# Decontamination of toxic chemical warfare sulfur mustard and nerve agent simulants by NiO NPs/Ag-clinoptilolite zeolite composite adsorbent

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A B S T R A C T

The present investigation describes the performance of NiO NPs/Ag-clinoptilolite zeolite as a novel composite adsorbent for the decontamination of two most known sulfur mustard and nerve agent simulants; chloroethyl ethyl sulfide (CEES) and dimethyl methyl phosphonate (DMMP). The reactions were carried out in both methanol and $n$-hexane solvents and monitored by GC-FID, $^{31}$PNMR and GC–MS analyses subsequently. Moreover, the SEM/EDAX, XRD and FT-IR techniques were applied for characterization of the as-prepared samples. The GC-FID results denoted that CEES was decontaminated on the composite in $n$-hexane solvent after 12 h at room temperature with a yield more than 86%. Besides, $^{31}$PNMR data illustrated that more than 89% of DMMP was decontaminated after 8 h under similar conditions. It seems that non-polar solvent aids the material transfer to the reactive sites on the surface of the composite without blocking them. The rate constant and half-life have been calculated $3.8194 \times 10^{-5}\,s^{-1}$ and $7.3055 \times 10^{-5}\,s^{-1}$, and $1.8640 \times 10^{4}\,s$ and $9.4860 \times 10^{3}\,s$ for CEES and DMMP, respectively. The hydrolysis products; hydroxyl ethyl sulfide (HEES) and methyl phosphonic acid (MPA) were also identified by GC–MS analysis. It was emphasized that NiO NPs/Ag-clinoptilolite zeolite composite has a high capacity and potential for the decontamination of CEES and DMMP molecules.

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## 1. Introduction

The threats of mass destructive weapons always have been posed renewed concerns to global community [1,2]. At present, neutralization and decontamination of chemical warfare agents (CWAs) is proposed for nonproliferation plans due to their nocuous consequences manifested in case of military activities, large worldwide stock of ammunition and definitely on the aspect of terrorist attack [3,4]. Recent reports from Middle East and especially Syria during the last four years have elucidated the vital crisis of CWAs namely sulfur mustard and phosphorus nerve agents utilized by terrorist organizations due to the availability of their component, being low cost and easy to manufacture. Sulfur mustard ((ClCH$_2$CH$_2$)$_2$S, abbreviated as H for arsenal grade and HD for distilled) has been considered as a persistent and potential CWA

which is of great concern for military defense and envisaging terrorism [5]. The usage history of HD refers to World Wars I and II and continued up to Iran–Iraq war of 1980s [6]. Since CWAs are extremely toxic, research studies have been generally performed with less toxic analogues (simulants) with physicochemical characteristics similar to those sorts of agents. Chloroethyl ethyl sulfide (CEES) is recognized as one of the most reputable sulfur mustard simulants. Exposure to this compound, leads to destructive effects such as skin blistering and mucous membranes [7,8]. According to Talmage et al. [9], and Devereaux et al. [10], CEES molecule acts as cytotoxin or mutatoxin via an intermediate form that binds to DNA, particularly in the bone marrow leading to blood disorders [11], Vorontsov et al. [12], advanced that high toxicity of these molecules is also associated with the ability of the SCH$_2$CH$_2$Cl group to alkylate proteins. CEES is known as a HD simulant due to owning a single chlorine atom on the β carbon atom related to HD as explained in Scheme 1a. Also, among the various lethal chemical warfare agents, the nerve agents (NAs) have had an entirely dominant role since the World War (II). All NAs belong chemically
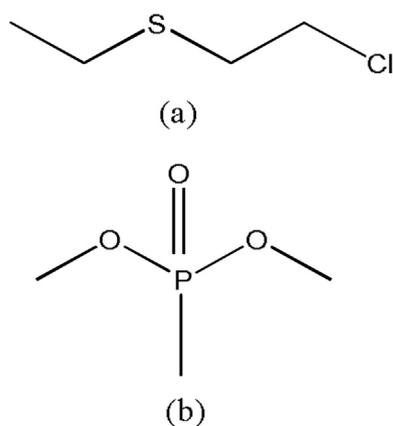
**Scheme 1.** The chemical structures of: (a) CEES and (b) DMMP.

to the group of organo-phosphorus (OP) compounds. They are stable and easily dispersed, highly toxic and have rapid effects both when absorbed through the skin and via inhalation [13,14]. Dimethyl methyl phosphonate (DMMP) is among the most hazardous organo-phosphorus compounds which has been widely applied as chemical weapons [15]. Scheme 1b represents the chemical structure of DMMP. Further, many advances have been made so far to design methodologies and strategies to neutralize harmful CWAs. Recently, the reports have revealed that there is a great interest to use solid sorbent decontaminants such as nano metal oxides in different scientific fields. Several nano-crystalline metal oxides like $ZrO_2$ [16], CuO [17], $MnO_2$ [18], ZnO-CdO [19] and $Co_3O_4$ and $MnCo_2O_4$ [20] have been synthesized as applying adsorbents and catalysts using in wide variant researches [21,22].

Plus, one of the known of those above mentioned solid sorbent s is aluminum-containing X- and Y-type zeolites [23–27]. Clinoptilolite (Cp) is one of those above mentioned zeolites with desirable features and advantages like being low cost, available and the most abundant natural zeolite. Further, it is in the chemical class of family of Heulandite (HEU-type), easily obtained from mines, appropriate as a sorbent due to its natural characteristics [28,29].

The combination of zeolites and metal oxide nanoparticles renders solid catalysts in which the high surface area of nanoparticles and the absorbent capacity provided by zeolites, cooperate to enhance the efficiency of the catalytic process [30]. Among the various transition metal oxides, Nickel oxide nanoparticles (NiO NPs) is specified as applying one and has attracted much tendency due to its convenient properties and applications [31,32]. NiO NPs display a large exciton binding energy and a wide band gap ranging from 3.6 to 4.0 eV [33,34]. Because of quantum size and surface effects, NiO NPs exert catalytic, optical, electronic, and magnetic properties that are significantly different from those of bulk-sized NiO particles [35,36]. There are many notable applications for both bulk and nano sized NiO such as; catalysis [37,38], electro chromic films [39,40], fuel cell electrodes and gas sensors [41,42], battery cathodes [43,44], magnetic materials [45,46] and photovoltaic devices [47] and also smart window [48], dye-sensitized photocathodes [49] and electrochemical super capacitors [50]. Also there are several methods to prepare NiO NPs including; hydrothermal, thermal decomposition, sol-gel, solvo-thermal and sonochemical [51–53]. $Ag^+$ is the only noble mono-positive cation that forms mononuclear species with appreciable stability in aqueous solution. Besides, silver is identified to have strong influence on the absorption properties of zeolites. In this

research, the combination of Ag-clinoptilolite zeolite as host and NiO nanoparticles as guest materials have utilized to synthesize an applying composite adsorbent to increase the efficiency of the catalytic process of CEES and DMMP molecules. To the best of our knowledge, there are no papers reporting the application of NiO NPs/Ag-clinoptilolite zeolite composite adsorbent used to decontaminate the sulfur mustard and nerve agent simulants.

## 2. Experimental

The natural clinoptilolite (NCp) zeolite employed in research was obtained from the region of the West Semnan, Central Alborz Mountains, Iran and its structural properties is as $(Na, K, Ca)_6$ $(Si, Al)_{36}$ $O_{72}·20H_2O$. Sodium chloride (NaCl), silver nitrate ($AgNO_3$), hydrochloric acid (HCl), nickel nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$), methanol, *n*-hexane, toluene and phosphoric acid were purchased from Merck (Merck, Darmstadt, Germany). The chloro ethyl ethyl sulfide (CEES) and dimethyl methyl phosphonate (DMMP) were obtained commercially from Sigma-Aldrich Co. (USA). All chemicals were used as received and were of chemical grade. Deionized water was applied for the preparation of all the solutions.

### 2.1. Instrumentation

The morphology, particle sizes and elemental composition of the prepared adsorbents were surveyed using a scanning electron microscope (SEM, HITACHI S-300N). Semiquantative analysis were carried out on an energy-dispersive x-ray spectrometer (EDAX) connected to LEO-1530VP XL30 Philips scanning electron microscope. The powder X-ray diffraction (XRD) patterns were recorded using a Philips X'pert Pro diffractometer equipped with CuKα radiation at wavelength 1.54056 Å (30 mA and 40 kV) at room temperature. Data were collected over the range 4–80° in $2\theta$ with a scanning speed of $2°\,min^{-1}$. The IR spectra were scanned on a PerkinElmer model 2000 FT-IR spectrometer (USA) in the wavelength range of $400–4000\,cm^{-1}$ using KBr pellets. A Varian Star 3400CX series gas chromatograph equipped with flame ionization detector (GC-FID) and an OV-101CWHP 80/100 silica capillary column (30m × 0.25 mm inner diameter (i.d.), 0.25 μm film thickness) was used to monitor the decontamination reactions of CEES. Helium (99.999% purity) was selected as the carrier gas with the flow rate of $1\,mL\,min^{-1}$. The injection was performed in the split mode. In order to investigate the reaction of the nerve agent simulant with the composite, phosphorous-31 nuclear magnetic resonance spectroscopy ($^{31}PNMR$, Bruker 250 MHz) and centrifuge (Universal, CAT. NO. 1004) instrument was used. The extracted products were analyzed by a HP-Agilent gas chromatograph-mass spectrometer equipped with a fused-silica capillary column (DB 1701, 30 m × 0.25 mm inner diameter (i.d.), 0.25 μm film thickness). In brief, the column temperature was initially held at 60 °C for 4 min and programmed at $20\,°C\,min^{-1}$ to 220 °C for 13 min to reach the final temperature which was then held for 6 min. The injector, MS quad and source temperatures were fixed at 60 °C, 200 °C and 230 °C, respectively.

### 2.2. Preparation of Na-clinoptilolite zeolite

5 g of the clinoptilolite zeolite was calcined before processing at 300 °C for 2 h in a furnace for excluding moister and impurities from the surface. To obtain the Na-clinoptilolite form, it was then chemically treated with 250 ml of 1 M sodium chloride (NaCl) at 90 °C for overnight and was washed with deionized water several times until chloride ions to be removed. Ultimately, treated clinoptilolite (sodium-clinoptilolite) was dried at 85 °C for 5 h.