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Self-driven microplasma decontaminates chemical warfare agent simulant in different gas environments

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Abstract

To develop and refine a self-driven plasma decontamination system, this study investigated the effect of different gas environments (air, Ar, Ar/O₂, and Ar/O₂/H₂O) on the degradation efficiency of 2-chloroethyl ethyl sulfide (2-CEES). A dielectricdielectric rotating triboelectric nanogenerator (dd-rTENG) was constructed to mechanically induce atmospheric plasma. The dominant active species of different plasmas were identified through spectroscopic and chemical probe diagnostic methods. The results revealed that Ar/O2 and Ar/O2/H2O plasmas generated higher levels of reactive O_x species (O_3 , O_2^- , and 1O_2) and OH radicals, respectively. Notably, the Ar/ O_2 and Ar/O₂/H₂O plasmas exhibited significantly higher decontamination efficiencies than the other plasmas. Moreover, the Ar/O₂/H₂O plasma featured an energy utilization efficiency of 0.962 µg/J, which is nearly twice that of the previously reported study. However, the Ar plasma exhibited minimal decontamination effect owing to its low electron energy and absence of active species. Further studies have indicated the vital role of reactive oxygen species in the 2-CEES decontamination process. Active Ox can promote the oxidation of 2-CEES, while OH can effectively mitigate the peroxidation process. Furthermore, the system exhibited low electron energy, which might play small role for 2-CEES decontamination. This study is vital for developing self-driven plasma decontamination devices and provides significant clues for understanding the 2-CEES decontamination mechanism.

Keywords: triboelectric nanogenerator, plasma, active species, gas environment, 2-CEES decontamination

1. Introduction

Chemical warfare agents (CWAs) were widely used on battlefields in the 20th century owing to their strong toxicity, rapid action, persistent effects, and broad range of harmful impacts ^[1, 2]. Among various CWAs, sulfur mustard (HD) can induce symptoms such as blistering, erythema, edema, erosion, and necrosis upon skin contact. Moreover, HD was known as the "king of poisons" during wartime owing to its ease of preparation, high toxicity, and low manufacturing cost^[3]. Despite the prohibition of its production, storage, and transportation by the Chemical Weapons Convention, HD still poses a significant threat to the security of the international community^[4, 5]. Therefore, it is urgent to develop CWA decontamination techniques and understand the decontamination mechanisms.

Low-temperature plasma is a highly promising technology for CWA decontamination, owing to its broad spectrum, high efficiency, and environmentally friendly characteristics^[6, 7]. High-energy electrons and active species generated in plasma interact with CWA molecules, leading to the decomposition or oxidization of CWAs into different substances through chemical bond-breaking or oxidation reactions^[8, 9]. Moreover, 2-chloroethyl ethyl sulfide (2-CEES) is commonly used as a less-toxic simulant for HD decontamination processes owing to their similar chemical properties^[10]. Traditional plasma excited by alternating current (AC) or pulsed power supplies has proven to be a powerful tool for 2-CEES decontamination. Li et al.[11] explored the use of a helium plasma jet to decontaminate 2-CEES and confirmed that OH was responsible for the production of 2-hydroxyethyl sulfide. Wang et al. ^[12] demonstrated that as plasma treatment time increased, the mineralized products of 2-CEES mainly comprised CO₂, H₂O, HCl, and H₂S. Chen et al. ^[13] further demonstrated that chemical bond breaking was responsible for 2-CEES decontamination under conditions of a high N₂/O₂ ratio, while oxidation played a significant role under conditions of a low N₂/O₂ ratio. The aforementioned studies indicated the vital roles played by both high-energy electrons and active plasma species in 2-CEES decontamination.

Although traditional plasma devices exhibit excellent decontamination performance for CWAs, their large and costly excitation power sources limit their practical applications ^[14, 15]. In contrast, triboelectric nanogenerators (TENGs) can absorb mechanical energy from the environment and convert it into electrical energy. Moreover, they are characterized by self-driving capabilities, broad energy sources, simple structures, and low costs^[16-20]. Previous studies have shown that TENGs have excellent degradation performance for 2-CEES, dimethyl methylphosphonate (DMMP) and malathion, and the degradation products can be well controlled^[21, 22]. Meanwhile, the self-driven property of this system allows a safe and manually operated system to do chemicals degradation. Therefore, this technology can also be used for degrading CWAs in extreme environments, such as the battlefield, where lacks power supply, not to mention high-voltage power supply. This self-powered decontamination system can work with the operation by a single soldier. However, owing to their high voltage and

low current output characteristics, the decontamination performance and mechanism of self-driven plasma decontamination systems using TENGs differed from that of traditional technology.

In this study, to further develop and refine the decontamination system, the effect of different gas components such as oxygen and water vapor on the degradation efficiency of 2-CEES and subsequent toxic by-products was investigated. The plasma was generated in different background gases, including air, Ar, Ar/O₂, and Ar/O₂/H₂O, using a dielectric-dielectric rotating triboelectric nanogenerator (dd-rTENG) as the power source. The active species generated in each plasma were identified through spectroscopic and chemical probe diagnoses. Finally, numerical simulations, active species detection, and analysis of the decontamination effect were combined to elucidate the differences in the decontamination efficiencies of different plasmas on 2-CEES and their corresponding mechanisms.

2. Experimental

2.1. Fabrication of self-driven plasma decontamination system

The self-driven plasma decontamination system comprised a dd-rTENG, a rectifier, a decontamination chamber, a needle-plate electrode, and a gas supply device (Fig. 1). The 2-CEES diluted by acetonitrile solvent was placed in the decontamination chamber. The bubbles in Fig.1 represented the 2-CEES molecules. To achieve a higher output voltage, a dd-rTENG was constructed using an entire sheet of paper instead of strips in a paper strip rotating triboelectric nanogenerator (ps-rTENG). The dd-rTENG exhibited a similar structure to that of a previously described ps-rTENG^[21, 23], comprising a stator, a rotor, and a charge supplementary layer. The stator and rotor had similar basic structures, but the charge supplementary layer was modified from a paper strip to a paper layer to further increase the friction area, thereby improving the power output and wear resistance.

The rectifier in the decontamination system included a full-wave rectifier bridge comprising four diodes (R5000, DO-1). The needle-plate electrode consisted of a tungsten needle and an aluminum crucible placed in a 250 mL glass chamber. The aluminum crucible featured a diameter, height, and thickness of 6.7 mm, 6 mm, and 0.2 mm, respectively. Moreover, it served as both the plate electrode and the container for the simulant. Furthermore, the system comprised a tungsten needle electrode that was 180 mm long, with a curvature radius of 0.22 mm at the tip. Tungsten needle electrode was fixed above the aluminum crucible. To optimize plasma energy utilization and prevent the needle tip from contacting 2-CEES, we've chosen a 1 mm spacing for the upcoming experiment. The gas supply device comprised a gas cylinder, a mass flow controller (MFC), a bubbler, and valves. MFC was responsible for regulating the content and flow rate of each component in the background gas, while the bubbler introduced water vapor into the Ar/O₂/H₂O background gas. The gas flow rate and replacement time are calculated using the following formula^[24]:

$$Q = xt = V ln \frac{A_0}{A} \tag{1}$$

where Q is the amount of gas consumed, x is the gas flow rate, t is the replacement time,

V is the chamber volume, A_0 is the percentage of air in the initial background gas, and *A* is the percentage of air in the background gas after replacement. At *t* of 1 min, the *V* was 250 mL, A_0 was 100%, and *A* was 1%, resulting in an *x* of 1.15 L/min. The degree of gas replacement in the chamber exceeded 99 %. Therefore, *x* in the experiment was 1.2 L/min, and *t* was 1 min.



Fig. 1 Schematic diagram of self-driven plasma decontamination system.

2.2. Working principle of the dd-rTENG

The dd-rTENG operates based on the principles of the triboelectric effect and electrostatic induction^[25], similar to the ps-rTENG^[23]. However, the dd-rTENG differed in the charge supplementary layer, which plays a significant role in enhancing the outputs. According to the triboelectric series, paper tend to lose electrons, while polytetrafluoroethylene (PTFE) tend to gain electrons^[26]. Therefore, PTFE and paper were used as friction materials, while aluminum foil served as the induction electrodes. Figure 2 shows the complete working cycle of the dd-rTENG. In Step I, the friction between PTFE 1 and the paper layer generated large amount of negative and positive charges each. Owing to electrostatic induction, the Al electrode 1 were induced with respective negative charges. As PTFE 1 went on sliding, the induced charges on Al 1 and Al 2 changed accordingly with the position of PTFE1, subsequently producing an external current (Step II-III). In fact, all PTFE sectors contributed to the charge generation and induction (Step IV). Thus, the dd-rTENG device was endowed with very high voltage and current output.



Fig. 2 Schematic of the working principle of the dd-rTENG.

2.3. Discharge characterization

The voltage and current of the dd-rTENG and plasma were measured using a highvoltage probe (Tektronix, P6015A, 1000:1), an oscilloscope (Tektronix, DPO2024B, 200 MHz), and a variable resistor box (MC-21-B, Zhicheng, China). The current in the circuit was indirectly measured through the observation of the voltage across a 4 M Ω resistor, and spectral acquisition was performed using an emission spectrometer (FX2000+RD, Fuxiang, China). To compensate for the low brightness in air, Ar/O₂, and Ar/O₂/H₂O plasmas, their spectra were obtained in an open environment, where 2 L/min of the relevant gas was blown between the needle plate electrodes to create a similar gas environment. A fiber optic was placed near the plasma during discharge to record the spectra with a 1000 ms integration time. The distance between the air, Ar/O₂, and Ar/O₂/H₂O plasma and fiber optic was 4 mm. However, owing to the high brightness of the Ar plasma, the spectrum was obtained inside a closed chamber with a 100 ms integration time. The distance between the Ar plasma and fiber optic was 33 mm. Ozone (O₃) in the surrounding environment was detected using a pump suction-type O₃ detector (XLA-BX-O₃, Pulitong, China).

2.4. Reactive free radical diagnosis

Benzenedicarboxylic acid and furfuryl alcohol were used as detection probes for hydroxyl radical (OH) and singlet oxygen ($^{1}O_{2}$), respectively. The 40 µL probe solutions were treated with plasma for 2 min and then subjected to detection to identify changes resulting from the treatment. The solution preparations and experimental procedures were performed according to the methods described in the literature [271]. The O₂⁻ and ONOO⁻ were diagnosed using the superoxide anion radical detection kit (Leagene, T01123) and peroxynitrite anion detection kit (BestBio, BB-461552-100T), respectively. The diagnosed samples comprised 40 µL of plasma-treated deionized water, and the experimental procedures were performed according to the instruction manuals provided with the kits.

2.5. 2-CEES decontamination and products detection

Four gas environments, such as air (30% relative humidity), Ar (dry, relative humidity <0.0187%), 79% Ar/21% O₂ (dry, relative humidity <0.0187%), and 79% Ar/21% O₂/H₂O (81% relative humidity), were used for decontaminating 2-CEES. Each plasma type represented a specific active species, in which air represented active NO_x, Ar represented electrons, Ar/O₂ denoted active O_x (O₃, O₂⁻, and ¹O₂), and Ar/O₂/H₂O represented OH.

Prior to decontamination, the aluminum crucible was cleaned with 40 μ L of acetonitrile to remove impurities. Subsequently, 40 μ L of 150 mg/L 2-CEES was added to the aluminum crucible, and the gas supply device replaced the gas in the chamber with the target gas. The dd-rTENG was activated to initiate the plasma treatment. After a specific duration of plasma treatment, the residual liquid was extracted and adjusted to 150 μ L with dichloromethane. The decontamination effect was analyzed using a gas chromatograph (Thermo Scientific Trace 1300) equipped with a DB-5MS (5% phenylmethyl polysiloxane) column (30 m × 0.25 mm × 0.25 μ m, Palo Alto, CA, USA). The gas chromatography–mass spectrometry (GC-MS) parameters were set as follows: a spitless injection model with an injection time of 1 min and an injection temperature of 220°C; a carrier gas (N₂) flow rate of 1.0 mL/min; a liquid sample injection volume of 1 μ L. The temperature control program was as follows: it was set at 50°C, maintained for 2.0 min, increased to 170°C at a rate of 10°C/min, further increased to 250°C at a rate of 40°C/min, and then maintained for 5 min.

Owing to its high polarity, the direct detection of 2-hydroxyethyl sulfide (the decontamination product of 2-CEES) using the GC column employed in this study was not possible. Therefore, N, O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was used as a derivatization reagent to modify 2-hydroxyethyl sulfide. The experimental process comprised the following steps: First, 40 μ L of 150 mg/L 2-CEES was treated with plasma, and the residual liquid was then extracted and dried at 50°C. Subsequently, 200 μ L of a 1:9 BSTFA/dichloromethane mixture was added and thoroughly shaken. Finally, 20 μ L of BSTFA was added, and the sample reacted at 70 °C for 30 min^[28].

3. Results and discussion

3.1. Electrical characteristics of dd-rTENG

The as-fabricated *dd-rTENG* exhibited an output open circuit voltage of 3.5 kV, a short circuit current of 156 μ A, and a transfer charge of 330 nC (Figs. 3a-c). Figures 3d-e illustrate the response of *dd-rTENG* to different external loads. Below 1 M Ω , both voltage and current remained relatively constant as the external load increased. Within the range of 1 M Ω -1 G Ω , the voltage output of *dd-rTENG* rapidly increased, while the current rapidly decreased, eventually reaching an open circuit voltage. At 30 M Ω , *dd-rTENG* achieved a maximum peak power of 0.2295 W. Additionally, the *dd-rTENG* exhibited excellent stability, maintaining nearly constant output voltage even after 10,000 s of continuous operation. This feature was beneficial for the continuous and stable degradation of 2-CEES.



Fig. 3 Characteristics of the *dd-rTENG*. (a-c) Voltage, Current, and charge output of the *dd-rTENG*; (d) variations in the current and voltage curves under the different external loads; (e) average power curve under the different external loads; (f) excellent stability of the *dd-rTENG*.

Furthermore, the electrical characteristics of the self-driven plasma system were investigated in four gas environments including air, Ar, Ar/O₂, and Ar/O₂/H₂O (Fig. 4). In all four gas environments, the plasma without the addition of simulant exhibited an arc discharge state. However, the plasmas featured significant differences in their breakdown voltage, current, and discharge frequency. At a distance of 1 mm between the needle and plate electrodes, the air, Ar, Ar/O₂, and Ar/O₂/H₂O plasmas featured discharge voltages of -2320, -1080, -1520, and -1600 V, respectively. These voltages corresponded to discharge currents of -340, -190, -240, and -250 μ A, discharge frequencies of 323, 969, 538, and 431 Hz, and average discharge powers of 0.073, 0.043, 0.055, and 0.051 W, respectively.

The internal resistance of the TENG led to a lower gas discharge voltage than its open-circuit voltage, and variations in the ionization energies of various gas components resulted in different breakdown voltages ^[29]. Among the four gas environments, N₂, O₂, and Ar comprised the main gas components. Previous studies have shown that under the same external conditions, the breakdown voltage values followed the order of $O_2 > N_2 > Ar^{[30, 31]}$. Therefore, the breakdown voltage values in the four environments (Air > Ar/O₂/H₂O \approx Ar/O₂ > Ar), which were consistent with this pattern. Additionally, as the difficulty of gas breakdown increased, a higher amount





Fig. 4 No-load output of *dd-rTENG* and the electrical characteristics of arc discharge for different plasmas.

To examine the effect of simulant addition on the electrical discharge of the plasma, the electrical characteristics and discharge images of different plasmas after simulant addition were evaluated (Fig. 5). The discharge state of plasmas shifted from arc discharge to corona discharge. At a distance of 1 mm between the needle and plate electrodes, the air, Ar, Ar/O₂, and Ar/O₂/H₂O plasmas exhibited discharge voltages of -2080, -560, -1440, and -1320 V, discharge currents of -155, -95, -130, and -130 µA, average discharge powers of 0.066, 0.035, 0.055, and 0.052 W, respectively. Additionally, the air, Ar/O₂, and Ar/O₂/H₂O plasmas featured discharge frequencies of 431, 754, and 754 Hz, respectively. Figure S1 compares the electrical characteristics of corona and arc discharge. The results indicated that the addition of simulant reduced the discharge voltages and currents of the four plasmas, but increased their discharge frequency. This was due to the reduced distance between the needle and plate electrodes by adding acetonitrile addition, thereby facilitating gas discharge. Nevertheless, the average discharge power of both arc and corona discharge remained significantly unchanged. Furthermore, the Ar environment featured a brighter plasma than the other gas environments. However, the discharge characteristics of the voltage and current plots were nonexistent in the Ar environment owing to the addition of the stimulant.



Fig. 5 Electrical characteristics of corona discharge for different plasmas.

3.2. Optical spectra of different plasmas

The plasma discharge process generated various active species through a series of chemical reactions. As the plasma was ignited, gas atoms and molecules at higher energy levels transitioned to excited states at lower energy levels, emitting photons^[35]. In this study, the emission spectrometer was used to obtain emission spectra from different plasmas, to identify the produced active species. Moreover, the simulant was placed between the needle and plate during spectral acquisition to study the effect of pollutants on active species production.

The emission spectra (Figs. 6a-d) of the four plasmas exhibited characteristic peaks corresponding to OH ($A^2\Sigma^+ \rightarrow X^2\Pi$) (306 to 309 nm), N₂ second positive system N₂ ($C^3\Pi_u \rightarrow B^3\Pi_g$) (330 to 420 nm), N₂⁺ first negative system N₂⁺ ($A^2\Pi_u \rightarrow X^2\Sigma_g^+$) (390 to 420 nm), and H- α (656.3 nm)^[36-38]. Notably, the spectra of air, Ar/O₂, and Ar/O₂/H₂O plasmas obtained in an open environment exhibited N₂-related peaks. Additionally, the spectra of Ar/O₂ plasma obtained in the presence of water vapor in the open environment featured OH and H_a characteristic peaks. However, the OH in the Ar/O₂ plasma featured a significantly lower emission intensity compared with the air plasma owing to dry gas purging. The higher humidity of Ar/O₂/H₂O resulted in significantly higher peak intensities for OH and H_a compared with air, indicating a higher generation of OH.



Fig. 6 Emission spectra of (a) air, (b) Ar, (c) Ar/O₂ and (d) Ar/O₂/H₂O plasma.

The spectrum of the Ar plasma was obtained in a closed chamber owing to its higher light intensity. However, despite the absence of N_2 in the background gas (Ar), the spectrum of the Ar plasma exhibited peaks corresponding to both Ar and N_2 . Therefore, it was hypothesized that the characteristic peak of N_2 was attributable to the N in acetonitrile (CH₃CN) present in the simulant. To confirm this hypothesis, the spectrum of the Ar plasma without the simulant was obtained in a closed Ar chamber, and the results are shown in Fig. S2. The spectrum of the Ar plasma did not feature a characteristic peak corresponding to N_2 , indicating that the interaction between acetonitrile and the plasma was responsible for the emergence of the excited state N_2 .

3.3. Active species of plasmas

The plasma discharge process generated various active radicals, including OH, ONOO⁻, O_2^- and 1O_2 [^{39]}, which can significantly affect the decontamination rate and products of 2-CEES. Therefore, different detection methods were used in this study to diagnose OH, ONOO⁻, O_2^- , 1O_2 , and O_3 .

The OH is considered the most oxidizing species in plasma, with an oxidation potential of 2.8 eV. Previous studies have indicated that OH played a cruial role in the 2-CEES decontamination. The OH generated by the Ar/O₂/H₂O plasma was 3.14 times that of the air (Fig. 7a). The OH generation was mainly attributed to the reaction between $O(^{1}D)$ and H₂O in a humid environment, as shown in reaction (2)^[40]. The air in the experiment displayed a relative humidity of 30%, while the Ar/O₂/H₂O plasma featured a higher relative humidity, reaching 81% after bubbling. An increase in the amount of water vapor in the background gas can significantly increase the amount of OH. Therefore, the OH detection was not conducted in the Ar and Ar/O₂ plasma environment owing to the absence of H₂O.

$$O(1D) + H_2 O \rightarrow 2OH \tag{2}$$

Furthermore, ${}^{1}O_{2}$ is a highly reactive species with an oxidation potential of 2.2 eV. Furfuryl alcohol was used as the probe, but the detection of ${}^{1}O_{2}$ was not repeated owing to the safety issues associated with furfuryl alcohol^[23]. Figure 7b shows the amount of ${}^{1}O_{2}$ produced by air, Ar/O₂, and Ar/O₂/H₂O plasmas. The similar amount of ${}^{1}O_{2}$ produced by these plasmas indicated that the differences in the background gas components did not significantly affect its production. The results of O₂⁻ detection are presented in Fig. 7c. The hydroxylamine oxidation method was employed to indirectly detect O₂⁻ through NO₂⁻ detection^[41]. However, NO₂⁻ generated by the air plasma could interfere with the O₂⁻ detection, leading to a higher O₂⁻ value for the air plasma. Nonetheless, this indicated that the air plasma produced a higher amount of NO₂⁻. Compared with the control group, the Ar/O₂ and Ar/O₂/H₂O plasmas featured lower levels of O₂⁻ However, the control group displayed slightly higher O₂⁻ levels than these plasmas. Moreover, the air plasma produced only a small amount of ONOO⁻, possibly owing to the low energy of the plasma (Fig. 7d). This indicated that plasma tended to produce O₃ at low input energies and more ONOO⁻ at high input energies^[42].



Fig. 7 Concentrations of (a) OH; (b) ${}^{1}O_{2}$; (c) O_{2}^{-} ; (d) ONOO⁻ at 2 min for different plasmas; (e) Variations in O₃ concentration at 0–320 s for different plasmas; (f) Comparison of O₃ concentration at 320 s for different plasmas (*: 0.01 < P < 0.05; **: 0.001 < P < 0.01; ***: P < 0.001).

The main generation reactions of O_3 (with an oxidation potential of 2.07 eV) in the plasma are as follows:

$$0 + 0_2 + M \to 0_3 + M, M = 0, 0_2, 0_3, N_2$$
(3)

$$O(1D) + O_2 \to O_3 \tag{4}$$

$$0_2^- + 0 \to 0_3 + e$$
 (5)

Figure 7e illustrates the changes in the O_3 concentration as a function of discharge time for the four plasmas. The Ar plasma did not generate O_3 owing to the absence of O_2 . However, in the other three plasmas, the O_3 concentration increased with increasing

discharge time. Figure 7f compares the amount of O₃ produced by the four plasmas at 320 s. The results revealed that the Ar/O₂ plasma featured the highest O₃ concentration at 42.43 ppm, followed by the Ar/O₂/H₂O plasma at 10.93 ppm, and the air plasma at 22.1 ppm. The higher O₃ concentration in the Ar/O₂ plasma could be attributed to the dry background gas. Water vapor in the air and Ar/O₂/H₂O environments could dissolve some of the O₃ (as O₃ was 25 times more soluble in water than in air). Additionally, the Ar/O₂ background mainly gas comprised Ar and O₂ components, which provided more electrons to facilitate the O₃ production.

In summary, the $Ar/O_2/H_2O$ plasma exhibited the highest OH concentration, while the Ar/O_2 plasma generated a higher amount of reactive O_x . Moreover, the air plasma produced higher reactive NO_x levels but featured lower OH and reactive O_x levels.

3.4. Numerical simulation and calculation

The electron density, type, and concentration of active species in the plasma significantly varied with different background gases. To further investigate these differences, the discharge process was simulated using COMSOL with the same model as reported in a previous publication^[21]. According to their electrical characteristics, the air, Ar, Ar/O₂, and Ar/O₂/H₂O plasmas exhibited input voltages of -2080, -560, -1440, and-320 V, respectively.



Fig. 8 Electron densities of (a) air; (b) Ar; (c) Ar/O₂; (d) Ar/O₂/H₂O plasmas.

Figure 8 displays the electron density clouds of the four plasmas. Figure S3 shows the corresponding properties of the plasmas at 0.1 mm above the liquid surface, where the decontamination process occurred. The Ar plasma exhibited the highest electron density, reaching 6.94×10^{17} m⁻³ at 1 µs, which accounted for its high intense. In contrast, the electron densities of the other three plasmas were one to two orders of magnitude lower than that of the Ar plasma. The air plasma featured an electron density of 3.5×10^{16} m⁻³ at 0.3 µs, while the Ar/O₂ and Ar/O₂/H₂O plasmas exhibited similar electron densities of 1.18×10^{15} m⁻³ and 1.32×10^{15} m⁻³ at 0.5 µs, respectively. Nevertheless, all four plasmas displayed electron densities below conventional levels^[43, 44].

Besides electron density, electron energy is also a vital property of plasma. The electron energy was calculated via the bi-spectral line method, and the spectrum of the Ar plasma (Fig. 6b) served as the source data. According to the principles of thermodynamic equilibrium or local thermodynamic equilibrium, the emission intensities of two spectral lines of the same atom or ion satisfy the following equation^[13]:

$$\frac{I_1}{I_2} = \frac{A_1 g_1 \lambda_2}{A_2 g_2 \lambda_1} exp\left(-\frac{E_1 - E_2}{k T_e}\right) \tag{6}$$

where the numbers 1 and 2 represent the spectral lines of the same atom or ion at different wavelengths, I is the spectral emission intensity, g is the statistical weight, A is the transition probability, λ is the spectral wavelength, k is the Boltzmann constant, E is the excitation energy, and T_e is the electronic temperature. The relevant values are shown in Table S1. The T_e of the plasma is calculated as follows:

$$T_{e} = \left| \frac{E_{2} - E_{1}}{k \ln(\frac{l_{1}A_{2}g_{2}\lambda_{1}}{l_{2}A_{1}g_{1}\lambda_{2}})} \right|$$
(7)

Two specific spectral lines, with wavelengths of 696.5 and 750.5 nm, were selected as the target spectral lines for calculating T_e . The T_e of the Ar plasma was calculated as 3980 K using equation (7).

The plasma electron densities in different gas environments were obtained by COMSOL simulation of the discharge process, and the electron temperatures of the plasmas were calculated. Not only the electron densities of the four plasmas are lower than the conventional level, but also the electron temperatures of the argon plasma are lower, which confirmed that the electron energy is not the main factor to cause the chemical bond breaking in this experiment^[13].

3.5. 2-CEES decontamination by different plasmas

To investigate the effect of different gas components such as oxygen and water vapor on the degradation efficiency of 2-CEES, subsequent formation of toxic byproducts, and degradation mechanisms, four plasmas types, such as air, Ar, Ar with 21% O₂, and Ar with 21% O₂ and H₂O were employed. For the decontamination and characterization experiments, 40 μ L of 150 mg/L 2-CEES was placed between the needle and plate electrodes. The plasma treatment durations varied from 0 to 320 s using different plasma types, and the decontamination effect of 2-CEES was analyzed via GC-MS.

Figures 9a-d show the chromatograms of 2-CEES at various treatment times. 2-CEES displayed a retention time of 6.1 min, and the mass spectra are presented in Fig. S4a. The decontamination results revealed that the peak intensity of 2-CEES gradually decreased with treatment time after plasma exposure, except for the Ar plasma. The peak areas of 2-CEES were calibrated and calculated using data processing software, and the results are illustrated in Fig. 9e. The results indicated that the peak area of 2-CEES rapidly decreased to 0 within 320 s after exposure to air, Ar/O_2 , and $Ar/O_2/H_2O$ plasma treatments. In contrast, the peak area of 2-CEES slightly decreased after exposure to the Ar plasma. The decontamination rate *D* of 2-CEES is calculated using the following equation:

$$D = \frac{P_0 - P_t}{P_0} \tag{8}$$

where P_0 is the initial peak area of 2-CEES, and P_t is the peak area of 2-CEES after t min of plasma treatment.

The calculation results of decontamination rates of 2-CEES are shown in Fig. 9f. After treatments with both Ar/O₂ and Ar/O₂/H₂O plasmas, 2-CEES reached a decontamination rate of 100% at 120 s. While the air plasma achieved a decontamination rate of 100% at 200 s. However, the Ar plasma exhibited a significantly low decontamination rate of only 16.8% at 320 s. To exclude the volatilization effect, samples exposed to air (without plasma treatment, 0~320 s) were also analyzed via GC-MS. A maximum 2-CEES concentration decrease of 14.6% was observed after 320 air exposure (Fig. 9e), which confirmed that plasma treatment was the main reason for 2-CEES decontamination. However, the change in the 2-CEES concentration in the Ar plasma as a background gas from 0 to 320 s was similar to that of the control group, indicating that the Ar plasma featured no decontamination effect on 2-CEES.



Fig. 9 Variations in 2-CEES chromatogram with time after (a) air; (b) Ar; (c) Ar/O₂; (d) Ar/O₂/H₂O plasma treatment; curve of (e) 2-CEES peak area; (f) decontamination rate with time.

Finally, the energy utilization efficiency (E_e) of the four plasmas was calculated. The E_e is obtained using the following formula:

$$E_e = \frac{M_0 - M_t}{Pt} \tag{9}$$

where M_0 is the initial amount of 2-CEES, M_t is the residual amount of 2-CEES after plasma treatment for *t* seconds, *t* is the plasma treatment time, and *P* is the average discharge power, which was 0.066 W in this experiment. The results revealed that the Ar/O₂/H₂O plasma featured the highest E_e , reaching 0.962 µg/J, which is nearly twice that achieved in previous studies. The air and Ar/O₂ plasmas exhibited E_e of only 0.455 and 0.909 µg/J, respectively, which are one order of magnitude higher than those of commercial power supplies.

Therefore, the Ar/O₂ and Ar/O₂/H₂O plasmas exhibited higher decontamination efficiencies for 2-CEES, possibly owing to the presence of more reactive oxygen species, which played a vital role in the decontamination process. Regarding energetic electrons, all four plasmas in this study exhibited a lower electron density and temperature than conventional levels. Chen *et al.* ^[13]compared the effect of high and low electron temperature plasmas on 2-CEES decontamination, and found that lower electron temperatures (4175 K) led to the generation of fewer small organic molecules through the breaking of chemical bonds. However, the Ar plasma used in this study featured an electron temperature of only 3980 K. This indicates that the lower decontamination rate of 2-CEES in the Ar plasma was likely attributed to the low electron energy and absence of active species in the plasma.

3.6. 2-CEES decontamination products by different plasmas

As the treatment time increased, the 2-CEES chromatogram featured two characteristic peaks, which were identified as 2-chloroethyl ethyl sulfoxide (2-CEESO) and 2-chloroethyl ethyl sulfone (2-CEESO₂) through mass spectrometry analysis (Figs. S4b and c). Previous studies have shown that 2-CEESO and 2-CEESO₂ comprised the primary oxidation products of 2-CEES, and they were formed as a result of the oxidation of sulfur (S) atoms, which produced S=O and O=S=O bonds through reactions with active species^[45, 46]. These reactions caused the loss of electron-assisting roles of the S atom, leading to the reduction of 2-CEES toxicity^[10].

Figure S5 depicts the generation of 2-CEESO after different plasma treatments, with a retention time of 10.8 min. Figure 10a shows the variation in the 2-CEESO peak area with treatment time. The absence of an oxidizing component in the Ar plasma hindered the formation of 2-CEESO. However, in the other three plasmas, the concentration of 2-CEESO gradually increased with time, reaching its highest level as 2-CEES was almost completely degraded. For example, the Ar/O₂ plasma achieved complete decontamination of 2-CEES at 120 s, resulting in the highest concentration of 2-CEESO at this point. As the treatment time was prolonged, the concentration of 2-CEESO in the plasma gradually decreased, indicating that 2-CEESO was further oxidized to 2-CEESO₂ ^[10]. Figure S7a compares the amount of 2-CEESO produced at 320 s with different plasma treatments. Generally, air plasma featured a higher 2-CEESO concentration, while Ar/O₂ plasma displayed the lowest 2-CEESO concentration owing to the differences in the active species in the plasma.

The chromatograms (Fig. S6) of 2-CEESO₂ exhibited a characteristic peak after different plasma treatments. 2-CEESO₂ featured a retention time of 11.18 min. After Ar plasma treatment, 2-CEESO₂ was not detected in the chromatograms (Fig. 10b). Additionally, in the other three plasmas, 2-CEESO₂ was not detected before 120 s because the oxidative species in the plasma were mainly used for generating 2-CEESO during this time. The concentration of 2-CEESO almost reached its maximum at 120 s, after which 2-CEESO₂ began to form. However, excessive oxidation of 2-CEES to 2-CEESO₂ can be harmful^[44]. Therefore, the decontamination system developed in this study was designed to precisely regulate the production of 2-CEES decontamination process.

Furthermore, the Ar/O_2 plasma generated the highest amount of 2-CEESO₂ at 320 s, while the air and $Ar/O_2/H_2O$ plasmas produced similar amounts of 2-CEESO₂ (Fig. S7b). The increased production of reactive O_x in the Ar/O_2 plasma promoted the formation of 2-CEESO₂. The addition of water vapor led to a significant decrease in the production of 2-CEESO₂, possibly owing to the higher concentration of OH radicals.



Fig. 10 Curves of (a) 2-CEESO; (b) 2-CEESO₂ peak areas with time; (c) variation curve of 2-hydroxyethyl ethyl sulfide concentration with time; (d) Comparison of the concentration of 2-hydroxyethyl ethyl sulfide after different plasma treatments for 1 min (*: 0.01 < P < 0.05; **: 0.001 < P < 0.01; ***: P < 0.001).

Previous studies^[11] have shown that OH can dechlorinate 2-CEES to form 2hydroxy ethyl sulfide (CH₃-CH₂-S-CH₂-CH₂-OH) through the interaction with the Cl atom. To further verify this hypothesis, the concentrations of 2-hydroxy ethyl sulfide were compared after different plasmas treatments (Figs. 10c and d). However, owing to its higher polarity, 2-hydroxyethyl sulfide underwent derivatization to form CH₃-CH₂-S-CH₂-CH₂-O-Si (C₃H₉). The derivatives featured a retention time of 7.82 min (Fig. S8), which was similar to the retention time of 7.95 min reported in the literature^[47]. These results indicated that the Ar/O₂/H₂O plasma produced a higher amount of 2hydroxy ethyl sulfide compared with the air plasma, indicating that the OH and reactive O_x followed different decontamination pathways for 2-CEES.

Table 1 summarizes the active species and degradation effects of the four plasmas. Similar to the previous results, the E_e of these plasmas was one order of magnitude higher than those of plasma decontamination technologies. However, the Ar/O₂/H₂O plasma exhibited an E_e , which is nearly twice that reported in previous studies. Moreover, the Ar/O₂/H₂O plasma produced more 2-hydroxy ethyl sulfide and less toxic sulfone owing to the presence of more OH. The Ar/O₂ plasma generated more toxic sulfone because more reactive O_x promoted the two-stage oxidation process of 2-CEES. The decontamination properties of different active species in plasma for 2-CEES are illustrated in Fig. 11. Therefore, the Ar/O₂/H₂O gas environment was the most conducive to the self-driven plasma decontamination of 2-CEES.

Plasmas	Power (W)	OH at 2 min (*10 ⁴ , a.u.)	O3 at 320 s (ppm)	Electron density (/m³)	2-CEES content (mg)	D at 2 min	2-CEESO at 320 s (*10 ⁵ , a.u.)	2-CEESO ₂ at 320 s (*10 ³ , a.u.)	2-hydroxy ethyl sulfide at 1min (a.u.)	<i>Е</i> е (µg/J)
Previous Study	0.064	-	10.93	-	0.004	>99 %	-	-	-	0.520
Air	0.066	5.34	10.93	3.5e16	0.006	83.78 %	3.26	7.07	0.101	0.455
Ar	0.035	-	0	6.94e17	0.006	8.85 %	0.68	0	-	-
Ar/O ₂	0.055	-	42.43	1.18e15	0.006	>99 %	2.69	17.12	0.085	0.909
Ar/O ₂ /H ₂ O	0.052	16.78	22.10	1.32e15	0.006	>99 %	3.04	6.97	0.376	0.962

Table 1. Active species and degradation effects of the four plasmas^[21]



Fig. 11 Effect of different active species on the 2-CEES decontamination

4. Conclusion

This study investigated the decontamination of 2-CEES using self-driven plasmas in different gas environments and elucidated the mechanisms responsible for the differences in active species among the four plasmas and their respective decontamination effects. The results revealed that air, Ar/O₂, and Ar/O₂/H₂O plasmas exhibited higher decontamination effects on 2-CEES, except for the Ar plasma. Moreover, the E_e of these plasmas was one order of magnitude higher than that of traditional plasma decontamination technologies. The Ar/O₂/H₂O plasma featured the highest degradation efficiency and E_e (0.962 µg/J), which is nearly twice that of previously reported studies. Additionally, the Ar/O₂ and Ar/O₂/H₂O plasmas generated more reactive O_x and OH, respectively, resulting in higher decontamination efficiency for 2-CEES. Conversely, the Ar plasma exhibited minimal decontamination efficiency indicated that electron-breakage chemical bonding was not the main decontamination mechanism in this system. The addition of H₂O and O₂ to this system can effectively improve the decontamination efficiency of 2-CEES. The $Ar/O_2/H_2O$ plasma generated higher levels of 2-hydroxy ethyl sulfide and lower levels of toxic sulfone owing to its higher OH concentration. However, Ar/O_2 plasma generated more toxic sulfone because more reactive O_x promoted the two-stage oxidation process of 2-CEES. Therefore, the $Ar/O_2/H_2O$ gas environment was the most conducive to the self-driven plasma decontamination of 2-CEES. This study is vital for further optimizing the selfdriven plasma decontamination systems and elucidating the decontamination mechanism of 2-CEES.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional of other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

Highlights:

- A self-driven plasma discharge system for sulfur mustard surrogate decontamination was developed.
- High level of reactive O_x species (O₃, O₂⁻, and ¹O₂) and OH radicals were produced with Ar/O₂/H₂O plasma.
- The low electron energy in this self-driven plasma system plays a minor role in 2-CEES decontamination.
- This work featured an energy utilization efficiency of 0.962 µg/J, nearly twice of the previous study.



Graphical abstract