with sarin [20, 75].

In these studies, commercially available TiO$_2$ was most commonly used [76]. However, to enhance the decontamination efficiency, TiO$_2$ was doped with metal or non-metal ions [77] or, alternatively, various nanocomposites were recently adopted [78]. Easily accessible carbon materials, with very high specific surface area, such as nanotubes, graphene or graphene oxide, GO, are among the most studied systems [79, 80]. Nevertheless, a robust and reproducible synthesis of these high-performance materials on large scale is still challenging, so far. Stengl et al. have previously reported two undemanding methods suitable for large-scale synthesis of TiO$_2$-based nanocomposites [80]. Water-compatible TiO$_2$/nanodiamond nanocomposites were studied in the rapid decomposition of soman in liquid phase, thanks to the abundance of oxygen-containing surface sites [81]. The materials exhibited improved adsorption, initial spontaneous dissociation of the CWA substrate (to products more prone to photooxidation) and solar-light photo-decomposition of vapours of the simulant dimethyl methylphosphonate, DMMP, coupled with beneficial electronic interfacial properties between TiO$_2$ and nanodiamond parts. Mesoporous TiO$_2$ aerogels coupled with plasmonic Cu nanoparticles, Cu/TiO$_2$, were tested in the degradation of the nerve CWA sarin under both dark and illuminated conditions. Cu/TiO$_2$ aerogels combine high dark degradation rates, which are facilitated by hydrolytically active sites at the Cu∥TiO$_2$ interface, with photo-enhanced degradation capability of semiconductor TiO$_2$ and the surface plasmon resonance (SPR) of the Cu nanoparticles. Accelerated hydrolysis of sarin occurs on Cu/TiO$_2$ aerogels under visible illumination (at > 480 nm) [82].

High surface-area mesoporous CeO$_2$ proved to be one of the most reactive oxides for adsorbing and degrading toxic organophosphorus compounds, including CWAs. Nanostructured CeO$_2$ aerogels, prepared using a facile, scalable and template-free sol–gel method, were tested to decompose DMMP. Enrichment of the aerogel surface with OH species led to an irreversibly binding of DMMP, which rapidly generates hydrolysis products. Exciting the CeO$_2$ bandgap with UV light in the 390–400 nm range, the DMMP degradation onto the surface of the materials is also accelerated, thus generating a high proportion of mineralized PO$_x$ products [83].

Nanosized NiO/Bi$_2$MoO$_6$ heterojunction photocatalyst was studied in the degradation of methyl parathion, obsolete pesticide and nerve agent simulant. The photo-decomposition reaction follows a pseudo-first-order kinetics with a high-rate constant of 1.7×10^{-3} min^{-1}, with the solid able to degrade more than 95% of parathion in *ca*. 120 min [84].

4.4 Decontamination over metal organic frameworks

Another class of materials that in recent years has attracted attention are metal organic frameworks, MOFs. They have emerged as an extensive class of crystalline materials with ultrahigh porosity (up to 90% free volume) and enormous internal surface areas, extending beyond 6000 m^2 g^{-1} [85]. These materials are formed by bonds between metal-based nodes and organic linkers with multiple coordination sites and feature tuneable pore size and adjustable internal surface properties. Tailored crystalline MOFs with accessible Lewis acid metal sites promote the catalytic hydrolysis of nerve agents both in aqueous solution and in the solid-state form, hence showing the relevant potential for MOF-based personal protection gears [86, 87]. Before discussing some of the earliest examples of divalent MOF catalysts, we need to distinguish between the absorption of nerve agents and their degradation. Among the first discovered and most popular MOFs in the world, MOF-5 has been demonstrated to be a promising material to absorb and capture sarin, as well as HD agent [88]. Though effective at absorbing the genuine nerve agent and its simulant, MOF-5 could not catalyse their hydrolysis. One of the prerequisites for MOF catalysts is the capability to promote the hydrolysis reactions, so that the MOFs do not get worn out and could be recycled for long-term usage in real life. One of the first examples of effective MOF catalysts dates back to 2011. The NENU-11 MOF, obtained from the Keggin-type polyoxometalate anion [PW$_{12}$O$_{40}$]$^{3-}$, is able to efficiently absorb and degrade DMMP, nerve agent simulant [89]. Then, HKUST-1 proved to be efficient in the hydrolysis of sarin [90]. A highly efficient bifunctional MOF, for the hydrolysis of organophosphorus agents, is Zn-MFU-4 l [91]. The combination of
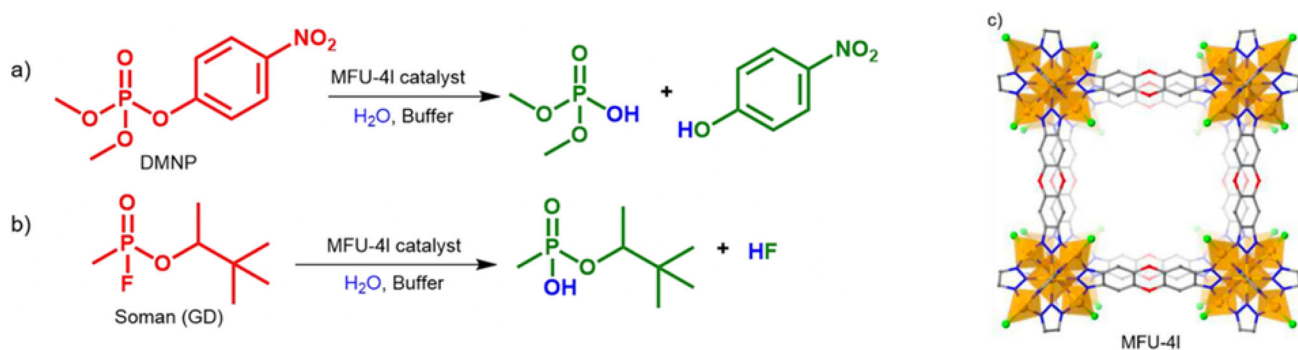
Fig. 12 Hydrolysis reaction of **a** the phosphonate-based nerve agent simulant DMNP and **b** nerve agent GD; **c** structural representation of MFU-4 l. Hydrogen atoms are omitted. Colour code: Zn (brown), Cl (green), C (grey), N (blue) and O (red); adapted from [91]

**Fig. 13** MOF (NU-1003)-enzyme carrier for the catalytic degradation of soman; adapted from [92]
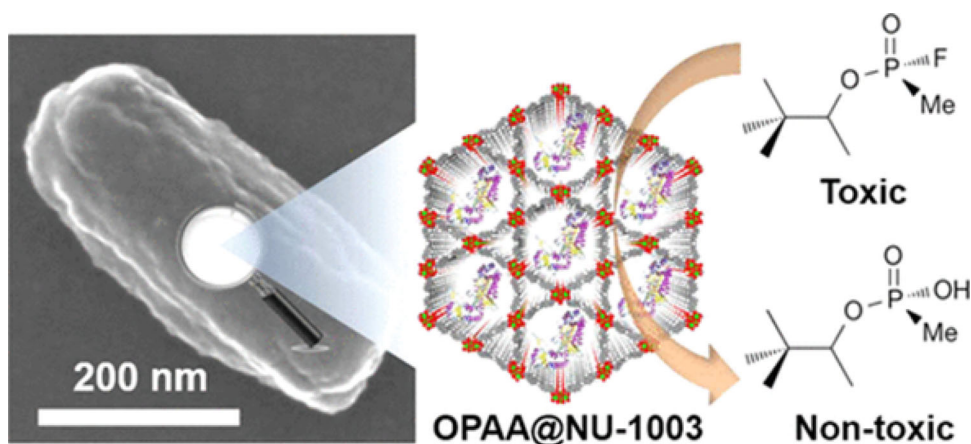
soft Lewis acidic Zn(II) and soft Lewis basic Zn-triazole-based building blocks on the linkers of MFU-4 l yields a heterogeneous catalyst suitable for the sarin and DMNP hydrolysis (Fig. 12).

Indeed, when MFU-4 l reaches a weight percentage of 6%, more than 80% of the DMNP is degraded in 3 min, which corresponds to a half-life of < 1 min, following a first-order kinetic process. This value is among the lowest values of DMNP hydrolysis half-life reported up to date. The half-life for the hydrolysis of sarin is 3.3 min, low enough for MFU-4 l to be considered promising for real-world applications. The recent development of water-stable mesoporous MOFs has paved the way to their use as enzyme carriers. Among them, NU-1003 has the largest mesoporous apertures (4.6 nm) known, so far, for a zirconium-based MOF. Within its porous network, it was possible to immobilize organophosphorus acid anhydrolase, OPAA, an enzyme capable to hydrolyse nerve agents [92]. The catalytic efficiency of immobilized OPAA in nanosized NU-1003, on soman, GD, was significantly increased with respect to the one of free OPAA in bis-trispropane buffer (Fig. 13).

Another work shows the development of MOF composites that structurally mimic active site and its ligated histidine residues in phosphotriesterase. Thanks to the incorporation of imidazole into the porous network of MOF-808, the final MOF showed the rapid degradation of the nerve agent simulant DMNP in H_2O and in a wet environment without a liquid base (Fig. 14) [93]. MOF-808 also recently proved to be a highly efficient and regenerable catalyst for the hydrolysis of Novichok nerve agents under basic conditions [94]. The introduction of missing linker and node defects in the structure of the UiO-66 MOF led to substantial improvement in the decomposition of organophosphorus toxic chemicals [86]. The CWA conversion after 40 min reached 88% and 50% for soman and VX, respectively, whereas a full degradation of soman was attained after 100 min. The fine balance among structure, hydrolytic capability and role of amino functionalities in the MOF framework showed that the intimate proximity of amino groups to the structural nodes is important for an effective chemical detoxification action. Detailed computational calculations have also excluded the possibility that the amino groups act as Brønsted basic sites, suggesting that micro-solvation around the defect sites affects the reactivity, thus giving useful insights for the design of novel and more effective MOF catalysts for the degradation of nerve CWAs.

The initial degradation rates of Novichok agents A-230 and A-232 were instantaneous, with half-lives of less than 30 s. In contrast with V- and G-series agents, the degradation of Novichok species follows a two-step hydrolysis pathway. First, P-F bond is very rapidly cleaved; then, the amidine group from the intermediate product is catalytically removed by the MOF. The intermediate therefore acts as a rate-determining competitive substrate for the entire two-step degradation sequence. Under acidic conditions, the amidine group of Novichok A-230 is more rapidly hydrolysed than the P-F bond, giving rise to a further moderately toxic intermediate.

Fig. 14 Schematic illustration of the catalytic hydrolysis of DMNP by incorporating imidazole bases into a MOF-808; adapted from [93]
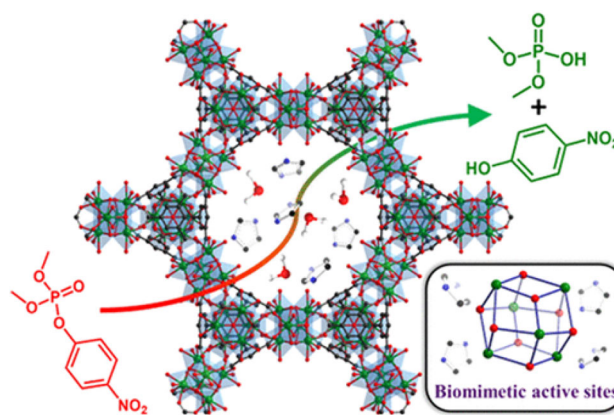
MOFs are therefore a promising class of porous nanostructured materials for many interesting applications in CWAs decontamination. For some classes of molecular sieve solids, there are still some issues in terms of robustness, costs, environmental safety and scalability of synthesis. Nevertheless, recent reports, at both academic and industrial levels, have shown that MOFs can be successfully integrated and embedded into textile fibres to obtain wearable protective garment with excellent capability in terms of in situ CWA degradation and detoxification [95–97].

5 Conclusions

The lists of highly toxic compounds that can be potentially and illicitly used as chemical warfare agents and are included in the set of banned or strictly controlled substances is regularly updated at international level, thanks to a periodic review of the Chemical Weapons Convention by the states adhering to it. Such ever-changing legal framework and the constant evolution of the geopolitical situation worldwide are, at the same time, a challenge and an incentive for the scientific community towards the search for new technologies, high-performance systems and innovative solutions to be applied to the safe, efficient and sustainable decontamination of CWAs.

Although none of the decontamination approaches developed so far are free from drawbacks or points of weakness, remarkable milestones have been reached in the last decades in the field of the design and development of efficient, stable, cheap, affordable and versatile decontamination systems. Indeed, only when novel and effective decontamination tools are available, an improved mitigation and reduction in the risk linked to the accidental or deliberate release of these substances can be achieved. All this, thus, corresponds to a step forward towards a safer society, free from chemical weapons.

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