

## Decontamination of mustard sulfur and VX by sodium percarbonate complexed with 1-acetylguanidine as a novel activator

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### ABSTRACT

The peroxide-based decontaminants had attracted great attention for degradation of chemical warfare agents (CWAs) because of their high performance, non-corrosive and environmental-friendly merits. Hydrogen peroxide can be activated by some organic activators to enhance the oxidation ability. In this work, a novel formula based on sodium percarbonate (SPC) complexed with 1-acetylguanidine (ACG) was investigated for decontamination of sulfur mustard (HD) and VX as CWAs. In the experimental results, the active species acetyl peroxide imide acid in the formula aqueous solution was detected *in situ* by Raman and <sup>13</sup>C NMR spectroscopy. The optimized conditions of the decontamination formula (SPC/ACG) were suggested that, the molar ratio of active oxygen and activator ([O]/[ACG]) was 1:1 while the pH value of the formula aqueous solution was about 9. To achieve the decontamination percentage over 99%, the molar ratio of active oxygen to CWA ([O]/[CWA]) needed to be at least 3 for HD and 7 for VX. Meanwhile, the degradation products detected by gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS) and ion chromatography (IC) indicated that the oxidation and elimination reactions should have occurred on HD molecule, while the degradation of VX mainly originate from the nucleophilic substitution and oxidation reactions.

**Key words:** 1-acetylguanidine, CWAs, decontamination, oxidation, sodium percarbonate

### HIGHLIGHT

- activation mechanism; activation of hydrogen peroxide; advanced oxidation of chemical warfare agents; hazardous waste treatment; water treatment

## 1. INTRODUCTION

The decontamination of chemical warfare agents (CWAs) is of great importance for nuclear, biological and chemical defense as well as counter-terrorism (Yang *et al.* 1992). In recent years, the chemical weapon was still sporadically used, such as the chemical attack that occurred on August 21, 2013 in the city of Damascus, Syria (Hakeem & Jabri 2015). In 2017, Novichok, as a series of nerve agents, entered into people's vision, which might be similar in toxicity to VX (O-ethyl-S-(2-diisopropylamino-ethyl)-methyl phosphonothioate) (Nepovimova & Kuca 2018; Kloske & Witkiewicz 2019). Therefore, many martial scientists still paid great attention to decontaminating chemical warfare agents (Love *et al.* 2011; Zhao *et al.* 2018; Bigley & Rauschel 2019).

It's a trend that the peroxide-based decontaminants were preferred by the researchers because of their high performance, non-corrosive and environmental-friendly merits. It has been clarified that the decontamination performance of inorganic peroxides, like H<sub>2</sub>O<sub>2</sub>, sodium percarbonate, sodium perborate, etc., was remarkably poorer than that of the organic peroxides, like magnesium monoperoxyphthalate (MMPP) (Lion *et al.* 1997). To achieve high decontamination efficiency and stability, a series of decontamination formula based on inorganic peroxides were developed where the catalysts, activators and surfactants were added, such as Decon Green (Wagner *et al.* 2001, 2002), DF-200 decontamination foam (Tucker & Comstock 2004) and the sodium percarbonate/tetraacetylenediamine (SPC/TAED) (Davies & Deary 1991; Qi *et al.* 2013) combined decontaminant. As an example, Decon Green as an environmentally benign decontaminant mainly composed of H<sub>2</sub>O<sub>2</sub>, potassium carbonate, potassium molybdate, propylene carbonate, and Triton X-100 additives (Wagner *et al.* 2001).

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The DF-200 decontamination foam developed by Sadia National Laboratory applied  $\text{H}_2\text{O}_2$  and glycerol diacetate as activator, this formula can generate peracetic acid ion in aqueous solution (Magnaud *et al.* 1998; Tucker & Comstock 2004), which was quite effective toward decontaminating soman (GD), sulfur mustard (HD) and VX. SPC as a solid form of hydrogen peroxide (Zhang *et al.* 2021) can react with TAED in aqueous solution to yield peracetic acid as a stronger oxidant which was used to decontaminate CWAs (Davies & Deary 1991; Qi *et al.* 2013). It's well known peroxide hydrogen and TAED as a bleaching agent had been widely used in treating fabrics. What's noted that, it has been found that the addition of an asymmetrically substituted alkyl or 1-acetylguanidine compound to the peroxide bleaching bath significantly enhances the peroxide bleaching performance, leading to a whiter and brighter end-product (Cai 2007). Compared with TAED, the guanidine-based bleaching activators would be apparent as one of the most popular activators on the cellulosic materials market. Therefore, guanidine derivatives as a potential activator with SPC might be applied for the decontamination of CWAs.

In this work, an aqueous decontamination formula based on the activation reaction of SPC and 1-acylguanidine (ACG) was researched for degradation of chemical warfare agents HD and VX. The active species was detected by Raman and  $^{13}\text{C}$  NMR spectroscopy. Some factors were optimized, such as the molar ratio of active to ACG ((O)/(ACG)), pH value, molar ratio of active oxygen to CWA ((O)/(CWA)), reaction temperature for decontamination efficiency and so on. The degradation pathways of HD and VX were discussed based on the detected degradation products.

## 2. EXPERIMENTAL

### 2.1. Materials

The toxic agents of HD and VX had a purity >95%, which were all attained from Institute of NBC Defense. Sodium percarbonate with 13% active oxygen content was purchased from Jinke Chemical Industry Co., Ltd in Zhejiang; ACG was obtained from Fisher Chemicals (Leicester, UK); Dichloromethane (GC grade) as solvent was obtained from Bafang Agents Inc. (Beijing, China). Because of their high toxicity, chemical warfare agents HD and VX were handled only by trained personnel using appropriate safety procedures.

### 2.2. *In situ* detecting on the activation process of SPC/ACG

#### 2.2.1. Raman spectrum

In a glass vial of 20 mL, 10 mL 0.3 mol/L–0.5 mol/L of SPC, ACG, SPC/ACG and peracetic acid solution were detected by Raman spectroscopy separately, in order to identify the generated active species at the room temperature ( $20 \pm 5$  °C). Raman measurements were performed on a portable Raman spectrometer (RFS1000, Shanghai Oceanhood Optoelectronics Tech Co., LTD) equipped with 785 nm laser source.

#### 2.2.2. $^{13}\text{C}$ NMR spectrum

All the samples were submitted to  $^{13}\text{C}$  NMR (AVANCE III HD 500 MHz, Bruker German) experiment, such as ACG and SPC/ACG solution. Samples of all substances were prepared in 5 mm NMR tubes, at concentration ranges between 40 and 150 mg/mL.

### 2.3. Decontamination reaction of HD and VX

The solid decontaminant was mainly composed of SPC, ACG and sodium phosphate buffer. The decontaminant solutions with difference concentration and pH value were prepared according to the different ratio of all ingredients. For the decontamination reaction, each decontamination ingredient was placed into a 50 mL flask and stirred for 5 min at 1,320 r/min under a certain temperature to achieve thermal equilibrium. Then, HD or VX liquid was injected into the flask with a micro-syringe under continuous stirring. Finally, sampling and sample preparation were accomplished at the different reaction time (e.g. 2, 5 and 20 min) in order to determine the decontamination efficiency and degradation products. Three drops of 10% sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution as terminator was added into each sample to neutralized the redundant peroxides before extraction.

### 2.4. Analysis of HD and VX as well as their degradation products

The residual CWAs and their non-polar degradation products could be quickly separated from the mixture of decontamination solution by organic solvent extraction (Davies & Deary 1991; Qi *et al.* 2012). To determine the residual HD and VX, the extraction agents ligarine and dichloromethane were used, respectively. The volume ratio of decontamination solution and extraction agent was 1:1, and the extraction time was 10 min. After the organic and aqueous phases were well separated,

the organic solvent was sucked out for analysis. The residual HD in ligarine was quantitatively analyzed with a colorimetric method (Franke 1977). The residual VX in dichloromethane was quantitatively analyzed by an Agilent 6890N gas chromatography (Agilent Technologies, Palo Alto, CA, USA), equipped with a flame ionization detector (FID) and a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm), employing the temperature ramp 70–280 °C at 15 °C/min (Qi *et al.* 2012).

For identification of the degradation products of HD and VX, dichloromethane was also used to extract the non-polar species in the decontamination solution. The samples were analyzed by an Agilent 7890A/5975C GC/MS, equipped with a HP-5-MS (30 m × 0.25 mm × 0.25 μm) capillary column employing the temperature ramp 40–280 °C at 15 °C/min. The polar degradation products in the decontamination solution were detected and identified by LC/MS. Firstly, the final solution was dried in a gentle stream of nitrogen, then the solid residue was extracted with methanol. The extractant was analyzed with an Agilent 1100 LC/MS equipped with a non-polar column (Zorbax SBC18 column, 30 mm × 2.1 mm × 3 μm). The mobile phase was 0.1% acetic acid aqueous solution at a rate of 0.2 mL/min, the column temperature was 40 °C, and the scan range was 50–1,000 m/z. In addition, the polar organic degradation products of VX were also analyzed by a pre-column derivatization method, where the aqueous sample was evaporated to dryness under a N<sub>2</sub> stream, the residue was alkylated via diazomethane (CH<sub>2</sub>N<sub>2</sub>) as an alkylation agent (Moore & Reed 1973), then dichloromethane solvent was used to extract the derivatized products. The dichloromethane sample was also analyzed by GC/MS with the same condition as above.

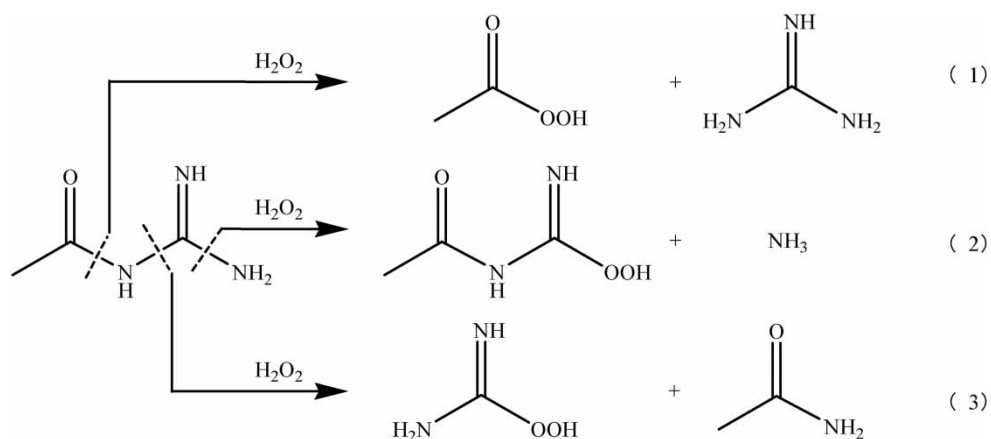
Ion chromatograph spectrometry (IC) was used to analyze the possible ionic products in decontamination solution upon long time of reaction. A Metrohm IC-761 ion chromatograph spectrometry (IC, Metrohm China Ltd, Hong Kong, China) equipped with a conductivity detector and an anion-exchange column Metrosep-A-Supp 5 (50 × 3 mm, Metrohm China Ltd, Hong Kong, China) was applied for analysis. The flow-rate of the eluent (3.2 mmol/L Na<sub>2</sub>CO<sub>3</sub> and 1.0 mmol/L NaHCO<sub>3</sub>) was kept at a rate of 0.7 mL/min.

### 3. RESULTS AND DISCUSSION

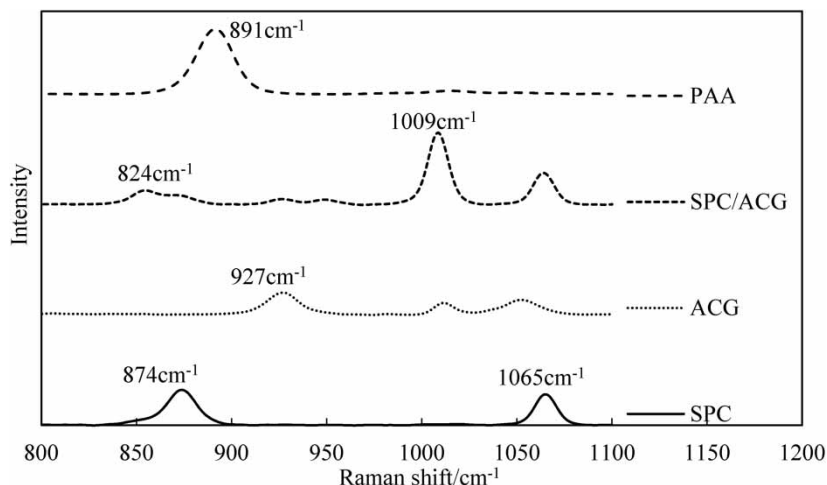
#### 3.1. Active reaction of SPC and ACG

It has been clarified that the compounds with structure of >C=N- or C≡N, such as guanidine, amidine, cyanogen, could be activated by hydrogen peroxide to generate some more active oxidation species (Palomeque *et al.* 2002; Nestler 2004; Malafosse). We suppose that hydrogen peroxide may be activated by 1-acetylguanidine. The active reaction pathways should be one of the three followings (Figure 1), which would be reconfirmed by the experiments.

As is well known that it is very difficult to separate the active species like peroxy ion from aqueous solution and verify their molecule structure. To clarify the activation pathway, a Raman spectrum method was applied to check the variation before and after the activation reaction. The solution of SPC, ACG and SPC/ACG were detected by Raman spectroscopy (Figure 2) separately, and the Raman spectrum of peracetic acid (PAA) was also tested for verifying the activation pathway (1) in Figure 1.



**Figure 1** | The possible activation pathways of SPC by ACG.



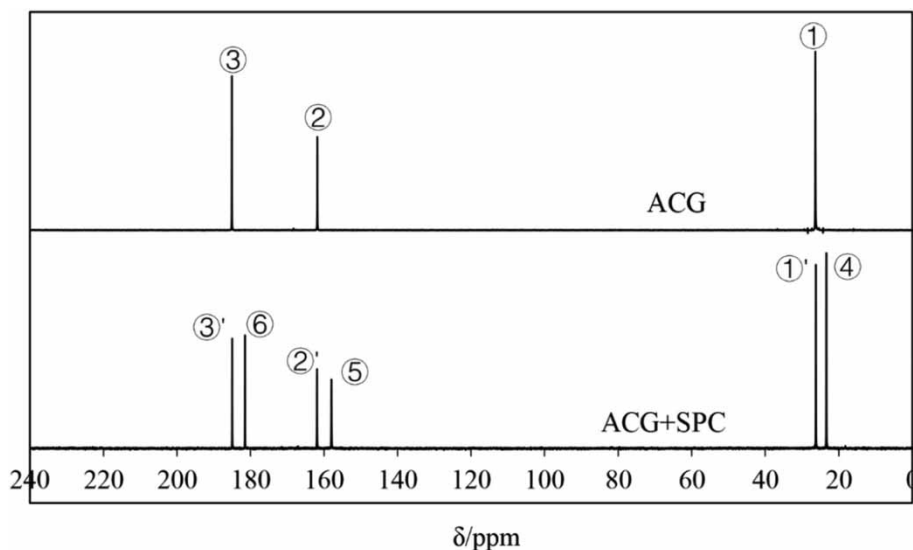
**Figure 2** | Raman spectrum of the ingredient solution of SPC, ACG, PAA and the complexed solution of SPC/ACG. The concentration of active oxygen in SPC and peracetic acid (PAA) was 0.5 mol/L while the ratio of active oxygen and ACG was 1:1.

It was known that hydrogen peroxide and sodium carbonate would be generated when SPC dissolved in water, so one can clearly observe the peak at  $874\text{ cm}^{-1}$  which was assigned to the stretching vibration of ‘-O-O-’ structure in  $\text{H}_2\text{O}_2$  molecule, and the peak at  $1,065\text{ cm}^{-1}$  which was assigned to the stretching vibration of  $\text{CO}_3^{2-}$  ion. In the Raman spectrum of ACG solution, the peak at  $927\text{ cm}^{-1}$  could be assigned to the stretching vibration of  $\text{N}=\text{C}-\text{N}$  structure. It should be noted that in the spectrum of complexed solution SPC/ACG, the peak at  $874\text{ cm}^{-1}$  and  $927\text{ cm}^{-1}$  disappeared, as well as two new peaks at  $824\text{ cm}^{-1}$  and  $1,009\text{ cm}^{-1}$  appeared. This suggested that some new activated species generated. As compared to the Raman spectrum of PAA, the characteristic peak at  $891\text{ cm}^{-1}$  was not found in SPC/ACG complexed solution. It indicated that the activation of SPC/ACG did not conduct by the pathway (1) in Figure 1. The peaks at  $824\text{ cm}^{-1}$  and  $1,009\text{ cm}^{-1}$  may be assigned to the stretching vibration of ‘ $\text{N}=\text{C}-\text{O}$ ’ and ‘-O-O-’ structure in the functional group of peroxy imide acid ( $\text{HN}=\text{C}-\text{OOH}$ ), respectively. Meanwhile, the peak of the shear vibration of ‘ $-\text{NH}_2$ ’ should be  $(1,590\text{--}1,650)\text{ cm}^{-1}$ , which was not detected in SPC/ACG complexed solution.

To further clarify the activation pathway, the aqueous solution of ACG and SPC/ACG complexed solution were detected by  $^{13}\text{C}$  NMR spectrometry, respectively. As shown in Figure 3, three single-peaks with chemical shifts of 26.35, 161.84 and 185.05 can be observed in the spectrum of ACG solution. It can be easily assigned to the three C atoms in ACG molecule, as listed in Table 1. In the spectrum of SPC/ACG solution, the three peaks of ACG can be obviously observed. In addition to that, three new peaks also can be observed beside the original three peaks of ACG, and the chemical shift decreased around 2.8–3.8 ppm. It indicated that the chemical structure of the generated activated product was quite similar to ACG. Thus, we suppose that the activation of SPC/ACG might be conducted by pathway (2) to produce acetyl peroxide imide acid, and the assignment of  $^{13}\text{C}$  spectrum is listed in Table 1.

### 3.2. Decontamination of HD and VX by SPC/ACG based formula

On the basis of the activation reaction between SPC and ACG, the generated species might behave to be more active towards decontaminating chemical warfare agents. Thus, the influence of molar ratio of active oxygen and ACG ((O)/(activator)), pH value, molar ratio of active oxygen and CWAs ((O)/(HD) or (O)/(VX)) were investigated in order to obtain an optimized decontaminant formula. For the decontamination of HD, the experimental results indicated that decontamination ratio of HD would increase while increasing the molar ratio of active oxygen and ACG ((O)/(ACG)) to around 1:1, then the decontamination ratio would not increase by increasing (O)/(ACG) ratio, as shown in Figure 4(a). It suggested that the optimized molar ratio of (O) and ACG was 1:1. Figure 4(b) gave the influence of pH value of the solution to the decontamination efficiency of HD; it indicated that the increasing of pH value would contribute to decontaminating HD. This result was quite consistent with that in hydrogen peroxide solution complexed with acetonitrile (Vacque *et al.* 1996) or benzonitrile (Popiel *et al.* 2005). As is known that the basic condition would be conducive to the hydrolysis and elimination reaction of HD, so increasing the pH value could promote the degradation of HD in aqueous solution. It can be seen in Figure 4(c)



**Figure 3** |  $^{13}\text{C}$  NMR spectrum of ACG and SPC/ACG complexed solution. The concentration of active oxygen in SPC was 0.5 mol/L while the ratio of active oxygen and ACG was 1:1.

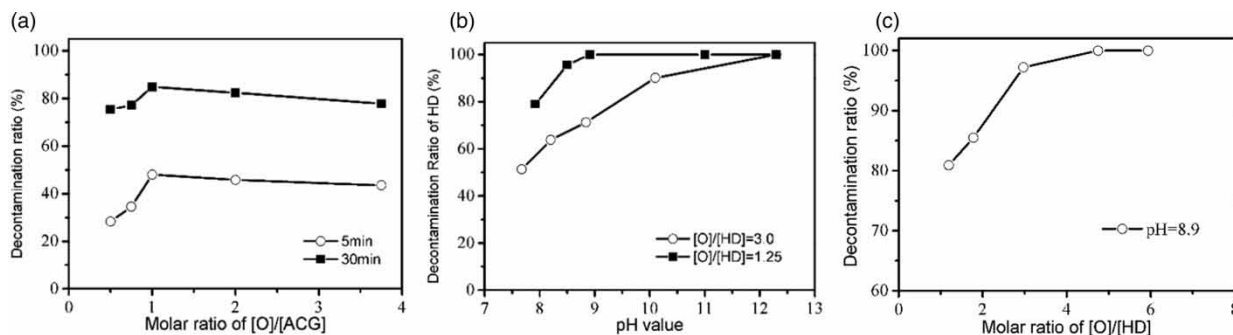
**Table 1** |  $^{13}\text{C}$  NMR spectrum data of ACG and SPC/ACG

| Solution | Number | $\delta_{\text{C}}/\text{ppm}$ | Assignment of C atoms |
|----------|--------|--------------------------------|-----------------------|
| ACG      | ①      | 26.35                          |                       |
|          | ②      | 161.84                         |                       |
|          | ③      | 185.05                         |                       |
| SPC/ACG  | ①'     | 26.23                          |                       |
|          | ②'     | 161.90                         |                       |
|          | ③'     | 184.99                         |                       |
|          | ④      | 23.44                          |                       |
|          | ⑤      | 158.11                         |                       |
|          | ⑥      | 181.46                         |                       |

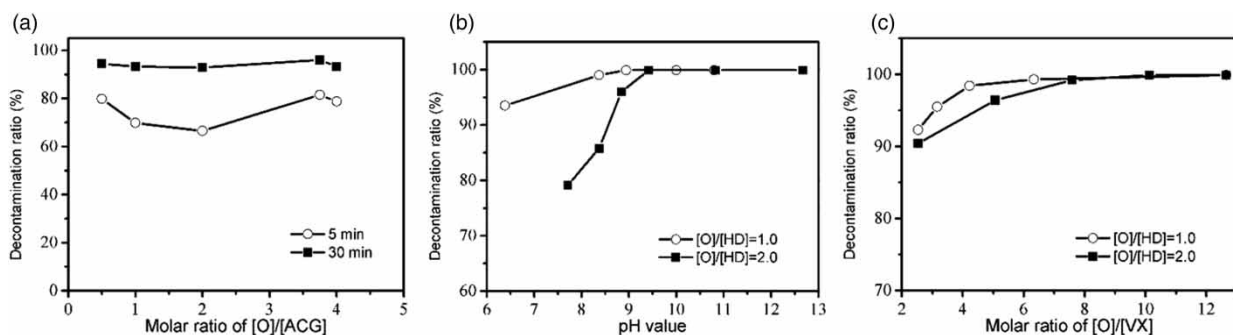
that the molar ration of (O)/(HD) should be more than 3 to achieve a high decontamination efficiency (>99%) in 30 min, where the (O)/(ACG) was 1:1 and the pH value of the complexed solution was about 8.9.

In the same way, the influence of pH value, molar ratio of ACG and VX were also investigated in SPC/ACG solution, as shown in Figure 5. The experimental data suggested that the effect of (O)/(ACG) was not remarkable for decontaminating VX (Figure 5(a)). Meanwhile, the optimal pH value for decontaminating VX should be no less than 9.5. Nevertheless, the (O)/(VX) should be no less than 7 to achieve a decontamination percentage over 99% in 30 min.

According to the above experimental results, a solid-state decontaminant formula based on SPC and ACG could be attained, where the mass ratio of SPC, ACG, sodium dihydrogen phosphate and disodium hydrogen phosphate was approximate to 1:1:1:1. Further, the decontamination performance of SPC/ACG formula was tested for HD and VX. When the concentration of the decontamination solution was 4% and the volume ratio of decontamination solution to CWAs droplets was 200:1, HD and VX were nearly completely degraded within 30 min at the temperature range from 0 °C to 45 °C, as listed in Table 2. Furthermore, it was verified in further experiments that the volume ratio of decontamination solution to CWAs could be decreased to 50:1 while the mass concentration of SPC/ACG formula was increased to 10%.



**Figure 4** | The decontamination efficiency of HD in SPC/ACG complexed aqueous solution under different conditions. The concentration of active oxygen (O) was 0.020 mol/L in all solutions; the concentration of HD was 0.016 mol/L and the pH value was 10.8 ( $\pm 0.1$ ) in (a); the pH value was adjusted by citric acid, phosphate and sodium hydroxide in (b); the decontamination time was 30 min in (b) and (c); the molar ratio of active oxygen and ACG was 1.0 in (b) and (c).



**Figure 5** | The decontamination efficiency of VX in SPC/ACG complexed aqueous solution under different conditions. The concentration of active oxygen (O) was 0.048 mol/L in all solutions; the concentration of VX was 0.004 mol/L and the pH value was 10.8 ( $\pm 0.1$ ) in (a); the pH value was adjusted by citric acid, phosphate and sodium hydroxide in (b); the decontamination time was 30 min in (b) and (c).

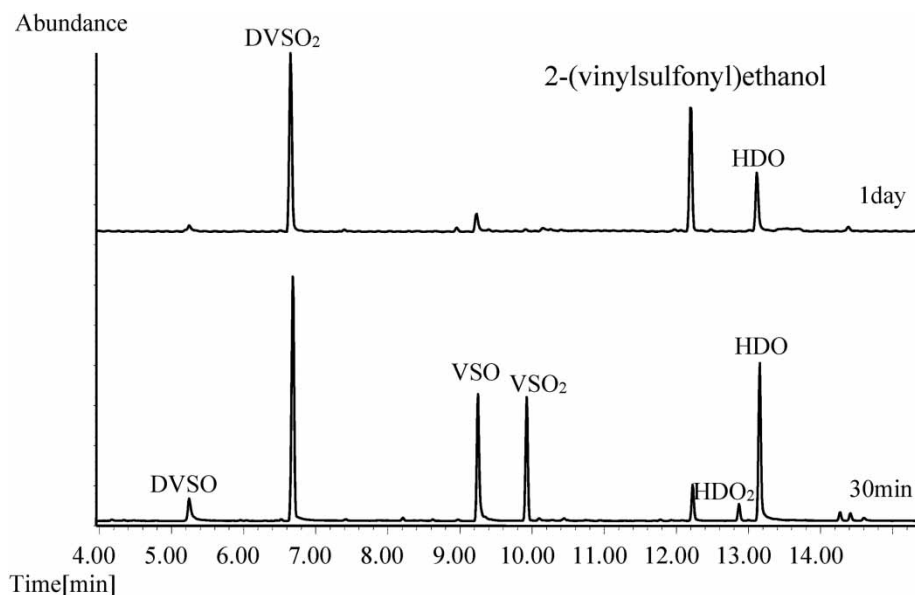
**Table 2** | Decontamination efficiency of HD and VX by SPC/ACG formula under different temperature

| CWAs | Temperature ( $^{\circ}\text{C}$ ) | Decontamination efficiency (%) |        |        |        |  |
|------|------------------------------------|--------------------------------|--------|--------|--------|--|
|      |                                    | 5 min                          | 10 min | 20 min | 30 min |  |
| HD   | 0                                  | 81.6                           | 93.5   | 99.0   | ND     |  |
|      | 20                                 | 99.0                           | ND     | ND     | ND     |  |
|      | 45                                 | ND                             | ND     | ND     | ND     |  |
| VX   | 0                                  | 79.2                           | 86.7   | 91.5   | ND     |  |
|      | 20                                 | 99.0                           | ND     | ND     | ND     |  |
|      | 45                                 | ND                             | ND     | ND     | ND     |  |

The mass concentration of decontaminant was 4%, pH value was 8.9. ND = not detected.

### 3.3. Decontamination products and pathways of HD and VX

In order to ascertain the degradation pathways of HD and VX in the SPC/ACG aqueous solution, the decontamination products had been detected and identified by GC/MS and IC approaches. Figure 6 had shown that the GC/MS total ion chromatography of the extracted degradation products of HD in SPC/ACG aqueous solution. It can be seen that a series of non-polar degradation products were detected and identified after reacting 30 min (Table 3), such as mustard sulfoxide (HDO) and mustard sulfone (HDO<sub>2</sub>), 2-(vinylsulfonyl) ethanol (VSO<sub>2</sub>-OH), vinyl 2-chloroethyl and divinyl sulfoxide/sulfone (DVSO and VSO/DVSO<sub>2</sub> and VSO<sub>2</sub>). Nevertheless, only divinyl sulfone, divinyl sulfone and mustard sulfoxide were detected



**Figure 6** | GC/MS total ion chromatogram for the degradation products of HD in SPC/ACG aqueous solution at pH 8.9, with 0.2 mol/L active oxygen and a molar ratio of active oxygen to HD of 4.7. (The particular compounds to the abbreviation marking the present peaks would be detailed seen in Table 3.)

**Table 3** | Possible degradation products of HD identified by GC/MS

| No. | Name                          | Abbreviation         | Molecular structure |
|-----|-------------------------------|----------------------|---------------------|
| 1   | Divinyl sulfoxide             | DVSO                 |                     |
| 2   | Divinyl sulfone               | DVSO <sub>2</sub>    |                     |
| 3   | Vinyl 2-chloroethyl sulfoxide | VSO                  |                     |
| 4   | Vinyl sulfone                 | VSO <sub>2</sub>     |                     |
| 5   | 2-(vinylsulfonyl)ethanol      | VSO <sub>2</sub> -OH |                     |
| 6   | Mustard sulfone               | HDO <sub>2</sub>     |                     |
| 7   | Mustard sulfoxide             | HDO                  |                     |

as non-polar degradation products in the decontamination solution after one day. It suggested that the oxidation and elimination reaction would proceed much deeper while prolonging the reaction time to one day. Meanwhile, the elimination reaction usually occurs easily when the pH value is much higher. Therefore, the elimination reaction would be appear in the SPC/ACG system with the pH value 8.9.

**Table 4** | Possible degradation products of HD identified by LC/MS

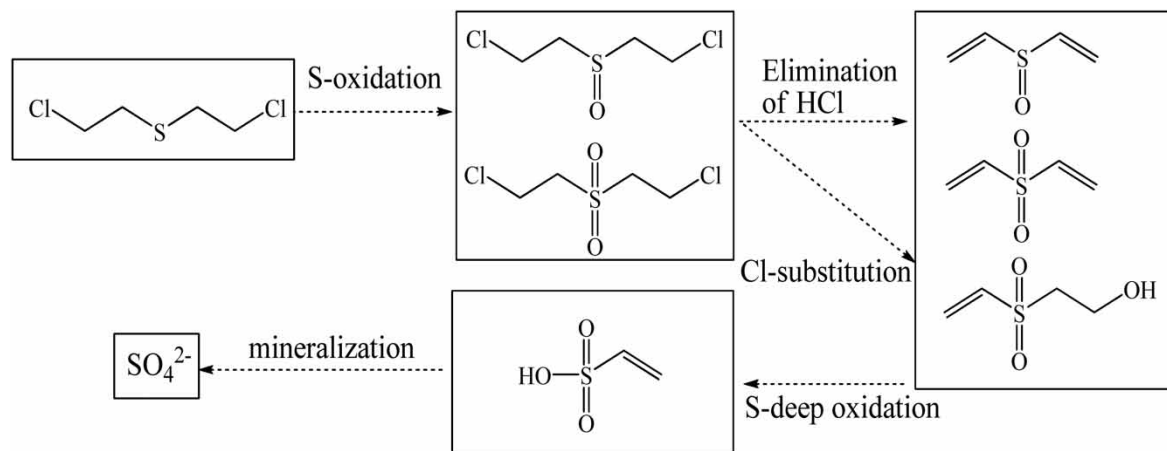
| No. | Name                | Structural formula | Mass                  |
|-----|---------------------|--------------------|-----------------------|
| 1   | Diethanol sulfone   |                    | M+H <sup>+</sup> =155 |
| 2   | Isethionic acid     |                    | M-H <sup>+</sup> =125 |
| 3   | Vinyl sulfonic acid |                    | M-H <sup>+</sup> =107 |

The polar compounds in the decontamination solution after one day were analyzed by LC/MS approach. Only three species were detected as negative ion ( $M \pm H^+$ ) in the decontamination solution. The obtained liquid chromatogram with extracted ion chromatograms ( $M \pm H^+$ ) were presented in Fig. S1. One could analyze these compounds based on the retention time and the  $M-H^+$  peaks. The possible structural formulas of the detected species were therefore deduced, as presented in Table 4. These detected sulfonic acid compounds were quite consistent with that observed in the references (Greenhalgh & Bannard 1959; Qi *et al.* 2013). Furthermore, S atom of partial HD would be finally oxidized to  $SO_4^{2-}$ , which was detected by IC. The mineralization ratio of S atom in the total of HD was calculated to be about 10% after one day.

In consideration of these results, a decontamination pathway involving oxidation of S atom, substitution of Cl atom and elimination of HCl by active oxygen (Figure 7) was deduced, which is quite similar to that in SPC/TAED decontamination solution (Qi *et al.* 2013). The pH value of the SPC/ACG system was about 9, but the elimination reaction occurred. This may contribute to strong nucleophilic of peroxy imide acid ion in the solution.

### 3.3.1. Decontamination products and pathways of VX

Similarly, the non-polar degradation products of VX extracted by dichloromethane, but only *N,N*-diisopropylformamide was detected by GC/MS, as shown in Fig. S2. However, several polar degradation products of VX were detected by LC/MS after one day of degradation, as seen in the extracted ion chromatograms ( $M \pm H^+$ ) in Fig. S3. The possible structural formulas of the detected species were therefore deduced, such as such as *N,N*-diisopropylhydroxylamine, diisopropylcarbamic acid, ethyl methylphosphonic acid (EMPA) and 2-(diisopropylamino)ethanesulfonic acid, 2-(hydroxy(isopropyl)amino)ethane-1-sulfonic acid, as presented in Table 5. These products were also detected by a precolumn derivation approach, as shown in Fig. S4.

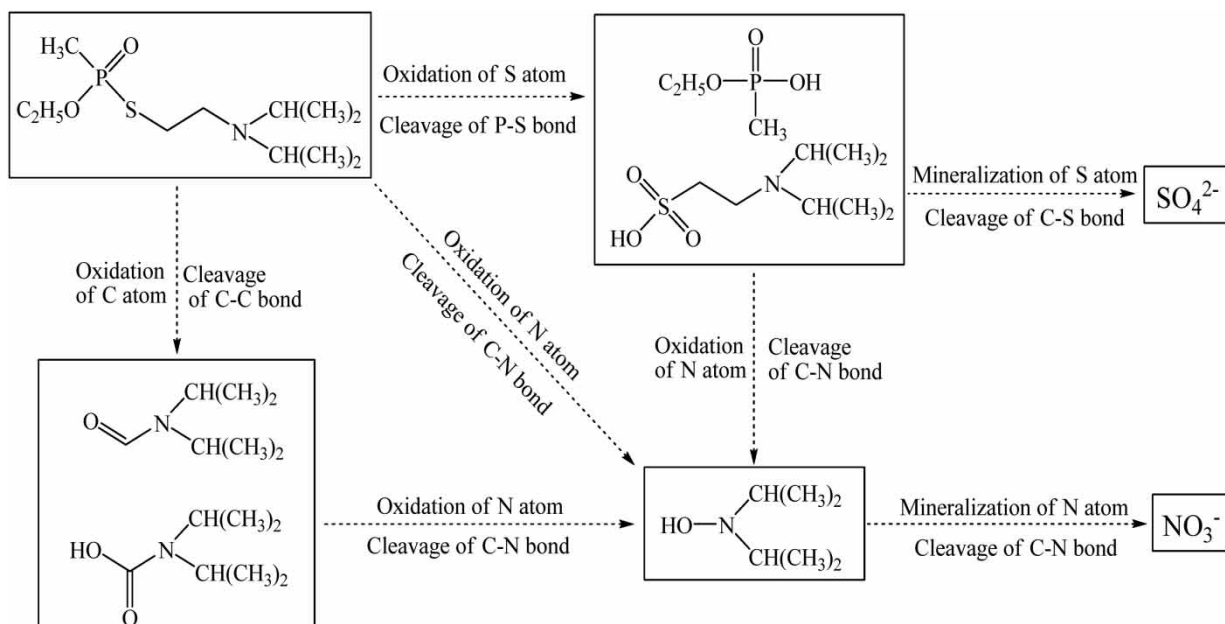
**Figure 7** | The degradation pathway of HD in SPC/ACG aqueous solution.



**Table 5** | Possible degradation products of VX identified by LC/MS

| No. | Name  | Molecular structure | Mass                  |
|-----|---|---------------------|-----------------------|
| 1   | N,N-diisopropylhydroxylamine                      |                     | M+H <sup>+</sup> =118 |
| 2   | ethyl methylphosphonic acid (EMPA)                |                     | M-H <sup>+</sup> =123 |
| 3   | 2-(diisopropylamino)ethanesulfonic acid           |                     | M-H <sup>+</sup> =208 |
| 4   | 2-(hydroxy(isopropyl)amino)ethane-1-sulfonic acid |                     | M-H <sup>+</sup> =182 |

Almost 16% of the S atoms were oxidized into  $\text{SO}_4^{2-}$  as detected by IC after one day. The mineralization ratio of S atom was less than that of VX in the SPC/TAED aqueous solution (Lion *et al.* 1997). The product ethyl methylphosphonic acid (EMPA) detected was consistent with the literatures (Greenhalgh & Bannard 1959; Winemiller *et al.* 2003; Qi *et al.* 2013). The  $\text{PO}_3^{3-}$  or  $\text{PO}_4^{3-}$  ion was not detected by IC, which suggested that the P-C bond appeared quite stable according to the products detected by GC/MS. It can be seen from the molecular structure of some of detected products that oxidation had occurred on the carbon atom next to the nitrogen ( $\alpha$ -C) in VX molecule to produce aldehyde, ketone and carboxylic acid. The nitrogen atom in VX molecule can be oxidized into oxime and  $\text{NO}_3^-$  ions which were detected by IC. The mineralization ratio of N

**Figure 8** | The degradation pathway of VX in SPC/ACG aqueous solution.

atom in VX molecule was calculated to be about 31%. Nevertheless, the  $\text{NO}_3^-$  ion was not detected by IC during the degradation process of VX in SPC/TAED aqueous solution (Qi *et al.* 2013).

In a word, the decontamination pathways of VX in the SPC/ACG aqueous solution mainly involved the oxidation of S, C and N atoms as well as the cleavage of the P-S, C-C, C-N bonds (Figure 8).

#### 4. CONCLUSION

In the aqueous solution, ACG as a peroxide activator could react with SPC to produce acetyl peroxy imide acid as proved by Raman and  $^{13}\text{C}$  NMR spectrum. The SPC/ACG complexed solution behaved quite efficiently towards decontaminating HD and VX. On the basis of the results on influence factors such as molar ratio of (O)/(ACG), (O)/(CWA), and the pH value, an optimized decontaminant formula was obtained, where the molar ratio of (O)/(ACG) was 1:1 while the pH value was about 9. To achieve the decontamination percentage over 99%, the molar ratio of active oxygen to CWA ((O)/(CWA)) needed to be at least 3 for HD and 7 for VX. What's important is that the SPC/ACG formula had good performance for decontamination of HD and VX, which would be used to decontaminate CWAs when the mass concentration was from 4% to 10% at the temperature range 0 °C to 45 °C. Meanwhile, based on the identified degradation products, the degradation pathways of HD and VX were deduced. It indicated that HD molecule was destroyed by oxidation and elimination reaction, while the degradation pathway of VX molecule mainly involved oxidation and nucleophilic substitution reaction.

#### ACKNOWLEDGEMENTS

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#### DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

#### CONFLICT OF INTEREST

The authors declare there is no conflict.

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