Active and Strippable PVA/Borax/NaBO₃ Hydrogel for Effective Containment and Decontamination of Chemical Warfare Agents

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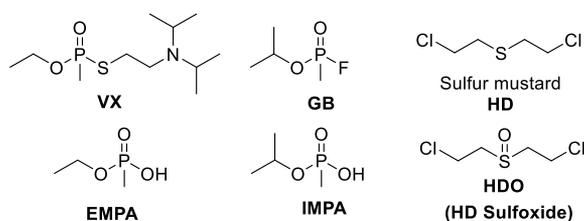ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Active gels present unique potential for the decontamination of chemical warfare agents (CWAs) as they strongly adhere to surfaces, thus allowing prolonged decontamination time. Herein, we present a decontamination hydrogel based on polyvinyl alcohol/borax, which contains sodium perborate (NaBO₃), as an in situ source of the active ingredient hydrogen peroxide. Developed as a binary formulation, this gel instantly forms and effectively sticks when sprayed on various matrices, including porous and vertically positioned matrices. The gel efficiently detoxified the CWAs sarin (GB), O-ethyl S-2-(diisopropylamino)ethyl methylphosphonothioate (VX), and sulfur mustard (HD) in test tubes (2 μL CWA/0.5 mL gel) to provide nontoxic products with reaction half-lives of <3, 45 and 113 min, respectively. The gel was also shown to efficiently decontaminate surfaces contaminated with VX (5−7 mg, 8−12 mL of gel, i.e., >99%) and to prevent GB evaporation, as proven by laboratory wind tunnel experiments. The universal decontamination abilities of this mild hydrogel, as well as its facile application and removal processes suggest that it holds high potential for future development as a new CWA decontamination tool.
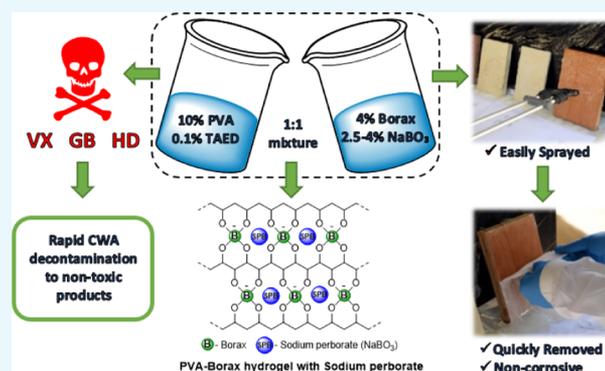
INTRODUCTION

Effective methodologies for the decontamination of chemical warfare agents (CWAs), such as the organophosphorus nerve agents O-ethyl S-2-(diisopropylamino)ethyl methylphosphonothioate (VX) and sarin (GB, isopropyl methylphosphonofluoridate), as well as the blister agent sulfur mustard (HD, bis(2-chloroethyl)sulfide), are required as evident from the recent usage of these extremely toxic and persistent chemicals (Figure 1).[1,2] Over the years, a plethora of formulations have been developed to effectively address these types of contamination scenarios.[3−5] These formulations include, for example, solutions based on hypochlorite, sodium hydroxide, and alkoxide/amine bases featuring a corrosive nature (suitable for terrain and infrastructures), as well as more delicate formulations, such as active powders and gels for indoor surfaces.[6,7] Gels specifically present a unique potential for the decontamination of vertical surfaces as they adhere to the contaminated platform while neutralizing the CWA, in contrast to active solutions that drip from the platform directly. Various gel formulations have been proposed by us and others over the years for mild decontamination purposes. These formulations include gels based on oxone and fumed silica (L-Gel),[8] polyalkylamines,[9] hypochlorite,[10] organogels containing oximate or peroxides,[11] ionic liquids[12] and polysaccharide hydrogels containing active fluoride species.[13,14] Notably, the decontamination gels reported to date were either corrosive, nonuniversal, and/or not strippable or required complicated removal methods. Aiming to achieve a hydrogel that would avoid such disadvantages, we have developed a new oxidizing decontamination gel based on polyvinyl alcohol (PVA)/Borax and sodium perborate as the active ingredient. PVA polymers are nontoxic, hydrophilic, biocompatible, and biodegradable[15]

Figure 1. CWAs used in this study and their decontamination products.

Table 1. Degradation Rates of VX, GB, and HD at 25 °C Using Various Compositions of PVA/Borax/NaBO$_3$ Active Gels

	gel components				$t_{1/2}$ [h]		
entry[a]	NaBO$_3$ [wt %]	TAED [wt %]	SDBS [wt %]	EG [wt %]	VX	HD	GB
1	1.25	0.05	0.25		0.5	NA[b]	<0.05
2		0.05	0.25		>22.3[c]	NA[b]	<0.05
3	1.25		0.25		0.6		
4			0.25		>3.6[d]		
5	1.5	0.05	1.5		2	6.3	<0.05
6		0.05	1.5		>24.6[e]	NA[b]	>0.05[j]
7	1.5	0.05			0.6		
8		0.05			>23[f]		
9	1.5		1.5		1.3	NA[b]	
10			1.5		>22.5[g]	NA[b]	
11	2	0.05	1.5	15	0.7	1.8	<0.05
12		0.05	1.5	15	>72[h]	NA[b]	>0.3[k]
13	2		1.5	15	0.9	2.9	
14			1.5	15	>5.7[i]	NA[b]	

[a]All formulations contained a total of 5 wt % PVA and 2 wt % borax with additives as indicated. [b]NA−not available - these values could not be obtained as HD was not miscible. [c]At 22.3 h, 79% VX, 14% EMPA, and 7% desethyl-VX were observed. [d]At 3.6 h, 97% VX and 3% EMPA were observed. [e]At 24.6 h, 91% VX, 6% EMPA, and 3% desethyl-VX were observed. [f]At 23 h, 90% VX, 8% EMPA, and 2% desethyl-VX were observed. [g]At 22.5 h, 97% VX and 3% EMPA were observed. [h]At 72 h, 78% VX, 18.5% EMPA, and 3.5% desethyl-VX were observed. [i]At 5.7 h, 100% VX were observed. [j]At 0.3 h, 22% GB was still present. [k]At 0.3 h, 90% GB was still present.
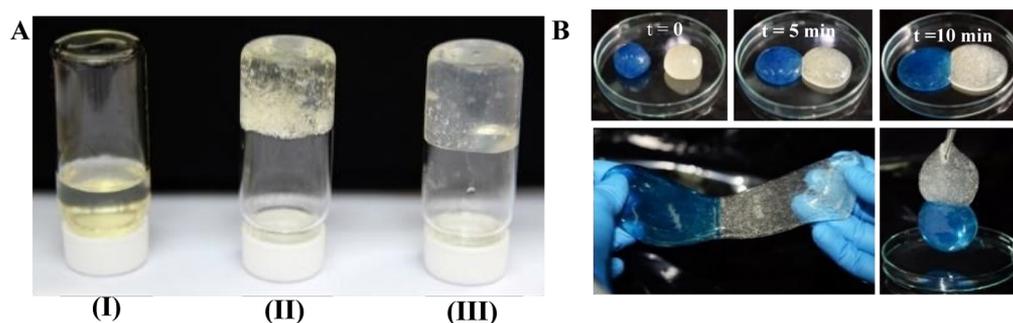
Figure 2. (A) Tube inversion test of (I) solution A and (II) active hydrogel, t = 0. (III) Active hydrogel, t = 2 weeks. (B) Self-healing ability of the PVA/borax/NaBO$_3$ hydrogel. To differentiate between the two hydrogel units, one was colored blue.

and hence seemed optimal for the intended purpose. To the best of our knowledge, these types of polymers have never been used in the context of CWA decontamination. PVA-based gels are typically formed by mixing PVA and borax. In water, the latter hydrolyzes to boric acid and tetrahydroxyborate anion to provide a buffer solution of pH ~ 9, which is noncorrosive. The borate anion further cross-links PVA to afford a hydrogel (Scheme S1 in the Supporting Information).[16] Because of their nontoxic and noncorrosive nature, peroxides are considered attractive decontaminants.[4] Among these types of derivatives, hydrogen peroxide has been extensively studied for its ability to decontaminate CWAs.[17−23] As it decomposes to water and oxygen, this reagent is regarded as environmentally friendly and has accordingly been used as the basis of various decontamination agents, such as Decon Green and DF-200.[17,19,24] However, the use of hydrogen peroxide has a few limitations, such as its instability in prolonged storage and difficult shipping and handling. With the aim of using peroxide chemistry while circumventing the disadvantages of hydrogen peroxide, we envisaged that sodium perborate (NaBO$_3$) could be utilized. As a solid generator of hydrogen peroxide, NaBO$_3$ features better storage stability, a longer shelf life, and easier handling.[25] Furthermore, it is a commercially available inexpensive reagent, is frequently added to household laundry detergents,[26] and is

used as a tooth bleaching agent.[27] NaBO$_3$ was previously shown to be effective in the degradation of organophosphate esters, including pesticides.[4,28] Herein, we describe the development of a PVA/borax/NaBO$_3$ oxidizing gel that effectively decontaminates CWAs and features facile application and removal.

RESULTS AND DISCUSSION

Gel Formulation Development. A gel that is easily sprayed seemed advantageous with respect to its application. Toward that goal, a binary system composed of two separate solutions that form a gel immediately upon contact on the desired surface was envisaged. To allow easy and reproducible spraying of such solutions, in the development process, their low viscosity and homogenous nature were emphasized. Various combinations of PVA (solution A) and borax (solution B) solutions differing in parameters such as the PVA molecular weight (MW), PVA weight percent, borax weight percent, and PVA/borax ratio were thus examined (Table S1 in the Supporting Information). NaBO$_3$, which dissociates in water to afford hydrogen peroxide and tetrahydroxyborate, a native part of the gel, was selected as the gel active ingredient (Scheme S1d in the Supporting Information). To further increase the gel's potential decontamination activity, a minute

amount of tetraacetylethylenediamine (TAED), which is known to accelerate the release of hydrogen peroxide from $NaBO_3$, was added.[29] Moreover, acyl transfer from TAED to hydrogen peroxide yields peracetic acid (PAA, CH_3CO_3H, Scheme S2 in the Supporting Information), a highly efficient oxidizing agent by itself.[18,26,30] A small amount of sodium dodecylbenzene sulfonate (SDBS) was also incorporated for the purpose of assisting in the dissolution of hydrophobic materials such as HD in aqueous media. Following the abovementioned optimization studies, the ideal formulation with respect to the gel physical characteristics was found to be a 1:1 mixture of the following aqueous solutions: solution A [10 wt % PVA (MW 22 KDa), 0.1 wt % TAED] and solution B (4 wt % borax, 2.5 wt % $NaBO_3$, 0.5 wt % SDBS); once the solutions are mixed to form the gel, the percentages of ingredients are divided by two (Table 1). TAED and $NaBO_3$ were deliberately incorporated into different solutions so that they would only meet once sprayed on the desired surface to generate the active species. Significantly, this gel formulation contains over 90% water, and the reagents added are common, inexpensive, and commercially available.

Surface Adhering Properties. The ability of the developed hydrogel to adhere to surfaces was first evaluated using the tube inversion test at 25 °C. Solutions A and B were thus placed in the same vial with no stirring to form the gel immediately. Direct flipping of the vial showed that the hydrogel strongly adhered to its glass walls and did not flow [Figure 2A(II)]. Solution A, in contrast, exhibited lower viscosity and instant flow upon inversion [Figure 2A(I)]. The strong adherence exhibited by a 2 week-old gel demonstrated the stability of the gel over time [Figure 2A(III)].

In addition to providing adherence, a gel should optimally provide full coverage of the contaminated surface. Self-healing is essential in that respect, as it allows the sprayed hydrogel to spread and fill up any empty spots left uncovered. To test this feature, two units of the hydrogel were placed on a glass surface 1 cm apart. As shown in Figure 2B, after only 5 min, the gel units adapted to the shape of the surface while autonomously moving toward one another until achieving contact. After a total of 10 min, the units adhered into one hydrogel, which was lifted and stretched without any rupture, showing that the hydrogel self-healed effectively. Next, the ability of the hydrogel to adhere effectively to and be removed easily from various matrices was examined. Accordingly, it was applied on a variety of vertically positioned surfaces relevant for indoor as well as outdoor decontamination scenarios. These surfaces included a glass window, wood, granite porcelain, marble, stainless steel, and smooth white-painted metal for the former type of decontamination and commercial red sidewalk brick, asphalt, polyurethane chemical agent resistant coating (CARC) painted metal, rough metal, and concrete for the latter. Solutions A and B were sprayed simultaneously on the surfaces to achieve full gel coverage (for details on the spraying device and all surfaces at different stages of the experiment, see Figure S1 and Table S2 in the Supporting Information). Gratifyingly, the gel adhered well to all surfaces and remained stable for 24 h, which was determined as the end point of the experiments. At that time, the gel was easily peeled from all surfaces, even from the more porous surfaces, such as asphalt and rough metal (Figure 3). Importantly, the surfaces were not damaged, suggesting that in accordance with its mild basic pH, the gel is indeed noncorrosive. Further exploration of the hydrogel abilities to
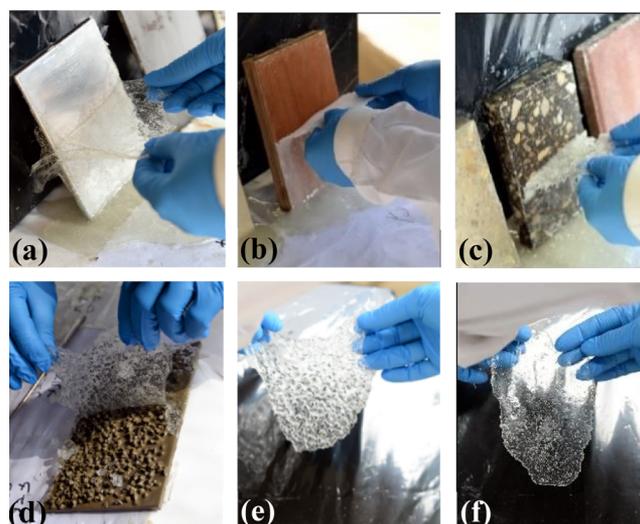
Figure 3. Gel removal after 24 h from various surfaces: (a) stainless steel, (b) wood, (c) asphalt, (d) rough metal. (e) Film of gel after removal from rough metal. (f) Film of gel after removal from smooth painted metal.

adhere, self-heal, and be pilled in various environmental conditions such as range of temperatures, humidity, and types of surfaces should be performed toward the advancement of the gel practical application.

Decontamination Studies in Test Tubes. As mentioned, our main target was to develop a gel that would effectively and universally decontaminate CWAs, namely, V agents, G agents, and blister agents, which are diverse in their nature. The ability of the gel to do so was examined by studying the decontamination kinetics of VX, GB, and HD, as representatives of these CWA families, in test tubes using ^{31}P and ^{13}C NMR. To assess the contribution of each gel component to the decontamination process, experiments lacking specific ingredients were also performed. Table 1 summarizes the degradation rates of the different CWAs obtained at 25 °C, when using the various gel formulations (for NMR spectra and data analyses, see Figures S2−S33 in the Supporting Information). The initial conditions (entry 1) were found to be highly effective for the decontamination of VX and GB, with reaction half-lives of 0.5 and <0.05 h, respectively. As expected, $NaBO_3$ was found to be essential for VX decontamination (entry 1 vs 2), unlike TAED, whose absence did not affect the reaction rate (entry 3). In the case of GB, however, similarly high rapid reaction rates were observed in the presence or absence of sodium perborate (entries 1 and 2, respectively). The hydrophobic blister agent HD was not miscible in the gel aqueous media despite the presence of SDBS, as was evident from its appearance as visible droplets; and accordingly, it was not decontaminated (entry 1). To address this issue, a gel formulation containing 6 times more SDBS than the initial conditions was developed (entry 5). Advantageously, the higher surfactant wt % enabled the addition of a slightly increased amount of sodium perborate. Indeed, these adjustments improved HD solubility (no droplets were observed in the test tube), affording its rather effective decontamination ($t_{1/2}$ = 6.3 h, entry 5). $NaBO_3$ was found to be essential for HD decontamination, as was observed with VX (entry 5 vs 6). TAED was also found to be important, as without this compound, HD decontamination did not occur (entry 9). GB decontamination was as fast as that obtained with the starting

conditions, although raising the amounts of sodium perborate and SDBS (entry 5 vs entry 1). In the case of VX, however, a slower reaction rate was obtained, namely, a $t_{1/2}$ of 2 h (entry 5) versus 0.5 h (entry 1). To verify that the increased amount of SDBS was responsible for the decrease in reaction rate, an experiment was also performed in the absence of SDBS (entry 7). Indeed, under these conditions, a shorter half-life of 0.6 h was obtained. Evidently, for VX decontamination, a small amount of this detergent is beneficial over an excess. To further improve the gel activity in both VX and HD decontamination, the addition of an organic cosolvent was next examined (entry 11). Various solvents, including ethanol, propylene glycol, 1-propanol, diethylene glycol monoethyl ether, dimethylsulfoxide, glycerol, isopropyl alcohol, PEG 400, and ethylene glycol (EG), were tested for their ability to promote the solubility of a known HD simulant (2-chloroethyl ethyl sulfide, CEES) in the gel. These studies suggested that EG is the optimal cosolvent for that purpose. Adding 30 wt % EG to solution B also allowed the dissolution of an increased amount of sodium perborate. Indeed, the formulation thus formed (entry 11) led to improved HD decontamination with a reaction half-life of 1.8 h, fast GB decontamination as previously obtained (<0.05 h), and high VX decontamination activity (0.7 h). The surface adherence and self-healing properties of this improved formulation was next examined as described above. Importantly, although presenting a slightly different texture, the gel formulation exhibited similar physical properties to those observed before.

Our three main gel formulations (entries 1, 5, and 11 of Table 1) were termed formulations I, II, and III, respectively (Table 2). Formulation III, which contains EG as a cosolvent,

provided the desired broad-spectrum decontamination of all three types of CWAs, with t_{total} values (time at which complete destruction of the agent was observed) of <0.2 h for GB, 3.9 h for VX, and 10 h for HD. These results are more than satisfactory, considering the proven ability of our gel to stick and cover surfaces for prolonged time (over 24 h).

Decontamination of Surfaces. Following examination of the activity of the gel in test tubes, we determined its ability to contain and decontaminate CWAs applied on surfaces. VX, the most toxic, most persistent, and least volatile CWA among those examined in this study, was accordingly spread (1.2 g/m^2) on both inert (glass) and porous (painted metal) surfaces. The surfaces were then simultaneously covered with formulation I solutions (2 L/m^2) to instantly provide full coverage of the matrices by the gel. After a period of 6 h, the gels were peeled off, and the surfaces were washed to extract any remaining VX. As controls, identical surfaces were contaminated without gel application, and VX was extracted using the same protocol. GC analyses of the extraction solutions showed that the gel effectively decontaminated these matrices, that is, 99.7 and 99.2% decontamination of the glass and metal surfaces, respectively, relative to the control (Table S3 in the Supporting Information). NMR analysis of the same solutions showed that ethyl methylphosphonic acid (EMPA) was the sole product obtained in this process. Namely, the gel effectively adsorbed and, based on our test tube studies, actively decontaminated the CWA from the contaminated surfaces.

Gel Containment/Sealing Properties. Next, we were interested in evaluating the capability of the gel to seal off a CWA and/or lower the concentration of the CWA in the air above a surface being decontaminated. To do so, we performed a set of experiments in our specialized laboratory-sized wind tunnel, which simulates evaporation of materials from matrices in an accelerated manner.[31] Accordingly, the conditions inside the wind tunnel include suction and high wind speed (1.6 m/s), which are challenging conditions for the hydrogel activity because the hydrogel is composed of more than 90% water, which may evaporate. GB was selected as the CWA for these experiments because of its rather low boiling point and expected quick evaporation, which we assumed would challenge the gel sealing capability.[32] Three separate experiments were performed at 25 °C. In each experiment, an inert

Table 2. Degradation Rates of VX, GB, and HD Using PVA/Borax/NaBO$_3$ Active Gel Formulations I−III

| formulation	VX		HD		GB	
	$t_{1/2}$ [h]	t_{total} [h]	$t_{1/2}$ [h]	t_{total} [h]	$t_{1/2}$ [h]	t_{total} [h]
I[a]	0.5	3.5	NA[d]	NA[d]	<0.05	<0.2
II[b]	2	3.6	6.3	>24[e]	<0.05	<0.2
III[c]	0.7	3.9	1.8	10	<0.05	<0.2

[a]Table 1, entry 1. [b]Table 1, entry 5. [c]Table 1, entry 11. [d]NA−not available - these values could not be obtained as HD was not miscible. [e]At the indicated time, 6% HD was observed.

Figure 4. (A) Evaporation profile of GB at 25 °C from stainless steel surfaces covered with formulation I hydrogel (green), commercial pad (blue) or uncovered control (red). The concentration of GB above the commercial pad covered surface is higher than that above the uncovered surface. The reason for that observation is that most (~70%) of the GB from the uncovered surface evaporated in the first 10 min of the experiment and respectively a much lower amount of GB remained on it to evaporate along the experiment time. (B) GB mass balance obtained over 24 h from the stainless steel surfaces.
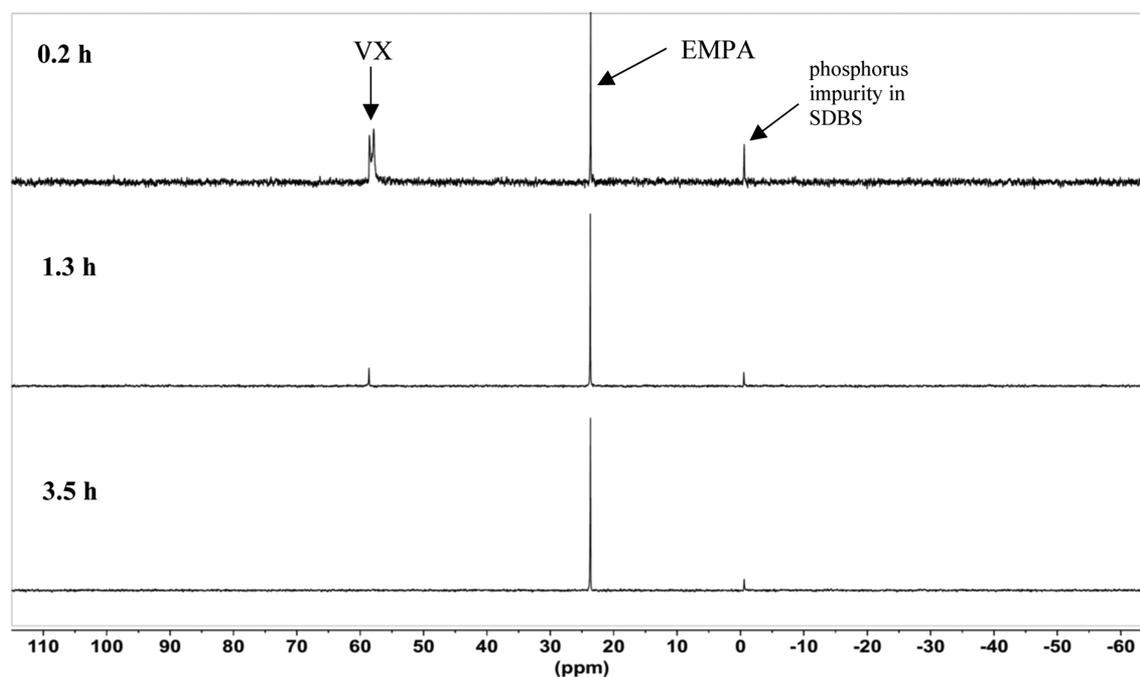
Figure 5. Selected ^{31}P NMR spectra presenting the degradation profile of VX by formulation I gel (Table 2, entry 1).

stainless-steel surface was contaminated with GB. In the first experiment, the surface was covered immediately with formulation I gel and introduced into the wind tunnel for continuous monitoring. The other two experiments included applying a commercial containment pad (holding a polyethylene layer) over the contaminated steel surface and a control where no form of coverage was applied. As seen in Figure 4A, despite the challenging conditions, the gel was able to immediately reduce the concentration of GB in the air by 2 orders of magnitude relative to the uncovered control and the commercial pad-covered surfaces. Furthermore, after only 12 h of decontamination, the concentration of GB in the air above the hydrogel was lower than the American threshold for exposure limit for the general population (GPL, 0.003 ng/L air).[33] In the other two experiments, however, this value was not reached even after 24 h. Figure 4B presents the mass balance results for these experiments, that is, the total amount of GB evaporated from the surfaces over 24 h. For the uncovered control and commercial pad-covered surfaces, almost all of the initially deposited GB (i.e., 92 and 100%, respectively) was collected by the system. In the case of the hydrogel-covered surface, however, only 3.6% was collected. These data suggest that 96.4% GB was actively decontaminated by the gel; and while doing so, the gel prevented GB evaporation from the surface, dramatically lowering its concentration in the air.

Decontamination Mechanisms. With respect to the decontamination mechanisms, both perhydrolysis (VX, GB) and oxidation (HD) appear plausible. In alkaline solutions such as those of the gel formulation (pH ~ 9), a significant part of the formed hydrogen peroxide is predicted to be in equilibrium with perhydroxyl anion (HOO$^-$, Scheme S1d in the Supporting Information). This anion is known to be extremely reactive toward organophosphate esters, that is, 10−100 times more reactive than hydroxide ion because of its α-nucleophilicity.[28,34] Accordingly, it is assumed that this anion is the major active species responsible for the gel's ability to

decontaminate VX and GB via perhydrolysis.[17,23,35] VX was previously shown to undergo rapid perhydrolysis by perhydroxyl anion to provide EMPA, while formation of the undesirable toxic compound S-2-(diisopropylamino)ethyl methylphosphonothioic acid (desethyl-VX), obtained through P−O bond cleavage, was avoided.[35] Consistent with a mechanism of VX perhydrolysis (Scheme S3A in the Supporting Information), the reactions with all three gel formulations (I−III, Table 2) led solely to EMPA, either directly or via a VX-oxide (VX-NO) derivative.[13,17,36] Toxic desethyl-VX was not observed (Figure 5).[13,36] The hydrolysis of VX in basic solutions is less effective and yields a part of EMPA a significant amount of desethyl-VX.[17,22,36] Indeed, we found that in the absence of NaBO$_3$, the mild basic media of the gel led to significantly slower VX hydrolysis rates, and in some cases, desethyl-VX was formed (Table 1, entry 2 and Figure S3 in the Supporting Information).

G agents can be detoxified rapidly by both perhydrolysis and alkali hydrolysis to provide isopropyl methylphosphonic acid (IMPA, Scheme S3B in the Supporting Information).[21,34a] Evidently, in all three gel formulations (I−III), nontoxic IMPA was obtained quickly as the sole product (Figures S16−S19 in the Supporting Information).[37] Interestingly, in the case of formulation I, hydrolysis in the absence of NaBO$_3$ was as fast as the reaction with NaBO$_3$ (Table 1, entries 1−2). Apparently, the fluoride atom, which serves as the leaving group, is labile in the mild basic formulation solutions (pH ~ 9), such that hydrolysis is quickly obtained, even without an additional active ingredient. In the case of formulations II and III, however, decontamination was much less effective in the absence of NaBO$_3$. The addition of detergent and mostly organic solvent evidently slowed the rate of hydrolysis (Table 1, entries 6 and 12).

Decontamination of HD using formulations II and III proceeded through an oxidation route, as evident from the products obtained, mainly the nonvesicant sulfoxide HDO,[17,18] as well as thiodiglycol sulfoxide (TGO) and thiodiglycol

sulfone (TGO$_2$)[20] derived from an additional oxidation step (Scheme S3C and Figures S20−S22 in the Supporting Information). In the case of formulation II (entry 5), divinyl sulfoxide was also obtained. The vesicant sulfone HDO$_2$ was not observed at any stage.[20] With respect to the active species, the oxidation of HD may be facilitated by either hydrogen peroxide, PAA, or both.[30b,38] As the presence of TAED appears to be important for the effective decontamination of HD (see entry 11 vs 13), it is assumed that PAA has a significant role in that process. In the absence of NaBO$_3$, although actual kinetic data could not be obtained because of limited solubility, the NMR spectra depicted a different profile of products, that is, mostly thiodiglycol (TG) and chlorohydrin TG (CH-TG), which are indicative of a basic hydrolysis mechanism (Scheme S4 and Figure S23 in the Supporting Information).[4]

CONCLUSIONS

A CWA decontamination hydrogel based on PVA/Borax, which contains sodium perborate as an active ingredient, was developed. These gel components and the additives (TAED, SDBS, and EG), are common, safe, environmentally benign, and frequently included in household products.[39−41] Importantly, once the binary formulation of the gel is mixed, the gel instantly forms; and hydrogen peroxide and PAA, powerful oxidants, are generated in situ, avoiding the need for their direct handling. These active species enabled the gel to effectively detoxify VX, GB, and HD. In accordance with its broad-spectrum CWA decontamination abilities, mild nature, and easy application and removal without specialized equipment, we believe that our gel holds great potential for future development as a new universal decontamination tool. Because the active components of the gel are known disinfectants, we expect our gel formulations to also be effective in the decontamination of biological threats. This aspect is currently being examined and will be reported in due time.

EXPERIMENTAL SECTION

Caution! These experiments should only be performed by trained personal using applicable safety procedures.

Chemicals. VX, GB, and HD* (^{13}C labeled) were obtained locally at the IIBR (>99% purity). PVA average MW 22 and 49 kDa were purchased from Fluka, PVA average MW 130 kDa, CEES, sodium perborate monohydrate, sodium tetraborate decahydrate (borax), TAED, sodium dodecylbenzenesulfonate (SDBS) and all solvents (HPLC grade) were purchased from Sigma-Aldrich and used without further purification. SPE (solid-phase extraction) NEXUS (Agilent) tubes of 6 mL (filled with 200 mg of sorbent) and 3 mL (filled with 60 mg of sorbent) were used for GB collection in the wind tunnel. Polyethylene-backed sorbent pad (Ultraclean BluePoly-backed-Gray Maintenance, 1UCGRL-PLY) was purchased from Evolution Sorbent Products, LLC.

NMR Spectroscopy. ^{13}C{^{1}H} and ^{31}P{^{1}H} spectra were obtained at 125 and 202 MHz, respectively, at 25 °C on a 11.7 T (500 MHz) Bruker spectrometer (AVANCE III HD). Chemical shifts were calibrated to TMS (for ^{13}C) and trimethyl phosphate (for ^{31}P) as 0 ppm. The spectra were recorded using the standard parameters of the TopSpin NMR software (version 3.5). Each data point was obtained from 100 to 128 scans, at a spectral width of 200 ppm and 2 s relaxation time. For comparison purposes, spectra of the kinetic experiments were recorded under identical conditions.

GC Analyses. All GC analyses were performed on an Agilent 6890 spectrophotometer, equipped with a flame photometer detector and a 7683B auto injector. Agilent ChemStation program was used for operating the GC and data analysis. A DB-5MS capillary column (Agilent J&W 122-5513), was used. Quantifications of GB and VX amounts were achieved using calibration curves of known concentrations ranging from 5 to 2000 ng mL^{-1}. The calibration curves were prepared in triplicate (±4.0% accuracy, ±1.5% reproducibility). The programs used for GB and VX analyses are specified in Tables S7−S8 in the Supporting Information.

Preparation of Gel Solutions. Three different gel formulations (I−III) were examined; each was composed of two solutions, A and B, of the same volume. Solution A was prepared by adding 10 wt % of PVA (average MW 22 KDa) powder to water and heating to 50 °C while stirring until dissolution. When used, TAED (0.1 wt %) was directly added to the PVA solution. Solution B was prepared by adding 4 wt % of borax to water and heating to 40 °C while stirring until dissolution. According to the specific formulation, sodium dodecylbenzenesulfonate and sodium perborate were added to this solution in different amounts, that is, between 0.5−3 and 2.5−4 wt %, respectively. In formulation III, EG was also added to solution B. Both A and B solutions, are stable at 25 °C. Sodium perborate was added shortly before use.

Decontamination Studies in Test Tubes. The CWA (2 μL) was carefully inserted into an NMR tube. Solution B (250 μL) of the examined formulation was then added to the tube, followed by solution A (250 μL). ^{31}P/^{13}C NMR spectra were taken periodically until completion of the reaction was observed (Figures S2−S23). Postacquisition data analyses to determine the average half-life times of the reactions were performed using GraphPad Prism analysis software using the one-phase decay function (Figures S24−S33).

Decontamination of Surfaces. VX was dispersed in a unified manner (0.5 μL drops) on an inert glass (7 mg VX, 67.5 cm^2) and porous painted (RAL7035 light gray) metal (5 mg VX, 63.5 cm^2) surfaces, to obtain a coverage of 1.2 g/m^2. After 10 min, the contaminated surfaces were covered by simultaneously applying solutions A and B (formulation I, 2 L/m^2, 12 and 8 mL for the glass and metal surfaces, respectively) to obtain the gel immediately. After a period of 6 h, the gels were removed, and the surfaces were washed with a solution of 10% triethylamine in a mixture of 30:70 ethanol/methyl tert-butyl ether (4−6 × 1 mL) to extract any remaining VX. Samples of these solutions after proper dilutions were then injected to GC to determine its residual amount based on a calibration curve and normalization to the control. Contaminated surfaces not covered with the gel were used as control and were washed immediately and analyzed using the same protocols. All tests were performed in duplicates.

Laboratory-Designed Wind Tunnel Experiments. Evaporation experiments were performed in a laboratory-sized wind tunnel. A detailed description of this setup was previously reported.[31] GB (16.5 mg, 15 μL) was dispersed as droplets of 3 μL over a 150 cm^2 piece of stainless steel to form surface contamination of 1.1 g/m^2. For the decontamination experiment, the two solutions of formulation I gel (A and B, total amount of 15 mL, 1 L/m^2) were sprayed simultaneously on the surface immediately after the contamination with GB. The contaminated surface, covered with gel, was then placed in the wind tunnel. The control and the commercial containment pad-covered surfaces were contaminated and examined in the

same manner. The relative humidity was set to 20%, wind speed to 1.6 m/s and the temperature to 25 °C. Two sets of collecting vessels allowed continuous air sampling into SPE (solid-phase extraction) tubes. In order to determine the amount of CWA in the air above the surface, the SPE tubes were disconnected periodically from the system and eluted with a mixture of 30:70 ethanol/methyl *tert*-butyl ether (1.0 or 1.5 mL for the 3 or 6 mL SPE tubes, respectively). Based on previous validation studies, the efficiency of GB extraction from the SPE tubes was evaluated as ~100%.[32] The measurements were performed in time intervals chosen in accord with the SPE ability to adsorb (500 μg) material with no risk of overloading. Indeed, no overload was detected when high concentrations of GB were used. The volume of the eluted solution was calculated according to the weight of each sample and the density of the elution mixture. Samples of these solutions were then injected into the GC, either directly or after the appropriate dilution to determine the amount of GB based on a calibration curve prepared in advance. The air concentration of GB was calculated according to eq 1

$$C = x/Qt \qquad (1)$$

where C is the air concentration of GB (ng L^{-1}), x is the amount of GB that was extracted from the SPE tube (ng), Q is the flow rate of air through the SPE tube (L min^{-1}), and t is the time interval of each measurement (min). For each time interval, three SPE tubes were measured in parallel, and the GB concentration was calculated using the average results of these three tubes. The evaporation data in all experiments are presented in the graphs as ln[GB] (ng L^{-1}) versus time. The data were fitted to a biexponential curve, which gave appropriate results according to previous studies. Detailed results of all experiments (concentrations and mass balance) are summarized in Tables S4–S6.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05493.

Decontamination kinetics—NMR spectra and data analyses, wind tunnel experiments, GC methods, and proposed mechanisms of CWA decontamination (PDF)

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Notes

The authors declare no competing financial interest.

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