

Sequestration and Decontamination of Chemical Warfare Agent Simulants by Ionic Liquids

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The ongoing use of chemical warfare agents (CWA) as weapons of destruction remains a dangerous threat in current times. In the aftermath of a CWA incident, it is vital to conduct a thorough decontamination of the surrounding environment, encompassing all exposed items. At the present time, decontamination systems continue to rely heavily on bleach-based solutions due to the broad range of decontamination action. The limitations of these systems include the potential for material destruction, high toxicity, generation of hazardous by-products, and the necessity for waste treatment prior to safe disposal. Herein, we report a decontamination strategy based on the use of a biodegradable ionic liquid (IL), cholinium acetate (ChIAce). ChIAce can be employed in either an immobilized form or as a standalone agent and is capable of sequestration *via* sorption (adsorption/absorption), confinement, solubilization, and/or decontamination (neutralization) of CWA simulants, dimethyl methylphosphonate (DMMP) and 2-chloroethyl ethyl sulfide (CEES), in their gaseous and

liquid states at relatively mild temperatures. The combination of ChlAce with choline hydroxide facilitates a more rapid neutralization reaction resulting in less toxic neutralization by-products. This approach offers a straightforward solution that circumvents the high toxicity, corrosion, and method complexity associated with current *in situ* decontamination methods.

The Chemical Weapons Convention, the world's first multilateral disarmament agreement,¹ was signed in 1997 and has since banned the production, storage, and use of chemical weapons. Unfortunately, the continued threat of active conflict and the high probability of chemical attacks, as evidenced by the Syrian civil war² and terrorism incidents³, demonstrate that humanity still lives in perilous times.^{4,5}

There are a wide variety of known chemical warfare agents (CWAs), and the process for their destruction and/or decontamination will depend on the type of agent, concentration, type of release, and location site.^{6,7} In the event of a CWA incident, after the threat is contained, considerable care needs to be taken for *in situ* decontamination. In an enclosed space, gaseous CWAs can be removed through active ventilation, or air filtration systems can also be employed, which combine filters that contain efficient adsorbents, such as modified impregnated activated carbon.^{8,9} Over the past decade, the quest for new and effective decontamination materials that can capture CWA in the gas phase has predominantly focused on porous catalysts, especially metal organic frameworks (MOFs)^{10–15}, single or mixed oxides/hydroxides^{16–22}, and zeolites^{23,24}. However, the manufacturing of these materials at a large scale has proven challenging, and their high cost has limited their widespread use. In the event of a CWA diffuse within a confined space, it is imperative that all objects and surfaces undergo decontamination through the application of

physical and/or chemical agents. The most common decontamination formulations are water- or foam-based, non-aqueous, or emulsions. Strong alkaline solutions and oxidants, such as peroxides and chlorinated solutions (e.g., bleach), are typically selected for a broad range of actions against CWAs.^{25–27} However, these methods present several disadvantages due to the high corrosive nature, toxicity, and large amount of toxic reactants in the majority of the solutions employed. Additionally, the reduced storage time of chlorinated solutions and the necessity of wastewater treatment after decontamination must be considered.^{7,28–31} The technology used for decontamination is crucial, and in recent years, continuous flow reactors have attracted considerable attention due to their rapid and selective neutralization of noxious substances. For instance, an upstream continuous flow setup configuration has been developed for the selective oxidation of organosulfur CWA simulants, which is capable of minimizing overoxidation to the highly toxic sulfones (less than 1 %).³²

Ionic liquids (ILs) have also been studied for CWA decontamination and neutralization. ILs are basically organic salts molten below 100 °C that present remarkable properties of low vapor pressure, chemical and thermal stability, tunability, nonflammability, biodegradability, and many other advantages. Their powerful solvation ability has been explored for CWA extraction from different surfaces. For example, a reactive gel based on an imidazolium IL has been used as a barrier to contain mustard agent simulant vapors in different surfaces, such as glass, wood, rubber, and painted steel.³³ Other ILs based on imidazolium cations have been reported for their rapid decontamination reactions when mixed with other reagents, resulting in alcoholysis, hydrolysis, and dehydrohalogenation processes.^{34–37} These outcomes showcase the high potential of ILs to solubilize CWA simulants, although they still require the addition of corrosive agents, which is a drawback, and imidazolium-based ILs can also be quite toxic. Another example of improved

solubilization was the incorporation of an IL, *N*-butyl-3-methylpyridinium dicyanamide, into a Zr-MOF catalyst. The presence of the IL not only enhanced the equilibrium adsorption capacities of the catalyst but also aided the *in situ* decontamination process of dimethyl 4-nitrophenyl phosphate (DMNP) and 2-chloroethyl ethyl sulfide (CEES).³⁸ ILs could also be used for chemosensing. One development is the room temperature fluorescence detection of sulfur mustard by a combination of luminol and 1-ethyl-3-methylimidazolium dicyanamide IL in water. In this particular case, the IL facilitated the reaction temperature decrease by enhancing the nucleophilicity of luminol and the electrophilicity of the sulfur mustard agent.³⁹ ILs-based molecular platforms are even being explored for the synthesis of acetylcholinesterase reactivators. This development has the potential to create antidotes for nerve agent poisoning.⁴⁰ A method for the destruction of toxic chemicals based on ILs or eutectic solvents was also developed and patented.⁴¹ However, the technique relies on mixing the agents in the liquid phase. While ILs sorption capacity to toxic gases has been explored, to our knowledge CWA sorption has remained relatively unexplored.^{42–47}

While assessing all of the work reported to date, it is difficult to compare decontamination systems due to the differences in objectives, application methods, operating conditions, reaction rates, and by-products, among other factors.⁴⁸ While several promising studies have highlighted the potential of ILs as effective liquid-liquid extractors for CWAs, challenges still remain within these decontamination systems, ranging from a narrow CWA range to complicated synthetic processes, unrealistic *in situ* applications, hazardous by-products that require waste treatment prior to disposal, and high-cost systems, among other disadvantages. Indisputable, ILs have the potential for defense, decontamination, and sensing of CWAs and their simulants. It should be noted that for research purposes, simulants are usually used instead of the real CWAs, since they have similar chemical composition and physical properties but have lower toxicity. Here, we report the

development of a sustainable CWA sequestration and decontamination (neutralization) system that can eliminate most of the aforementioned drawbacks. This practical and simple system is based on the environmentally friendly and low toxicity IL, cholinium acetate (ChlAce).^{49–51} This ChlAce-based decontamination system is capable of sorption, confinement, solubilization, and/or neutralization of the CWA simulants, dimethyl methylphosphonate (DMMP) and CEES, in their liquid and gas phases (Fig. 1). This is most useful for gentle on-site decontamination where relative care is necessary to avoid the destruction of contaminated materials and surfaces. The low vapor pressure of the ILs is a great advantage, as it can contain the agents and limit their tendency to evaporate, unlike some water- or alcohol-based decontamination formulations. The sorption or solvation of the simulants by ChlAce can then be neutralized by a mild thermal treatment. In this decontamination reaction, it is the acetate anion that inactivates the CWA simulants, unlike known decontamination systems. At room temperature, decontamination can be performed by combining ChlAce with choline hydroxide in a 7:3 stoichiometry, resulting in faster decontamination. In this scenario, some material corrosion may occur, although significantly less than that observed with a commercial bleach decontaminant. When using the ChlAce-based decontamination system, the neutralization reaction by-products are less harmful than the simulants. This work presents the scope of this novel CWA simulants decontamination and neutralization system based on the IL, ChlAce.

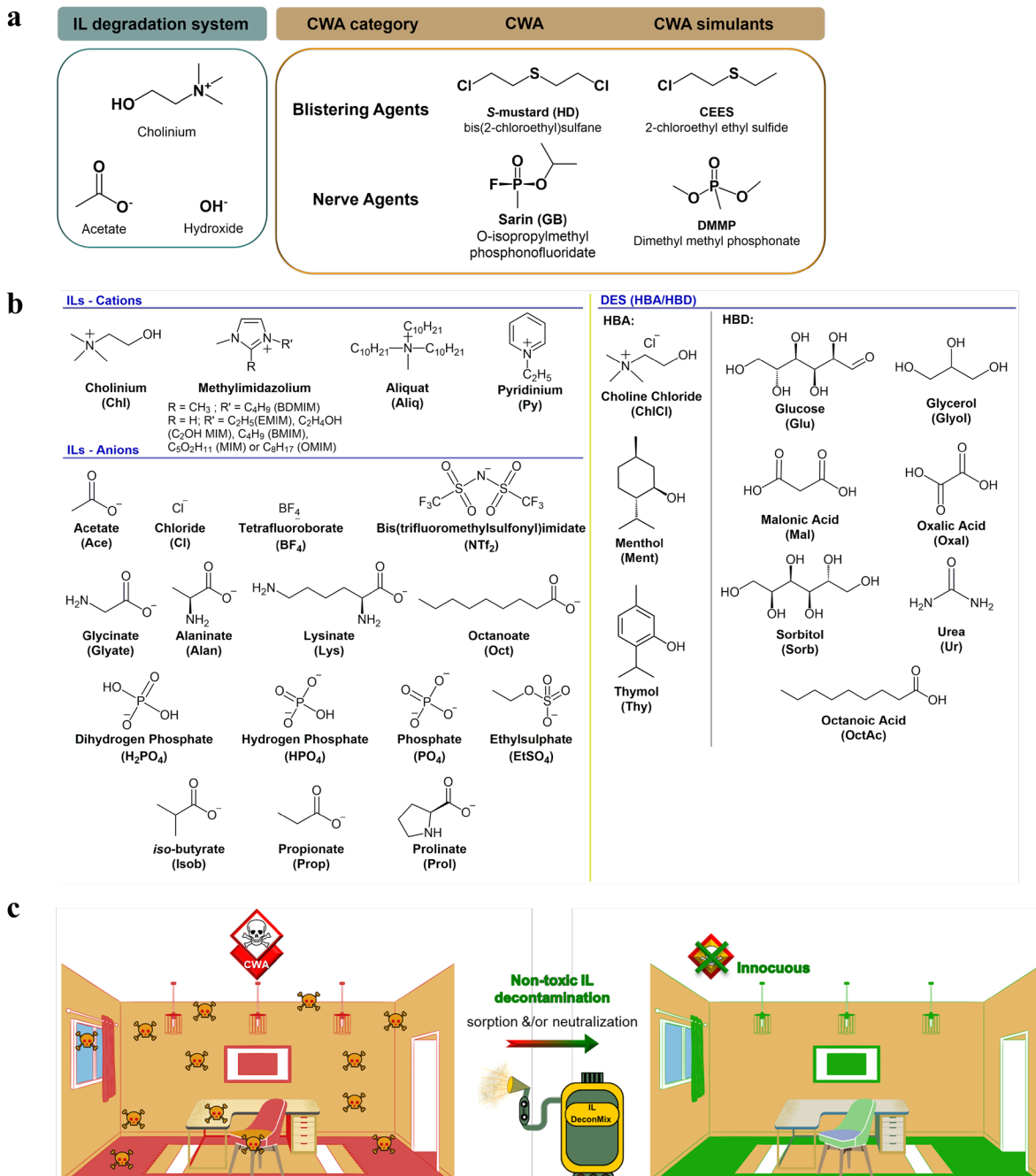


Fig. 1| CWA simulants decontamination system by ILs and deep eutectic solvents (DES). **a**, Representation of the IL decontamination systems and the simulants tested in this work. **b**, General structures of tested systems composed by the conjugation of cations and anions in ILs and of the pairing of hydrogen bond acceptors and donors in DES. **c**, Schematic representation of the IL sorption/decontamination system.

Results and Discussion

The IL decontamination system for DMMP and CEES was demonstrated by systematic studies of sorption and neutralization. DMMP is a surrogate of the nerve agent sarin, while mustard gas simulant CEES is a blistering agent (Fig. 1a).²⁵ Since the CWA simulants still have high associated toxicity, all experiments involving them were performed in a controlled laboratory at the Portuguese Army facilities.

Sorption Analysis

A wide variety of ILs (cholinium, imidazolium, pyridinium, and aliquat®-based) were studied for their simulant sorption capacity. This first step was crucial for the selection of the IL decontamination system. Deep eutectic solvents (DES) were also analyzed, most of which were based on choline chloride as a hydrogen bond acceptor. Sorption capacity was studied with the simulants in a gas phase and in contact with the IL, determined by headspace sampling and quantified by GC/MS (see Supplementary Information for methods and conditions, section 2).

ILs sorption results for DMMP and CEES are depicted in Fig. 2. This screening shows that there is generally a greater sorption capacity for DMMP than for CEES. Nevertheless, these results indicate the potential for an efficient dual simulant sorption system. Cholinium cation (Chl) based ILs have a higher sorption affinity for both simulants compared to other IL cations or to DES (Supplementary Fig. 3). Due to the hydrophobic nature of CEES (partially soluble in water)⁵² a higher affinity for hydrophobic ILs (NTf₂ anion based) or DES (choline chloride/urea, thymol/octanoic acid (Thy/Oct), menthol/octanoic acid) was to be expected. However, the best CEES sorption results are observed for cholinium-based ILs, namely ChlIsob and ChlOct (sorption

> 90 %). In the scope of ILs/DES, the DMMP sorption capacity has an average of circa 80 %, with the best results being obtained with ChlOct and ChlProl (sorption > 90 %) (Supplementary Fig. 3).

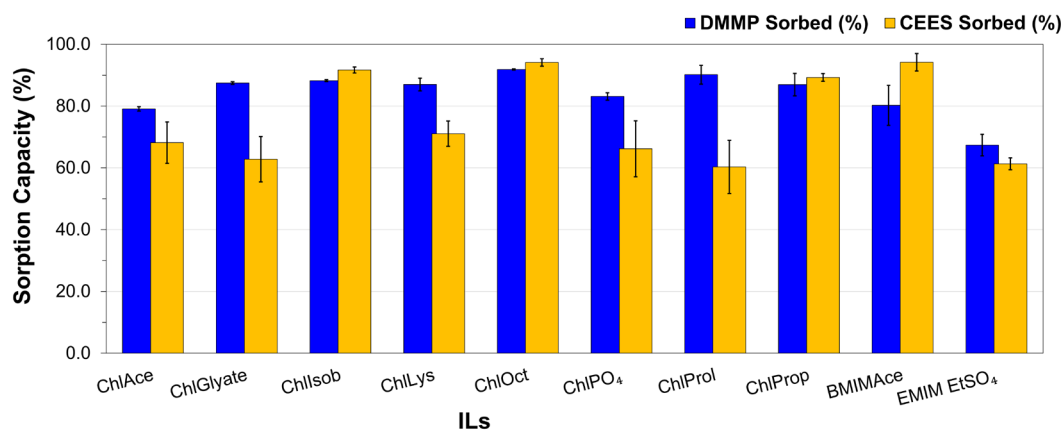


Fig. 2| Selection of ILs sorption capacity for the CWA simulants, DMMP (blue filled) and CEES (yellow filled). Sorption capacity of cholinium- and imidazolium-based ILs. Sorption assays were performed with the simulants in gas phase and in contact with the respective IL system. Results were obtained using a headspace encapsulation coupled to gas chromatography-mass spectrometry (HS-GC/MS). Displayed error bars indicate the standard deviation ($n=3-8$). Compound abbreviations (Fig. 1b): cholinium acetate (ChlAce), cholinium glycinate (ChlGlyate), cholinium isobutyrate (ChlIsob), cholinium lysinate (ChlLys), cholinium octanoate (ChlOct), cholinium phosphate (ChlPO₄), cholinium proline (ChlProl), cholinium propionate (ChlProp), 1-butyl-3-methylimidazolium acetate (BMIMAce) and 1-ethyl-3-methylimidazolium ethyl sulfate (EMIM EtSO₄). See Supplementary Information for further experimental details.

In this sorption scope, ChlAce demonstrates good sorption features for both DMMP and CEES. While its sorption may be slightly less efficient as other ILs, it does offer the most cost-effective solution. Furthermore, the cholinium core, which contains a quaternary ammonium cation with a polar hydroxyl group, has been previously reported to have lower toxicity when compared to the imidazolium cation.⁵³ Additionally, ChlAce is water soluble and *in vitro* skin assays classified it as non-irritant (in accordance with the UN GSH and EU CLP “No Category” (UN, 2009;

No.1272/2008, EU, 2008). See Supplementary Information for methods and conditions).

Hereafter, due to the substantial benefits it offers, all studies were centered around ChlAce.

In sorption studies, the role of water is also an important factor to consider. In real-life atmospheric conditions, relative humidity is variable and can potentially modify the sorption process. For this reason, the sorption capacity of ChlAce was analyzed under different water content conditions, ranging from basic ambient storage level (water content of 8.4 %) up to a 30 % water increase (Supplementary Fig. 4). The results show that the sorption of DMMP by ChlAce is not significantly influenced by the increase of water content, in contrast to CEES, where a decrease of about 20 % was observed. This decrease is probably due to CEES partial solubility in water, which slows down the sorption rate.

ChlAce simulant neutralization with temperature

The efficacy of ChlAce as a decontamination system was demonstrated by its sorption capacity. Furthermore, its ability to neutralize simulants single-handedly was also confirmed by the application of a mild temperature treatment. This outcome was observed upon simulant sorption and neutralization studies performed at 70 °C for 18 h in ChlAce (see Supplementary Information for methods and conditions). The simulants were present in the gas phase throughout the course of the assay. As illustrated in Fig. 3a, the decrease in DMMP quantity does not correspond to the amount of DMMP sorbed by ChlAce, except at approximately the half-hour mark. After this time, the quantity of unaccounted DMMP continues to increase, and given that these assays are conducted in a closed system, this indicates that DMMP is not only being sorbed but also neutralized. In the particular case of CEES, this neutralization is so complete that after a period of 1 h, nearly half of the simulant has already been sorbed and neutralized (Fig. 3b). Additionally,

189 CEES sorption assays were performed at room temperature for an extended period of time (72 h,
190 Supplementary Fig. 6). At the conclusion of the 72 h period at room temperature, CEES was not
191 fully volatilized. Nevertheless, at this point in time, ChlAce demonstrated the capacity to confine
192 22 % and to have simultaneously sorbed and neutralized approximately 65 %.

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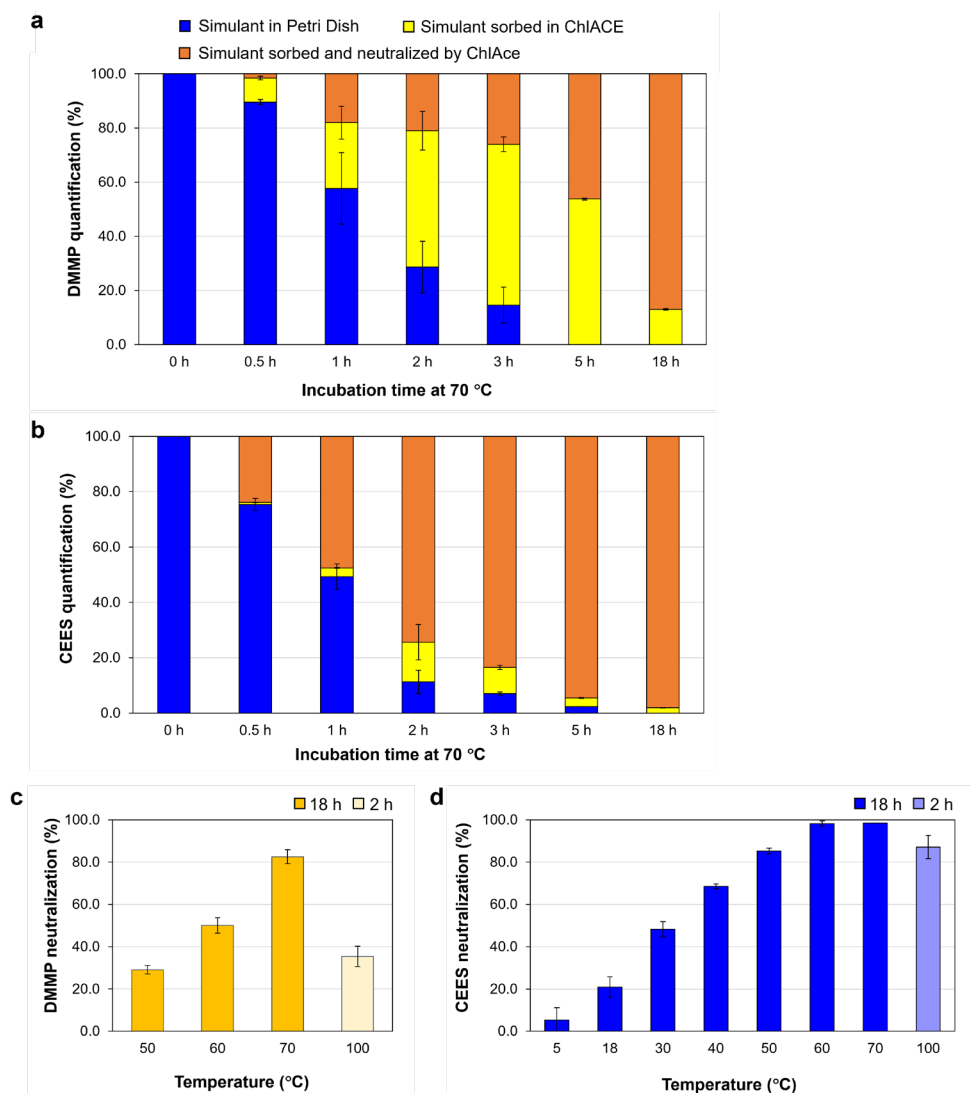


Fig. 3| Simulant sorption and/or neutralization in ChIACE. **a**, DMMP quantification at 70 °C at different incubation times. **b**, CEES quantification at 70 °C at different incubation times. For a-b see Supplementary Information for experimental details. Bar colors indicate the non-volatilized simulant (blue), the presence of simulant in ChIACE (yellow), and the difference between these two values relates to the simulant that was sorbed and neutralized (orange). Displayed error bars indicate the standard deviation ($n=2$). **c**, DMMP neutralization at different temperatures for incubation times of 18 h and 2 h. **d**, CEES neutralization at different temperatures for incubation times of 18 h and 2 h. For c-d, see Supplementary Information for experimental details. Bar colors indicate the incubation time of 18 h (dark color) and 2 h (light color). Neutralization assays were performed with the simulants in liquid phase and in direct contact with the respective IL system. Results were quantified by GC/MS. Displayed error bars indicate the standard deviation ($n=3$).

Based on the aforementioned sorption/neutralization outcomes, direct liquid-liquid contact assays were conducted (see Supplementary Information for methods and conditions). During the course of these assays, neat ChlAce and the simulants, were kept in contact for a period of 18 h at a range of temperatures. Fig. 3c shows that DMMP starts to neutralize at temperatures circa 50 °C. At 70 °C and 18 h of contact, the DMMP maximum neutralization efficiency reaches its peak at around 80 %. For CEES (Fig. 3d), the neutralization temperature is significantly lower, with some decontamination already observed at 5 °C. CEES neutralization is almost complete at 60 °C after 18 h. By reducing the assay time to 2 h and increasing the temperature to 100 °C, the neutralization efficiency for both simulants is comparable to that achieved after 18 h at 50 °C for each respective simulant.

The neutralization products resulting from the application of ChlAce as a decontamination system for DMMP and CEES were analyzed by NMR. The decontamination of DMMP revealed the presence of neutralization products, methoxy(methyl)phosphinate, methanol, and methyl acetate (Supplementary Fig. 9). These products derive from the nucleophilic attack of the carboxylate anion on the methyl ester group of DMMP. As for CEES decontamination products, the analysis revealed the formation of 2-(ethylsulfanyl)ethyl acetate (Supplementary Fig. 10), which is derived from the acetate nucleophilic substitution on the C-Cl bond.

ChlAce simulant neutralization at room temperature

Implementing ChlAce as a neutralization system at room temperature requires the incorporation of a nucleophile to enhance the efficiency and speed of the decontamination process. The room temperature neutralization assays were performed by placing the simulant in a liquid phase in direct contact with the IL for a period of up to 5 h. The Supplementary Information comprises

236 preliminary studies of the incorporation of ChlAce into several neutralizing systems, including
237 commercial decontamination systems. These studies also examine the effects of different
238 nucleophiles (hydroxide, polyamine, and imidazole) and oxidant (oxone®) on the decontamination
239 of DMMP. After thorough research, the most efficacious system was identified as the
240 incorporation of ChlAce with choline hydroxide (ChlAce/ChlOH) in a 7:3 stoichiometry
241 (Supplementary Fig. 11). The hydroxide anion presence in this decontamination system promotes
242 the hydrolysis of the simulants. Despite the analysis of different stoichiometries, the neutralization
243 outcomes remained similar. Therefore, it is preferable to use the lowest possible amount of
244 hydroxide to minimize toxicity and corrosion risks.

245 Afterwards, the selected room temperature neutralization system, comprising ChlAce/ChlOH (7:3)
246 with different water content, was assessed over a 5 h period for the neutralization of DMMP and
247 CEES (Supplementary Fig. 12). In the particular case of CEES, the neutralization process is
248 instantaneous. The neutralization efficiency of DMMP increased with an rise in contact time for
249 all water incremented systems. Nevertheless, the ChlAce/ChlOH (7:3) system exhibits the greatest
250 neutralization capacity under water saturated conditions, with an average efficiency increase of
251 8 % for each additional contact time. Ultimately, the system achieved a DMMP neutralization of
252 80 % at 5 h. The neutralization efficiency still remains between 70 and 80 % for 5 h, even when
253 the water content is increased from saturated conditions up to a 20 % water increment. These
254 findings substantiate the efficacy of ChlAce/ChlOH (7:3) in neutralizing CEES and DMMP, the
255 latter even in the presence of a 20 % water increment.

256 The ChlAce/ChlOH (7:3) neutralization mixture was also tested for its sorption capacity, with the
257 simulant being in the gas phase. This study was performed with variable water content. Under
258 saturated conditions, the mixture exhibits sorption/neutralization of 96 % and 85 % for DMMP

259 and CEES, respectively (Supplementary Fig. 13). When compared to the same ChIAce assay
260 (Supplementary Fig. 4), there is a 17 % increase in decontamination efficiency for both simulants.
261 This efficiency increase was expected due to the neutralization mixture's ability to not only sorb
262 but also neutralize the simulants through the presence of the hydroxide anion and thereby enhance
263 the sorption capacity. In the DMMP decontamination, it was observed that the increase in water
264 content does not significantly decline the neutralization process. This is not the case for CEES
265 decontamination, as it experiences a significant decrease in efficiency of around 25 % with just a
266 10 % increase in water content. As CEES hydrolysis is dependent on its dissolution, an increase
267 in the water ratio will hinder its solubility in the decontamination system, resulting in a loss of
268 efficiency.

269 The reaction between ChIAce/ChIOH (7:3) and DMMP was analyzed through a kinetics study by
270 NMR (Supplementary Fig. 14). After a minimum of 5 min of contact, the neutralization products
271 observed were methoxy(methyl)phosphinate (MMP) and methanol. These products are derived
272 from the nucleophilic attack of the hydroxide anion on DMMP. After 4.5 h, the simulant was
273 nearly neutralized (Supplementary Fig. 14). Generally, DMMP degradation products vary
274 depending on the reaction process and can result in a number of compounds, including phosphates,
275 acids, and gases. While MMP is not commonly reported, it has been identified by mass
276 spectrometry in studies examining site selectivity with several anions in gas phase reactions with
277 DMMP.^{54,55}

278 In the presence of the neutralization mixture ChIAce/ChIOH (7:3), CEES hydrolyzes to the well-
279 known ethyl 2-hydroxyethyl sulfide (HEES) (Supplementary Fig. 15). For comparison purposes,
280 the hydrolysis of CEES was also tested in the presence of an alkaline sodium hydroxide solution.
281 After 13 days, a residual amount of CEES was still observed. Additionally, an excess of NaOH

282 was also added into this reaction, and no notable difference was observed. As for CEES in the
283 presence of ChlAce/ChlOH (7:3), it significantly accelerates the neutralization, requiring only 24 h
284 to achieve the same results that took 13 days with the alkaline solution. It is therefore evident that
285 ChlAce/ChlOH (7:3) is a highly effective room temperature neutralization system. ChlAce/ChlOH
286 (7:3) DMMP neutralization efficiency was further evaluated after a 6 months period under basic
287 storage ambient conditions. The results indicate a gradual decline in efficiency, with circa 2 % loss
288 per month probably due to some reduction of hydroxide content derived from Chl degradation via
289 Hofmann elimination (Supplementary Fig. 16).

290 One drawback of current neutralization systems is the corrosion of materials. Therefore, a
291 corrosion assay was devised to analyze the possible material damage when using ChlAce/ChlOH
292 (7:3) system. Nine different metals (aluminum, brass, bronze, copper, mild steel, pure lead,
293 stainless steel AISI 304, tin, and zinc) were coated with ChlAce/ChlOH (7:3) and compared with
294 those coated with sodium hypochlorite containing 6.5-6.8 % of active chlorine. After a 22 day
295 period at 26 °C and 60 % humidity, the plates were analyzed using an optical microscope and
296 scanning electron microscope (see Supplementary Information for methods and conditions). The
297 majority of metal plates coated with ChlAce/ChlOH (7:3) (Supplementary Tables 5-13) exhibited
298 less corrosion compared to those coated with sodium hypochlorite, with the exception of copper,
299 pure lead, and zinc. While copper and pure lead display similar corrosion behavior with respect to
300 both coatings, the corrosion of zinc metal plates was more pronounced with the ChlAce/ChlOH
301 (7:3) layer. No corrosion was noticeable in the stainless steel plates. Upon extending the assay
302 time and increasing the temperature (50 °C for 2 months), the stainless steel plate coated with
303 ChlAce/ChlOH (7:3) remained with no observable corrosion, while the coating with bleach
304 solution caused staining (Supplementary Table 14).

ChlAce/ChlOH (7:3) as a neutralization mixture has proven to be highly effective, although it may require more time than the typical bleach solutions to achieve maximum decontamination. However, bleach solutions are known to be corrosive, toxic, and can produce highly toxic neutralization byproducts. A comparison between ChlAce/ChlOH (7:3) and sodium hypochlorite with 6.5-6.78 % of active chlorine revealed that the former has a reduced corrosive effect. This, coupled with the relatively lower toxicity of ChlAce/ChlOH (7:3) by-products, highlights a significant advantage of our system, thus showcasing the superior performance and relative safety of using ChlAce/ChlOH (7:3) as the decontamination method for DMMP and CEES.

Immobilization studies

Several materials have already been reported as suitable solid matrices for immobilization and destruction of CWAs, with a particular emphasis on activated charcoal as an efficient absorbent.⁹ Our study also focuses on the immobilization of ChlAce within various solid matrices, which could potentially be employed in air filtration systems for contaminated environments or as a protective barrier. The aim of this particular study is not only to develop a safe and effective method for capture and confinement of CWAs but also to provide a safer environment for the disposal of simulants. By trapping the simulants within the solid matrix that comprises ChlAce, it is possible to neutralize the simulant at moderate temperatures (as demonstrated in the aforementioned studies, see Supplementary Information for methods and conditions). Granulated activated charcoal combined with ChlAce exhibits the highest sorption capacity for both simulants (Supplementary Fig. 17). In this instance, the addition of up to 20 % of ChlAce to the solid matrix resulted in an approximate 80 % increase of DMMP and CEES sorption capacity. A surprising yet effective immobilization matrix was ChlAce in gelatine (circa 100 % for DMMP). In the right

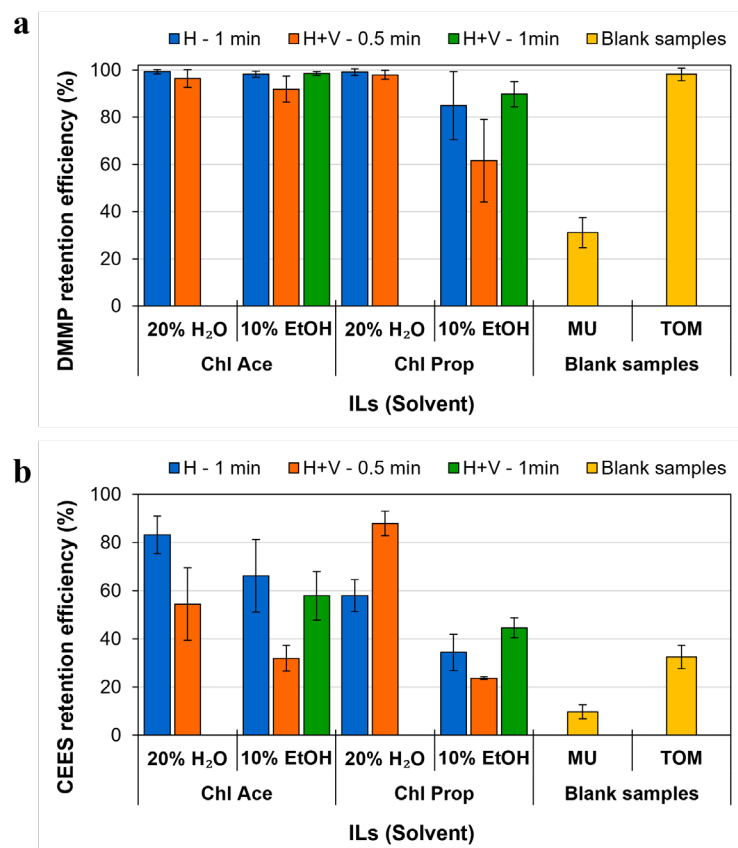
conditions, gelatine can be used to create a biodegradable film that provides a gas protective barrier. This flexible film can protect various surfaces, ranging from simple door handles to electronic equipment. The sorption of DMMP in this matrix is independent of the amount of ChlAce present, however its presence provides a solid consistency to the gelatine.

ChlAce barrier on fabric surface

Regarding a possible application of ChlAce as a barrier to protect against toxic agents from skin contact, a direct IL spray solution application onto the surface of military uniform (MU) samples was developed. After the fabric drying process, the retention capacity for DMMP and CEES was quantified (see Supplementary Information for methods and conditions).

As can be observed in Fig. 4, CEES retention efficiency in all samples is lower than that for DMMP. The ILs that were dissolved in 20 % of water exhibited higher retention efficiency for both simulants than the ones dissolved in 10 % of ethanol, probably due to a more effective spray dispersion. When compared with the blank samples (MU), it is evident that the fabric samples treated with the ILs have a significant simulant retention improvement, particularly for ChlAce (sprayed for 1 min in a horizontal direction) and ChlProp samples (sprayed for 0.5 min in a horizontal and vertical direction), both with 20 % water. In the case of DMMP retention efficiency, the IL spray application is shown to be comparable to the TOM protective suit. However, when regarding CEES, the fabric treated with the IL displays a greater retention improvement when

347 compared with the fabric of the Paul Boyé Technologies protective suit TOM, which is a CBRN
 348 (chemical, biological, radiological, and nuclear defense) suit compliant with NATO AEP-38.



349
 350 **Fig. 4| Simulant retention efficiency in fabric samples of military uniform with ILs, ChlAce**
 351 **and ChlProp. a, DMMP retention. b, CEES retention.** The fabric samples (64 cm²) were treated
 352 with a direct IL spray solution, with the IL being dissolved in water (20 %) or ethanol (10 %) and
 353 dispersed in different directions (H – horizontal, V – vertical) and time conditions (0.5 min and 1
 354 min). Blank samples of the tested military uniform (MU) and the TOM Protective Suit (TOM,
 355 CBRN suit NATO AEP-38 compliant) were also analyzed. The fabric samples containing the
 356 dispersed IL solution were dried before being subjected to simulant quantification by GC/MS.
 357 Displayed error bars indicate the standard deviation ($n=5$). See Supplementary Information for
 358 further experimental details.

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360 In a CWA incident, rapid response is necessary, and providing any protection in a prompt manner
361 is crucial. In this case, a portable spray system which can pulverize these ILs solutions on short
362 notice into a simple military uniform could probably save lives, specially since protective suits
363 such as TOM are not so readily available for a large number of personnel. In this line of thought,
364 and with the results presented, diverse prototypes could be developed. For example, with just
365 ChlAce immobilized in activated charcoal (20-35 mesh ASTM), it is possible to create air
366 purification systems and even face mounted filters to be adapted to personal protective equipment
367 filter masks as air-purifying respirators. The main advantage of this key filter layer is that the CWA
368 can be destroyed *in situ* and disposed of without prior specific treatment.

369 In summary, we report here a decontamination strategy that employs a biodegradable IL based on
370 ChlAce. This system, which can be immobilized, used as a standalone agent, or combined with a
371 nucleophile, has the capacity to remove and/or neutralize CWA simulants, DMMP and CEES. The
372 IL system is capable of sorption, confinement, solubilization, and/or neutralization of the CWA
373 simulants at mild temperatures. The results showed the efficacy of ChlAce in capturing and
374 decontamination (neutralization) CWA simulants in both their gaseous and liquid phases.
375 Furthermore, when combined with ChlOH at room temperature, it accelerates the decontamination
376 (neutralization) process, yielding less toxic by-products. The development outlined in this reported
377 study presents a simple, less toxic, and non-corrosive alternative to conventional decontamination
378 methodologies.

379

380 **Online content**

381 Any methods, additional references, Nature Portfolio reporting summaries, source data, extended
382 data, supplementary information, acknowledgements, peer review information; details of author

contributions and competing interests; and statements of data and code availability are available at <http>

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Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files. Source data for figures 2-4 are provided with the paper.

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Author contributions

A.A.R. and C.A.M.A. applied for funding, managed and supervised the project and devised experiments. A.A.R. and R.A.L.S. prepared the ionic liquids and analyzed the obtained data. I.C., T.G and P.N. prepared the methodology and performed all experiments involving CWA simulants. All authors contributed to the preparation of the manuscript.

Competing interests

544 The authors have filed a patent application (n° PT120011, 28 January 2025), under Faculty of
545 Pharmacy, University of Lisbon, to provide commercial protection for this technology of
546 sorption/decontamination of CWA simulants by ionic liquids.

547

548 **Additional information**

549 **Supplementary Information** is available for this paper.

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