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ULTRASONIC DECONTAMINATION OF CHEMICAL WARFARE AGENTS

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Abstract: *Sonochemistry studies the physical and molecular level changes induced by ultrasonic energy on solutions. Sonochemical degradation of the chemical warfare agents (CWA) may occur due to three successive phenomena based on the principles of acoustic cavitation phenomena: nucleation, growth, and implosive collapse of microbubbles. The sonolytic degradation of CWA was quantified by GC-MS technique, considering the variation of some parameters such as frequency of ultrasonic waves, power control, temperature, and addition of nanoparticles as catalysts to the solution.*

Keywords: chemical warfare agents, ultrasonic decontamination, sonolysis, sonochemical degradation

1. Introduction

Since the first use of sulfur mustard in World War I, significant efforts have been made to develop materials and technologies for the adsorption and decontamination of all categories of chemical warfare agents (CWAs).

The decontamination procedures generally consist of applying a decontamination agent on the contaminated surface, followed by the physical removal and collection of the reaction products. All these procedures have one common problem that is often neglected: high quantities of water solutions containing toxic compounds that were not completely neutralized and moderately poisonous degradation products. Even if we talk about a critical CWA event or a military training facility, the high quantity of post-decontamination waste has acute ecological effects.

Nowadays, the development of efficient liquid-phase technologies for the decontamination of CWA, as well as improved catalysts to work under mild reaction conditions, represent a new challenge for researchers [1], [2].

The sonochemical disintegration of organic pollutants in aquatic environments has received much attention nowadays [3], [4]. Sonolysis is often carried out by OH· radicals, which are produced when an aqueous solution is subjected to ultrasonic irradiation [3]. The formation, oscillation, growth, and collapse of micro-bubbles during ultrasonic irradiation of water is known as acoustic cavitation [3]. To provide energy to the liquid phase, ultrasonic waves create a repeated sequence of compressions and rarefactions as they travel through a liquid medium [5]. Cycles of compression and rarefaction apply

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positive and negative pressure to the liquid, forcing or repelling molecules in different directions [5]. This process generates a locally concentrated energy powerful enough to split water molecules into OH· radicals and hydrogen atoms [3].

Previous studies found that the introduction of heterogeneous surfaces increases the extent of interfacial cavitation [6]. Thus, the addition of solid particles serves as an additional nucleus, increasing the numbers of cavitation events and accelerating the decomposition rate of contaminants [7], [8]. Metal catalysts permit using environmentally friendly oxidants such as molecular oxygen, resulting in simply water as a byproduct. Gold nanoparticles have shown outstanding catalytic performances in the selective oxidation of alcohols in the presence of a base [1]. The catalytic activity in alkaline-free conditions is generally an order of magnitude lower than the catalytic activity obtained in high-pH solutions, which highlights the critical role of the base as a promoter in gold-assisted catalysis [1].

Here we report a preliminary study on the investigation of the ultrasound-assisted degradation of 2-chloroethyl ethyl sulfide (2-CEES) in an alkaline alcoholic solution (isopropyl alcohol) encompassing gold nanoparticles. These investigations aimed to identify the key features to be addressed in future thorough research studies on the sonolytic process of CWA degradation.

2. Materials and equipment

Reagents used for the laboratory tests and sample preparation are 2-chloroethyl ethyl sulfide (Sigma-Aldrich, Missouri, USA), 97% purity; sodium hydroxide pellets (Merck Millipore, Massachusetts, USA); isopropanol (Sigma-Aldrich, Missouri, USA), 99% purity; water for chromatography (Merck Millipore, Massachusetts, USA), LC-MS grade; dichloromethane (Sigma-Aldrich, Missouri, USA), 99.8% purity; sodium sulfate anhydrous (Merck Millipore, Massachusetts, USA) and gold nanoparticles (Aldrich, Missouri, USA), 5 nm diameter, stabilized suspension in citrate buffer, OD 1. For ultrasonic decontamination, a high-intensity ultrasound equipment (Hielscher UP400S, Germany, power 400 W, frequency 24 kHz) was used and gas chromatography - mass spectrometry analyses were performed on a GC Focus-MS DSQII, Thermo Electron Corporation (Waltham, United States).

3. Methods

For the decontamination process, four experiments were designed (Figure 1). Five specimens of 10 mL of aqueous hydroalcoholic solution (HA_{Ref}) containing 5% NaOH and 10% isopropanol were contaminated with 10 µL of 2-CEES. First specimen was homogenized for 1 minute, prepared for GC-MS analysis, and served as the reference sample. One specimen (HA_0) was magnetically stirred at 500 rpm and 20°C. This decontamination test simulates the classic decontamination process. Three specimens were subjected to a high-intensity ultrasonication procedure, representing a new approach for CWA decontamination involving sonolysis and sonocatalysis chemical process. The first specimen (HA_{50}) was ultrasonicated at an amplitude of 50 % and 0.5 cycle and the second one (HA_{100}) at 100 % amplitude and 0.5 cycle. In the third specimen, 1 mL of gold nanoparticles suspension in citrate buffer was added. The specimen (HA_{50NP}) was ultrasonicated at an amplitude of 50 % and 0.5 cycle. For each decontamination process, 3 samples were collected for GC-MS analyses after 2, 10, and 30 min from the beginning of the decontamination process. For analysis, 200 µL HA_{probe} were taken and extracted with 3.8 mL of dichloromethane (DCM) under 1 min shaking. Samples were dried over anhydrous sodium sulfate, filtered on Sartorius filter and analyzed by GC-MS, electron impact ionization.

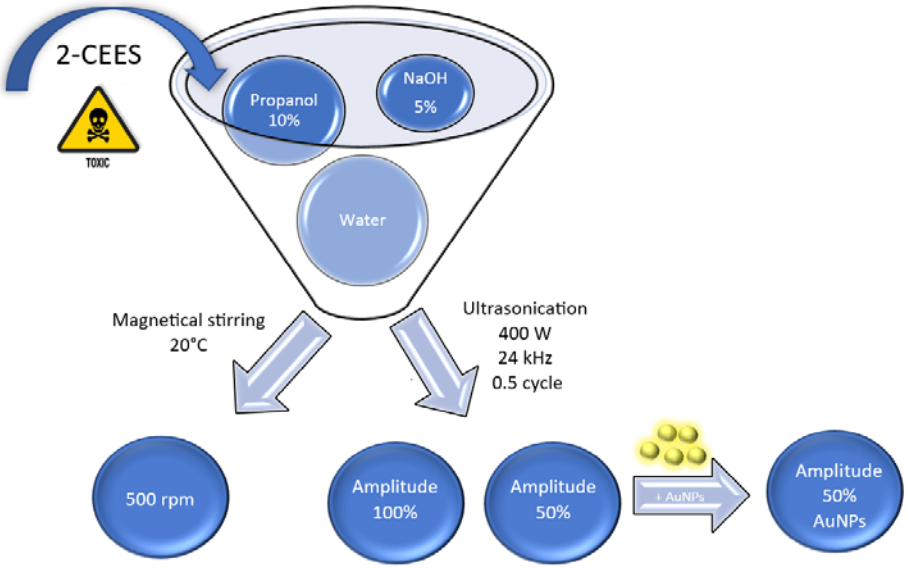

Figure 1: Overview of the decontamination processes designed

4. Characterization

A high-resolution transmission electron microscope (HRTEM), type TECNAI F30 G2STWIN (Fei Company, Oregon, USA), was utilized to obtain the image of the gold nanoparticles (300 kV acceleration voltage, resolution 1Å). The optimized structures (DFT, B3LYP/6-31+G** level of theory) of HD and 2-CEES were obtained with Gaussian®16 computational chemistry software package [9]. The graphical representation of molecular orbitals - MOs (HOMO and LUMO) for HD and 2-CEES were extracted from checkpoint files (*.chk) visualizable in GaussView®6.

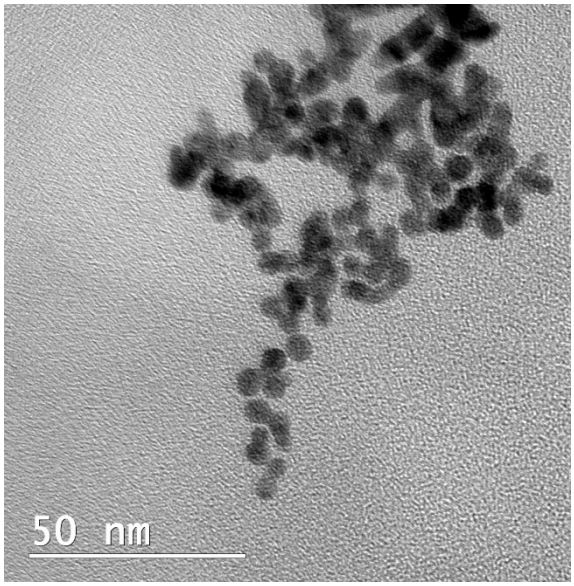

Figure 2: TEM image of gold nanoparticles

5. Results

TEM imaging (Figure 2) offered information on the shape and size of the gold nanoparticles employed in the experiments. As can be observed, the diameter of these gold nanoparticles is approxymatelly 5 nm; thus, this higher specific surface will presumably ensure a higher probability of cavitation events promoting a more efficient degradation of CWAs.

It has already been discovered that gold nanoparticles with diameters smaller than 5 nm possess more significant catalytic activity toward CWAs than bigger gold particles [10]. Figure 3 illustrates the optimized structure of mustard gas (HD) and an analogous simulant (2-CEES) and the corresponding molecular orbitals (MOs). The visualization of MOs helps to predict the reactivity of the compounds and supports understanding molecular properties.

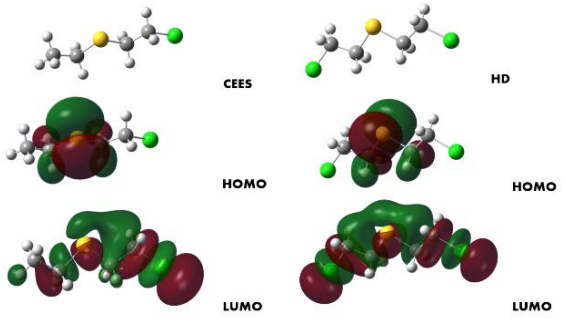

Figure 3: MOs of 2-CEES and HD

GC-MS analyses showed an improvement of the decontamination efficiency in several stages. Comparing the results between the classic decontamination process assisted by magneting stirring and the ultrasonication at a power of 400 W and a frequency of 24 kHz, we observed an improvement of about 10 to 25% in favor of ultrasound assisted procces, and depending on parameters such as amplitude and temperature achieved during the process. On the other hand, comparing the ultrasound assisted decontamination process at amplitude of 50 % and 100 %, we observed an improved process at a higher amplitude. An almost similar improvement degree was observed between results obtained from the decontamination process at an amplitude of 50 % and the addition of gold nanoparticles as catalyst. In addition, several future tests should be performed to optimize the amplitude and the amount and type on nanoparticles to be used in decontamination. Finally, in Figure 4 a degradation mechanism was proposed for 2-CEES under tested conditions presented in this paper.

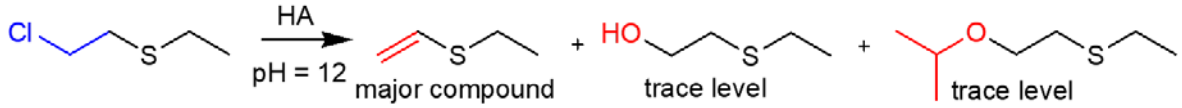

Figure 4: Degradation mechanism proposed for 2-CEES under tested conditions

6. Conclusions

The influence of applied ultrasonic power on the successful degradation of CWAs can be attributed to various factors.

Varying ultrasonic energy will lead to a change in the bubble population, average bubble size, the growth process of bubbles, the structure of the clustering bubble clouds, and a variety of chemical effects induced by the interactions established in this configuration.

Future perspectives to continue this study involve the combination of sonolysis with other advanced oxidation processes, i.e., photocatalysis, which has been commonly recognized as a suitable tactic to overcome the limitations of the unaccompanied sonochemical degradation process of organic pollutants. Thus, the ultrasound-assisted degradation process of CWAs could be improved further by combining it with photocatalytic strategies. An integrated sonophotocatalytic system may ensure a faster degradation of CWAs.

Acknowledgments

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