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Decontamination agents for chemical neutralization of organo-phosphorous poisonous compounds: Literature Review

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Abstract

Organophosphorus compounds (OPC) are highly toxic substances that are used as pesticides, active pharmacological ingredients, components of chemical weapons, etc. Many of them are neurotoxic agents, possible carcinogens, have acute or chronic toxic effects, suppress immunity, cause disorders of the endocrine, central and peripheral nervous systems. These compounds are inhibitors of acetylcholinesterase, a key enzyme for the regulation of central and peripheral nervous systems. The review considers mostly chemical and some physical approaches to the development of OPC decontamination methods, summarizes the preexisting and new strategies of individual decontamination of OPC. Hydrogen peroxide-based systems have been shown to be effective decontaminants for OPC, mild in nature and environmentally safe. Introduction of activators into the system tenfold increases the reactivity of hydrogen peroxide due to the formation of active peroxoanions. It has been shown that modified aluminosilicates accelerate the process of decomposition of OPC, and the relative instability of peroxoanions requires the search for alternative ways to optimize decontamination systems.

Keywords: Decontamination system; Degassing; Individual decontamination; Organophosphorus compound; Hydrogen peroxide; Peroxysolvates

1. Introduction

The relevance of research regarding the development of modern agents for decontamination of organophosphorus esters, that manifest neuro-paralytic action, is dictated by a number of priority tasks related to protection from chemical hazard. Toxic effects of organophosphorus compounds [1] pose a considerable threat to both human health and environment. A significant number of active ingredients of pesticide products possess either known or potential carcinogenic effect, exhibit acute or chronic toxic effects, suppress immunity, cause disorders of the endocrine, central and peripheral nervous systems [2, 3]. Previous studies have also confirmed that organophosphorus compounds (OPC) adversely affect reproductive functions, lead to fetal developmental disorders and pose an increased risk to children health. [1, 4, 5].

In 1993, the International Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on Their Destruction was administered [6], which set up the deadline for the planned complete reduction of existing stockpiles by 2007. A number of directives have also been adopted, regulating the assortment of organophosphorus pesticides, as well as the procedures for their application, circulation, disposal, and safety

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precautions. [7–11]. The need to use pesticides has led to agro-industrial countries facing the problems with safe storage of the waste of these substances, as well as the elimination of consequences of accidental spilling [9]. In developed countries, the problems of waste and contamination with organophosphorus pesticides and active pharmaceutical ingredients are mainly related to contamination of wastewater, recycling or disposal of packaging after the use of pesticides and pharmaceuticals, and remediation of contaminated soils. According to the results of inventory measurements, about 20 thousand tons of obsolete pesticides have been accumulated in Ukraine alone. Accumulation of obsolete and unusable pesticides leads to the fact that, according to various estimates, OPC poisoning is the cause of 200-300 thousand deaths in the world annually due to soil and water contamination, as well as unintentional consumption of pesticides [1, 3, 9].

Furthermore, there were registered incidents of neuro-paralytic and other OPC use in military operations in Syria (2017), terrorist attacks in Matsumoto and Tokyo subway (1994, 1995), Salisbury (2018), Russia (2020). The specificity of such terrorist attacks necessitates equipping rescue teams with means of individual decontamination of OPC, which would be safe for life and health of victims [12–14]. According to "The Concept for Raising the Level of Chemical Safety", published by the Cabinet of Ministers of Ukraine (decree № 1571-p), scientific and technical advances in development and introduction of safe technologies for disposal of hazardous chemical wastes and substances are necessary to reduce the likelihood of adverse effects of chemicals on public health and environment.

In this regard, in addition to the problem of large-scale industrial disposal of chemical weapons components and banned pesticides, rises an issue of effective decontamination of toxic compounds released during terrorist acts or due to chemical and pharmaceutical industrial accidents. At the same time, special attention should be paid not only to the decontamination of surfaces, walls and other interior elements of the premises for further safe operation, but also to the removal of toxic substances from skin of humans and animals. Thus, the development of fast-acting decontamination formulations, environmentally safe and with mild impact on human body, is a necessary and urgent task in the process of creating new technological solutions for the disposal of OPC.

2. Organophosphorus Compounds: Properties and Toxicity

Intensive studies on the organic chemistry of phosphorus have led to the invention of various groups of organophosphorus compounds, such as phosphates, phosphonates, phosphinates and phosphorothioates, as well as countless other structurally and toxicologically different OPC [15, 16]. Detailed classification of toxic OPC based on their chemical structure was provided by *Mukherjee* and *Gupta* [2]. The authors note that organophosphorus pesticides are predominantly thiols, amides, or esters of either phosphoric, phosphonic, phosphinic or thiophosphoric acid that incorporate two extra side chains – phenoxy, cyanide or thiocyanate functional groups [2]. Several OPC including S-substituted phosphorothioates and phosphonofluoridates are used as nerve agents, also known as chemical warfare agents. The main neurotoxic OPC are commonly known by their military identifiers, which are given to them according to NATO regulated standards, and fall into four categories [2]:

G-series compounds, first synthesized by German scientists, include compounds like tabun (GA, O-ethyl-N,N-dimethylphosphoramidocyanidate), sarin (GB, O- isopropyl-methylphosphonofluoridate), soman (GD, O-pinacolyl-methylphospho-nofluoridate) and cyclosarin (GF, O-cyclohexyl-methylphosphonofluoridate)/

V-series compounds, which include VE, VG, VM and VX agents, where: VX – O-ethyl-S-[2-(Diisopropylamino)ethyl]-methylphosphonothioate; VR (also known as Russian VX) – O-isobutyl-S-[2-(Diethylamino)ethyl]-methyl-phosphonothioate);

GV-series compounds, which demonstrate properties inherent to both G and V series. A good example of those would be 2-dimethylaminoethyl-(dimethylamido)-fluorophosphate [9]. As a general rule, G-series compounds have more moderate levels of toxicity compared to V-series;

«Novichok»-series compounds – A230, A232 and A234, which are synthesized as a liquid and further converted into a powder by adsorption of liquid droplets on carriers such as silica gel, pumice, talc, etc. [12]. In [13] *Harvey et al.* reported that the chemical and enzymatic decomposition of OPC «Novichok» occurs slower compared to agents of G- and V-series. Currently there is a debate regarding the structure of these compounds, and therefore variety of different versions of the structures are assumed to be accurate.

It is known [2] that OPC easily cross epithelial and dermal membranes of the respiratory tract and are distributed in different parts and systems of living organisms, especially in adipose tissue. Most of the OPC undergo biotransformation through oxidation of functional groups - sulfur (parathion and malathion), thioether (eg, disulfoton), amides (schradan

and dichrotophos) and hydroxylation of the alkyl group (tri-o-cresylphosphate), yielding active derivative forms of the initial biologically inert compound.

A comprehensive understanding of OPC toxicity is fundamental to the development of decontamination techniques as well as effective therapies, therapeutic concepts, and treatment regimens. *Sidell et al.* note [17] that the primary mechanism of acute toxicity of OPC is covalent binding to the active site of acetylcholinesterase (ACE), which leads to inhibition of ACE and subsequently to the development of cholinergic crisis.

In studies published by *Worek* [16], OPC are classified as either nerve agents or ACE-inhibiting pesticides. ACE activity can be affected differently, as the specificity of the inhibitory action of organophosphorus agent depends on the nature of functional groups attached to the central phosphorus atom. In vitro determination of the bimolecular inhibition rate constants k_i, performed using isolated human ACE, makes it possible to quantify the inhibitory effect of specific agents, and can provide an initial assessment of the toxic potential of a particular OPC.

As shown in table 1 there is a significant range of k_i values, which indicate that, for example, chlorpyrifos oxone is a more potent metabolite than the neuroparalytic agent tabun. Knowing these characteristics one can run an initial rough assessment of potential toxicity in vivo. However, the actual in vivo toxicity, as established by *Rice* [18] and *Young* [19], is determined by a number of interrelated factors, including volatility, chemical and biological stability, lipophilicity, and the mechanism of action of a particular OPC.

Table 1 Kinetics of ACE inhibition by OPC

OPC	k_i	**OPC**	k_i
Fenamiphos	0.002	TEPP	59.7
Propophos	0.03	Methylsarin	105
Tetrachlorvinphos	0.03	Dimethyl-VE	125
Metamidophos	0.05	Leptophos	134
Monocrotophos	0.06	Tabun	182
Trichlorfon	0.07	Dimethyl-VX	222
Dicrophos	0.15	Chlorpyrifos-oxone	269
Omethoate	0.16	Ethylsarin	327
Etoprophos	0.23	Di-iso-propyl-VE	368
Heptenophos	1.38	PPDB	377
Bromfenvinphos	1.43	Sarin	398
Chlorfenvinphos	1.72	VE	433
Pirimiphos-methyloxon	2.81	Diethyl-VX	551
Dichlorvos	3.55	VX	1150
Profenophos	4.08	n-Propylsarin	1260
Malaoxon	4.74	Soman	1930
Mevinphos	6.64	n-Butylsarin	2790
N-diethyltabun	7.77	Chinese VX	3210
Dimethylamiton	8.57	n-Pentylsarin	3240
Paraoxon-methyl	11.3	Cyclosarin	4390
N-n-Propyltabun	11.8	Russian VX	4580
Amiton	18.9	sec-Pentylsarin	4870
Di-iso-propylamiton	27.4	iso-Butylsarin	5330

O-Methyltabun	32.1	iso-Pentylsarin	5460
Paraoxon-ethyl	33.0	n-Pentylsarin	9500

Vapor pressure and volatility of neuroparalytic agents largely determine the key pathway of their toxic influence. For example, *Worek* [16] and *Rice* [18] showed that due to its high volatility and water solubility, sarin has an increased percutaneous toxicity with delayed signs of poisoning. In general cases, OPC-pesticide poisoning occurs mainly orally, while its toxicity is determined by:

- Indirect conversion of organophosphontioates into active oxons as a result of exposure to cytochrome P450 [20];
- Specific inhibitory effect of OPC on ACE, which causes either rapid or delayed manifestation of toxic symptoms [21];
- Detoxification of the OPC and its active metabolite by endogenous enzymes such as paraoxonase [22];

lipophilicity of a pesticide as the main factor determining its stability in adipose tissue and long-term redistribution in the systemic circulation [23, 24].

OPC are characterized by significant variability of toxic effects, which depend on the structure and individual physicochemical and biological properties of a particular toxic substance (Table 2). Therefore, for the development of optimized decontamination systems it is necessary to take into account a significant number of variables [25].

Table 2 Differential toxic effects of OPC*

OPC	**Primary source of influence**	**Occurrence of intoxication**	**Stability of OPC**
Sarin	Inhalation	Rapid (minutes)	Low
Tabun	Inhalation	Rapid (minutes)	Low
Soman	Inhalation	Rapid (minutes)	Low
VX	Percutaneous	Delayed (hours)	High
Diazinon (parathion)	Oral	Rapid (minutes)	Moderate to high
Malathion, dimethoate	Oral	Delayed (hours)	Moderate to high
Profenofos	Oral	Delayed (hours)	Unknown

Note.* The extent of ACE inhibition is dose-dependent

As already noted, organophosphorus compounds (OPC) are mostly used as: components of chemical warfare agents [2], pesticides in agriculture (paraoxon (PO), methylparathion (MR), diazinon, chlorophos, metaphos, glyphosate), active pharmaceutical ingredients (armine, nibufin) [2, 6, 7, 13–18] (Fig. 2). While two of those categories have very specific and limited areas of application, exposure to pesticides poses a much more probable threat to general public, therefore their toxicity is a matter of numerous studies.

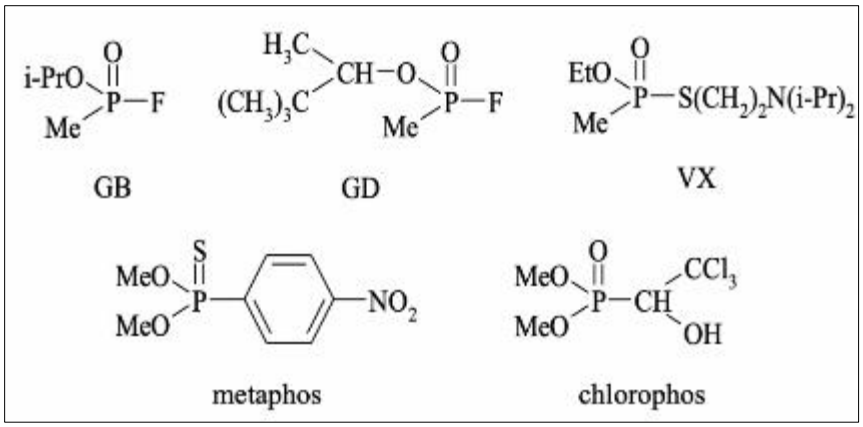

Figure 1 Structural formulas of organophosphorus compounds

Toxicity of organophosphorus pesticides has been studied in detail by *Davisson et al*. [26]. Based on their level of toxicity (Table 3), organophosphorus compounds can be classified as follows: extremely toxic (LD_{50} < 50 mg/kg): thiophos, octamethyl; highly toxic (LD_{50} – 200 mg/kg): methylmercaptophos, dichlorvos; moderately toxic (LD_{50} – 200–1000 mg/kg): chlorophos, carbophos, cyanophos; low-toxic (LD_{50} > 1000 mg/kg): bromophos, demuphos, temephos. The maximum allowable concentration for different organophosphorus compounds varies from 0.02 to 0.5 mg/m^3. Even in very small doses, OPC can disrupt vital organs and systems function, and cause lethality [27].

Within the framework of modern approaches to the search for chemically active components that rapidly and irreversibly break down OPC, special attention is paid to the creation of universal systems with oxidative nucleophilic mechanism of action. Thus, although nucleophiles are effective when one is working with esters and acyl halides of organophosphorus acids (GB), in order to effectively split substances such as VX or mixtures of compounds (GB and VX) oxidative nucleophilic systems are preferred [28, 29, 30].

Table 3 Estimated toxicity* of OPC [26]

Toxic compound	LD_{50} mg/kg of body mass	LC_{50}, ppm	LCt_{50}, mg·t/m^3	IDLH, ppm
GA (tabun)	1	2	100–400	0.03
GB (sarin)	1.7	1.2	50–100	0.03
GD (soman)	0.35	0.9	25–70	0.008
GF (cyclosarin)	0.03	–	–	–
VX	0.01	0.3	5-50	0.002

Note. * LD_{50} (percutaneously): the average lethal dose of a toxic substance required to kill half of subjects in the test population; LC_{50} (inhalation): the average lethal dose of a toxic substance required to kill half of subjects in the test population; LCt_{50} (inhalation): dose that will cause incapacitation rather than death; IDLH: concentration of toxin in the air, which is immediately dangerous to life and health.

Analysis of disposal methods [31–34] demonstrates several advantages of using systems based on hydrogen peroxide and its derivatives, given the dual nature of such compounds: as an α-nucleophile in the form of HOO^--anion [32] and as a soft oxidant in H_2O_2 form [34, 35].

3. Decontamination Methods for Organophosphorus Toxic Compounds

Important conditions for ensuring safety of OPC disposal process are: choose the most optimal disposal technology, comply with environmental and hygienic requirements for the organization and management of the process, control over the completeness of destruction.

The existing methods of OPC decontamination can be divided into four categories [1, 36, 37]:

- physical – methods aimed at removing the contaminant from any surface (biotic or abiotic), e.g., adsorption, dissolution, evaporation or leaching of the agent while maintaining its chemical structure;

- mechanical involves isolating toxic substances by covering it with sand or other inert material, and can be used in cases, where other methods are not available;
- chemical is the neutralization of the agent by means of chemical transformations (hydrolysis, alcoholysis, oxidation, reduction, etc.);
- enzymatic is carried out using enzymes that promote decomposition of OPC.

For more efficient and faster decontamination, combining physical and chemical methods is a recommended course of action - simultaneous removal and neutralization [1]. This approach should minimize the negative consequences for human health, and environmental risks. Recent trends in research and development of chemical protection against OPC usually imply the use of nanotechnology in the design of decontamination methods [1, 36]. Results of a study by *Carniato et al*. [37] demonstrated the catalytic activity of nanosized materials, including nano-clays, which have a significant surface area to adsorb toxic substances, and simultaneously accelerate the process of nucleophilic substitution.

3.1. Means for Individual Decontamination of OPC

The term "individual decontamination" should be understood as purification of contaminated areas of the body, clothing, materials and equipment immediately after contamination [38, 39].

Usually, individual decontamination of victims includes collecting liquid droplets by adsorbents, washing contaminated areas with water and detergent, chemical neutralization using available means [1, 37]. This whole set of procedures takes certain amount of time, which can have fatal consequences for both health and life of the victims.

Given the extreme toxicity of OPC (Tables 1–3), one of the main criteria for selecting a decontamination formulation is the rate of chemical decomposition of the substrate. Among the common technological approaches to the destruction of OPC, the most popular are alkaline hydrolysis using sodium hydroxide, oxidative chlorination with sodium hypochlorite, studied by *Affam et al.* [40], as well as alcoholysis by monoethanolamine or potassium butylate, described by *Sahu* [41] and *Tuorinsky* [42].

Singh et al. [43] investigated decontamination of OPC with a solution of sodium hypochlorite at a concentration of 0.5% for personnel and 5% for equipment. Such low concentrations of deactivator do not provide the required rate of decomposition of the toxic substance, while increasing them is impossible due to the strong irritating effect for eyes, skin, open wounds. Sodium hydroxide, in turn, breaks down organophosphorus esters yielding the corresponding phosphonic acids at moderate rates, but causes significant chemical burns to skin and eyes with consequences being irreversible in some cases. Combining hypochlorites with alkalis (93% calcium hypochlorite and 7% sodium hydroxide) makes a mixture characterized by high efficiency in decontaminating OPC [42]. Sodium phenolate or sodium cresolate, chloramines in alcohol solution, potassium permanganate and other chemical nucleophilic oxidizing compounds are also used to decontaminate OPC. Table 4 presents the composition of commercial decontaminants used in world practice in cases of exposure to organophosphorus toxic agents.

Information obtained from literary sources [36, 44, 45] suggests that a combination of physical and chemical methods of decontamination is usually used for decontamination of OPC. As a general rule, at first the substance will be adsorbed by Fuller's earth or other materials (clays, napkins). The collected material is then treated with decontamination systems to neutralize toxic substances, as shown by *Tazrart* [46] and *Thors* [47] *et al*.

Table 4 OPC decontamination systems

Commercial name	Chemical composition
DS2 [1]	70% diethylenetriamine, 28% 2-methoxyethanol, 2% sodium hydroxide
DF-200 [45]	Quaternary ammonium compounds, 8% hydrogen peroxide, glycerol diacetate
RSDL [48]	2,3-butanedione monoxime, Dekon 139, polyethylene glycol methyl ester
M291 [44]	0.5% sodium hypochlorite, 1% soap water
IPP-95 [38]	chloramine B, zinc oxide, magnesium stearate, zeolite, magnesium stearate, urea, silicone oil
IPP-8 [38]	ethoxyethanol, iso-propanol, dimethylformamide, sulfolane, sodium

The study published by *Worek* [16] provides data (Table 2), showing that the rate of distribution of nerve agent in the body is so high that decontamination and treatment should be carried out as early as possible: optimally during transportation to appropriate medical facilities [44]. At this stage, the importance of individual decontamination kits and requirements for those in terms of environmental safety and decontamination efficiency increase significantly. Individual kits must meet the operational requirements and therefore must have the best possible ratio of size, weight, ease of use and, of course, decontamination rate.

According to [49], the M258 skin decontamination kit (used in the United States since 1970) consists of two packages, one of which contains a napkin pre-moistened with phenol, ethanol, sodium hydroxide, ammonia and water; while the second one contains a napkin impregnated with chloramine-B and a sealed glass ampoule filled with zinc chloride solution.

M291 kit for skin decontamination, adopted by US military in 1989, is a non-woven fibrous applicator pad filled with absorbent and resin. Absorbent is a carbon compound with large contact surface area, applied to remove the product from skin. The resin itself consists of two ion exchange resins, one anionic and the other cationic, capable of neutralizing contaminant by hydrolysis reactions [44, 50]. This technology was used by US military until it was gradually replaced by RSDL reactive lotion for skin decontamination [48]. Its effectiveness is very low against VX and limited against soman compared to other decontamination methods [51, 52]. In addition, this method is not suitable for treating eyes and open wounds.

RSDL is one of the solutions provided to civil security personnel to address the problem of local impact of OPC [49]. The technical solution is made up of a sponge, separately packaged and impregnated with a solution containing diacetylmonoxim and Decon 139 – a patented mixture dissolved in monomethyl ether of polyethylene glycol [53]. This composition allows to desorb neurotoxic agent from the skin and chemically decompose it by a nucleophilic reaction. For V- and G-series agents, the time required to complete decontamination is less than three minutes [54]. Its effectiveness exceeds that of M291 against agents such as VX and soman [51, 52]. RSDL protection factor against VX (defined as the ratio of LD_{50} for the treated group to that of the untreated group) in guinea pigs is approximately 60 times higher than M291 factor (66,4 and 1,1 respectively) [51]. Against soman protection factor for RSDL is 5 times higher than that of M291 (14 and 2,7 respectively) [52]. RSDL is effective for decontaminating the skin if applied a few minutes after exposure. Same as M291, RSDL is strictly prohibited for treating eyes and open wounds [44].

The effect of Fuller's earth decontamination system is based only on passive physical adsorption of OPC. Fuller's earth mainly consists of fine aluminum silicate powder with large surface area, which provides good local adsorption of contaminants [55].

There is information [49] regarding the development of barrier decontaminant cream based on perfluorocarbon compositions. This cream, applied to skin with a layer thickness of 0.15 mm, should provide protection against liquid organophosphorus agents, including HD, Lewisite, GD and VX for at least four hours. To increase decontamination efficiency of the cream, attempts were made to include into its composition several oxidative-nucleophilic and enzymatic components [49]: polyoxometalates, cross-linked enzyme crystals (hydrogen phosphorus hydrolase and phosphoric acid anhydrolase), nanometal oxides (MgO, CaO, TiO_2, MnO_2), metal alloys with polymer coating (titanium-iron-manganese, manganese-nickel, calcium-nickel), potassium persulfate, metals with zero valence (iron-palladium, zinc-palladium), 2,3-butanedione monoxime, thermophilic bacterial enzymes and benzoyl peroxide. Even after introducing various modifications, barrier decontamination cream did not find wide use for chemical protection, because the extreme thickness of cream layer, as well as direct prolonged contact of chemicals with the skin, pose a serious limitation – they interfere with normal integuments function.

Decontamination of equipment, premises and areas is usually carried out using harsher chemicals [1, 49]. DS2 is an organic liquid consisting of 70% diethylenetriamine, 28% ethylene glycol monomethyl ether and 2% sodium hydroxide. Decontamination component here is a conjugated $CH_3OCH_2CH_2O^-$ base with high levels of nucleophilicity. DS2 is a highly effective OPC decontaminant, but ethylene glycol monomethyl ester demonstrates teratogenicity in mice. As a result of interaction between DS2 and mustard gas, hydrogen chloride is released, while reactions with GB agents occur through the formation of diesters with their subsequent decomposition into the corresponding phosphonic acids.

Standard decontaminators for equipment usually include hypochlorite bleaches. One example of such compositions is a mixture of 93% calcium hypochlorite and 7% sodium hydroxide described by *Wartell* [49]. Bleach reacts with mustard gas by oxidizing sulfide to sulfoxide and sulfone, while simultaneously a dehydrochlorination reaction occurs resulting in formation of non-toxic compounds. G-agents are converted by hydrolysis into the corresponding phosphonic acids. In turn, in an acidic solution VX is rapidly oxidized at the sulfur atom and decomposes through the protonation of

nitrogen atom. However, at high pH values, the solubility of VX is significantly reduced, and deprotonated nitrogen is oxidized, which leads to the consumption of oxidant exceeding the stoichiometric amount.

C8 German decontamination system [1, 44] is a microemulsion that consists of 76% water, 15% tetrachlorethylene, 8% calcium hypochlorite and 1% mixture of anionic surfactants. Due to its solubilizing properties, C8 increases the solubility of OPC, yet it contains chlorinated hydrocarbons, resistant to decomposition in the environment, and forms toxic by-products such as vinyl chloride – a known carcinogen [49].

Currently there is a lack of non-corrosive solutions acceptable for decontamination of both sensitive equipment and personnel. Most of the available methods can eliminate the threat of OPC poisoning, but then themselves cause a catastrophic chemical contamination. Therefore, it is extremely important to choose methods that allow rapid sequestration and destruction of neurotoxic agents an at the same time ensure the formation of harmless OPC breakdown products.

Common disadvantages of these methods of chemical detoxification are also: toxicity of materials used, multicomponent composition (some systems are supplied in two or three components) and low reactivity of decontaminants. It is possible to increase the rate of OPC decomposition by using α-nucleophiles [56–58], a typical representative of which is peroxide anion HOO^- and its derivatives – peroxoanions.

In addition to its high reactivity, hydrogen peroxide (H_2O_2), as a decontamination agent, provides versatility of action by nucleophilic and oxidative mechanisms, and meets the basic norms and requirements of "green" technologies, the so-called «Decon Green» systems [56]. The use of solid sources of hydrogen peroxide - peroxysolvates, reactivity of which with OPC was studied in detail [56, 59], opens new prospects for creating effective decontamination systems suitable for long-term storage.

In study by *Vakhitova et al*. [59] the following DS system was chosen for OPC decomposition: urea hydrogen peroxide / boric acid / cetylpyridinium chloride, as it best meets aforementioned requirements. Garamite 7303 and Cloisite Na^+ nanoclays were added to the decontamination system in order to enhance levels of adsorption of organophosphorus substrates from contaminated surfaces, and their solubility. The choice of system components was not random, it was based on prior research results [60–62]. Urea hydrogen peroxide ($CO(NH_2)_2 \cdot H_2O_2$, UHP) was used as the nucleophile. It is known that hydrogen peroxide, in forms of H_2O_2, HOO^--anion or peroxoanions, demonstrates high reactivity and universality of action against ecotoxicants of two main types – mustard gas analogues, and pentavalent phosphorus compounds [60]. However, the use of concentrated aqueous solutions of H_2O_2 for applied purposes creates additional risks during storage and transportation, as well as for operation at subzero temperatures. Therefore, it is advisable to use solid (anhydrous) reactants, such as UHP, as an alternative sources of H_2O_2; it is an industrially produced non-toxic, storage-stable crystalline substance.

Table 5 demonstrates the values of apparent second-order rate constants of nucleophilic substitution reactions for paraoxon (PO) and methyl parathion (MP) (k_{HOO^-}, $M^{-1}s^{-1}$) in the studied reaction medium – DS decontamination system. Due to the complex mechanism of chemical transformations in micellar systems in the presence of boric acid and nanoclays, the constants are calculated based on the total concentrations of HOO^- anion at fixed pH levels of the decontamination system.

Table 5 OPC deactivation rate k_{HOO^-} ($M^{-1}s^{-1}$) for various decontamination systems

Decontamination system	**k_{HOO^-}, metal**	**k_{HOO^-}, polystyrene**	**k_{HOO^-}, cloth**	**$\tau_{1/2}$, s***
Paraoxon				
DS [59]	19.4	20.6	23.0	17
Methyl parathion				
DS [59]	16.1	18.6	20.5	20
VX-series OPC				
Decon Green [63]: 0.75 M $NaHCO_3$, 0.743g UHP, 1.0 ml t-BuOH, 1 ml H_2O	–	–	–	450
M291 [44]	–	–	–	90

DS2 [1]	–	–	–	600**
DF-200 [45]	–	–	–	600***

Note: *calculated for [UHP] = 1 M; **conversion > 99,9%; ***97,8 % conversion.

A comparison of the half-lives ($\tau_{1/2}$, s) of PO and MP in DS systems [59] with those in known and NATO units-used decontamination systems (M291 [44], DS2 [1], DF-200 [45]) shows that decontamination rates in the suggested solutions are either higher or not inferior. The suggested systems based on a solid source of hydrogen peroxide have advantages in terms of environmental safety, manufacturability, chemical stability.

Regardless of how universal of an agent H_2O_2 is, its application is associated with several potential limitations. Those include: the low solubility of hydrophobic substrates in aqueous media – the most favorable type of media from the standpoint of "green" chemical engineering; the fact that the maximum rate of oxidation reactions in studied reaction media can only be achieved at different levels of acidity than those required for efficient nucleophilic substitution in the same system; and lastly, the unsatisfactory reactivity of hydrogen peroxide in the sulfoxidation of mustard gas analogues [15].

This issue was addressed using the nucleophilic degradation of paraoxon (O,O-diethyl-O-(4-nitrophenyl) phosphate) and the oxidation of methylphenyl sulfide as model systems. The efficiency of decontamination was investigated for blistering and nerve agents. Hydrogen peroxide solutions in "oil-in-water" type microemulsions were chosen and studied as reactive decontamination systems, which additionally contained Laponite EP synthetic nano-clay and polyvinylpyrrolidone. The base of the microemulsion consisted of: an aqueous phase, a co-surfactant (isopropanol), a non-polar phase (hexane), and various surfactants – cetylpyridinium chloride, sodium dodecyl sulfate, and Triton X-100.

It was shown that in the studied microemulsions, the solubility of paraoxon and methylphenyl sulfide increased on average by a factor of 100 or more compared to their solubility in water. Moreover, the substrate binding constants were 2-3 times higher than those in similar microemulsion systems. It was found that the presence of nano-clay in the microemulsion provides a catalytic effect by at least doubling the decomposition rate of paraoxon and methylphenyl sulfide. In addition, the nano-clay additive thickens the microemulsion and, together with the polymer, increases the viscosity of the reaction medium, which was beneficial for the system's efficiency. Kinetic parameters of decontamination and substrate solubility, determined by the authors of the reviewed study, allow to conclude that the use of the studied microemulsion system accelerates nucleophilic substitution and oxidation reactions by a factor of 150–350 compared to the reaction rates in water.

4. Conclusion

Despite the general compliance with the requirements of Chemical Weapons Convention and various Directives governing the range, use and circulation of organophosphorus pesticide compounds, there is a risk of contamination with these toxic substances for both population and environment. The most dangerous of all OPC are organophosphorus neurotoxic agents, as poisoning with such agents leads to irreversible consequences. According to scientific sources covered in this review, to date there are no universal decontamination systems for individual use, which would've guaranteed rapid and effective decontamination and degradation of OPC.

From the analysis of literature data on the comparison of different decontamination systems, the following conclusions can be drawn: systems based on hydrogen peroxide are effective decontaminants for OPC, which at the same time are mild in nature and environmentally safe; introduction of activators (bicarbonates, borates, etc.) into the system drastically increases reactivity of hydrogen peroxide due to the formation of active peroxoanions; modified aluminosilicates accelerate the process of OPC decomposition; relative instability of peroxoanions requires additional research on the alternative ways to optimize decontamination systems.

Compliance with ethical standards

Disclosure of conflict of interest

There is no conflict of interest.

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