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Study on the effective decontamination and hydrolysis of sulfur mustard agent simulant using tenorite (CuO) nanoparticles as a destructive catalyst

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Abstract

In the present study, tenorite (CuO) nanoparticles have been assayed for their catalytic properties. The decontamination reaction of chloro ethyl ethyl sulfide (CEES) as an surrogate of sulfur mustard have been accomplished on the surface of CuO NPs with different weight ratios at ambient temperature and monitored by Gas chromatography equipped with Flame ionization detector (GC-FID) and Gas chromatography coupled with a mass spectroscopy (GC-MS). CuO NPs were successfully synthesized via precipitation method in the absence and presence of polyvinylpyrrolydone (PVP) and copper (II) nitrate as the precursors. PVP was used as a capping agent to control and reduce the agglomeration of the nanoparticles. The synthesized CuO NPs were characterized by Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. The GC analysis results revealed that the decontamination of CEES occurred in *n*-hexane solvent with the weight ratio of 1:40 (CEES: CuO NPs) after 12 h with more than 90% yield. The hydrolysis product such as hydroxyl ethyl ethyl sulfide (HEES) was also identified by GC-MS analysis.

Keywords: Tenorite (CuO) nanoparticles; chloroethyl ethyl sulfide (CEES); decontamination; hydrolysis; precipitation; polyvinylpyrrolydone (PVP).

Introduction

The chloroethyl ethyl sulfide (CEES) as a sulfur mustard agent simulant is among the toxic pollutants and poses inevitable threats to the environment and the persons who contact with, thereby causes health hazards. This compound is considered as a powerful irritant and blistering agent that damages skin, mucous membranes, eyes and respiratory treatment. It also damages DNA, a vital component of cells in the body. In some cases CEES smells like garlic and onions, while sometimes does not have any odor [1-6]. It exists as a vaporizable species and does not find naturally in the environment. The chemical structure of CEES is illustrated in Scheme 1 [4].

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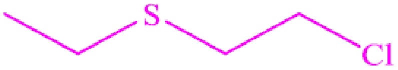


Scheme 1. The chemical structure of chloroethyl ethyl sulfide CEES [4]

Different methodologies have been designed for the decontamination of CEES through the recent years [7-9]. A series of materials including bleach, potassium per sulfate, oxone, sodium perborate have been long used as active detoxification agents along with surfactants and micro-emulsions for the decontamination of chemical agents [1]. Certain disadvantages exist with the use of these materials, as the most important one is environmental contamination.

As in the recent years, interests have been inverted toward the application of nanomaterials and nanotechnology, more nano-crystalline inorganics like metals and metal oxides with adsorptive properties have been assayed as solid reactive catalysts to replace the liquid detoxification of organo-sulfurous chemical agents [10-14]. The intriguing properties of nanomaterials are expected to be aroused owing to the increased fraction of the surface atoms as their size decreasing occurs under certain conditions which is different from that of the bulk atoms. The surface atoms are unsaturated and have high chemical activity and adsorption capacity to many substances [15,16]. High surface area and the reactive sites tailored in the form of edge and corner defects, unusual lattice planes, etc, react in a stoichiometric way, thereby rendering the adsorbed toxic agents into non-toxic ones. Besides, the reactions are analogous to their solution behavior. Recent investigations have explored the promising decontamination applications of the nano-sized metal oxides such as MgO, CaO, Fe_2O_3, Al_2O_3 and MnO_2 [17-22]. Among metal oxides, tenorite (CuO) nanoparticles actuated our attention due to their low cost and availability of the starting materials and also high certainty and purity compared with other applied metal oxides [23].

Tenorite (copper oxide) nanoparticle as a p-type semiconductor exhibiting narrow band gap (Eg=1.2 eV), have attracted a great deal of research interest in this decade. These nanoparticles are also utilized in a wide range of applications: such as electronic, optoelectronic and sensing [24-28]. Several physical and chemical methods have been reported for the preparation of CuO NPs including sonochemical method [29], sol–gel technique [30], one-step solid state reaction method at room temperature [31], electrochemical method [32], thermal decontamination of precursors [33] and co-implantation of metal and oxygen ions [34], precipitation method [35] and so on. In the present work, CuO NPs are successfully synthesized by precipitation method in the presence of PVP as the capping agent. Then, we investigated the adsorptive and catalytic properties and the performance of the surface of CuO NPs as catalyst for the decontamination of CEES. To prevent increasing in the particle size and size distribution, a capping agent, often a polymer is used, either natural or synthetic with a degree of affinity for metals. The polymer is adsorbed on the cluster in the solution and reduces the surface tension. These agents also control both the reduction rate of metal ions and the aggregation of final particles. It is reported that polyvinylpyrrolidone (PVP) can stabilize the colloidal particles in water and many non-aqueous solvents through adsorbing onto a broad range of materials such as metals (e.g., Ag, Au and Fe) and metal oxides (e.g., Al_2O_3, Fe_2O_3 and TiO_2) [36,37].

Experimental

General

Copper nitrate ($Cu(NO_3)_2.3H_2O$), sodium hydroxide (NaOH), polyvinylpyrrolidone (PVP) were obtained commercially from Merck (Merck, Darmstadt, Germany). The chloroethyl ethyl sulfide (CEES), *n*-hexane and toluene were purchased from Sigma-Aldrich Co. (USA). All the chemicals and reagents were of chemical grade and were used without further purification. Deionized water was used for the preparation of all the solutions.

The synthesized CuO NPs were subjected to various characterization instruments. The morphology and the size of the catalyst particles were determined *via* SEM micrographs using a scanning electron microscope (SEM, LEO-1530VP). Transmission electron microscope (TEM) micrograph was taken on a FEI Tecnai G2 20 S-TWIN. The X-ray diffraction (XRD) analysis was carried out on a Philips X-ray diffractometer using CoKα radiation (40 kV, 30 mA and λ=0.15418 nm). Samples were scanned at 2°/min in the range of 2θ=0-80°. A Varian Star 3400 CX series gas chromatograph equipped with a FID detector and a SATURN4D series gas chromatograph-mass spectrometer were used to investigate the reaction of CEES on the surface of CuO NPs. The GC and GC-MS analyses were carried out on an OV-101CWHP 80/100 capillary column (2m × 1.8 in, DB 5MS, 0.1μm film thickness, 30m × 0.25mm internal diameter). In brief, the column temperature was initially hold at 60°C for 4 min and programmed at $20°C.min^{-1}$ for 13 min to 220 °C to reach the final temperature which was then hold for 4 min. Helium (99.99 % purity) was used as the carrier gas with the flow rate of $1\ mL.min^{-1}$. The detector temperature was fixed at 230 °C. The injection was performed in the split mode.

Synthesis of CuO NPs catalyst

CuO NPs were prepared by precipitation method in the presence of polyvinylpyrrolidone (PVP) as capping agent to control the agglomeration of the nanoparticles. At first, An appropriate amount of Cu $(NO_3)_2.3H_2O$ (2 g) as the source of Cu^{2+} ions and 8 g of PVP were dissolved in deionized water and heated to 40°C. While the solution was being stirred rapidly, 20 mL of 0.1 M NaOH was added to the solution. After 30 min the reaction was halted, and then the mixture was filtered and washed with deionized water until the pH of the mixture was equal to 7. As a result, CuO precursors i.e., Cu $(OH)_2$ were produced which were left at 60°C±10°C for 24 h to dry. The clean and dry precursors were then calcined at 300 °C for 2 h after which CuO powder was formed. The ionic equation of the reaction is as follows (1) [38]:

$$6Cu^{2+} + 12OH^{-} \rightarrow 6Cu\,(OH)_2\downarrow \rightarrow 6CuO + 6H_2O \quad (1)$$

Decontamination procedure of CEES onto the surface of CuO NPs

Approximately 10 μL of toluene as the internal standard and 10 μL a 5:1 (v/v) ratio of sulfur mustard simulant samples ($CEES/H_2O$) were added to 5 mL of *n*-hexane as solvent in a 20 mL Erlenmeyer flask. All samples were vortexed for 1 min to give blank samples. Then, various amounts of CuO NPs sample (5, 50, 100 and 150 mg) of CuO NPs were added to above solutions. No efforts were made to control ambient light or humidity. To do a complete reaction between catalyst and organo-sulfurous compound, all samples were shaken for about 12 h on wrist-action shaker. After agitation of solution samples, they left until the precipitation process fulfilled. Finally, 10 μL of upper solution of each samples brought out by a micro-syringe and injected to GC-FID and GC-MS instruments for quantitative analysis. The reactions were investigated at ambient temperature (25±1 °C) and pH equal 7.

Results and discussion

SEM and TEM of tenorite nanoparticles

The SEM micrographs of CuO NPs in the absence and presence of PVP are shown in Figure 1. Analyzing the morphology aspect of nanoparticles by studying the micrographs indicates that smaller particles (less than 100 nm) have been synthesized *via* the incorporation of PVP as the capping agent. A primary purpose of the introducing PVP was to protect the CuO NPs from growing and agglomerating.

With the introduction of PVP, particles would coordinate with N or O in PVP, and a covered layer would generate on the surface of the particles. This layer inhibits the growth and agglomeration of the particles. Also, Figure 2 shows the TEM micrograph of as prepared nanoparticles. TEM studies reveal that the CuO nanoparticles/PVP are in the range of 6-7 nm.

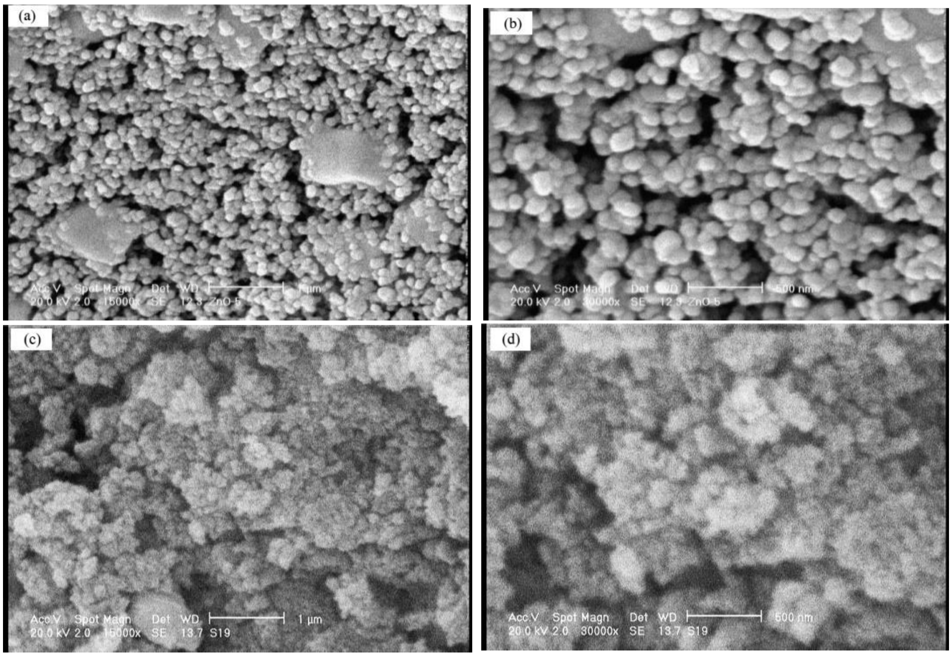


Figure 1. SEM micrographs of the synthesized CuO NPs in the (a) and (b) absence, (c) and (d) presence of PVP with different resolution (15000X and 30000X).

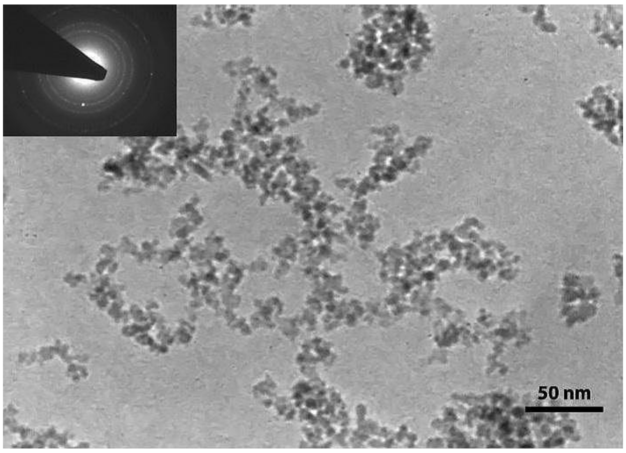


Figure 2. TEM micrograph of the synthesized CuO NPs/PVP

X-ray diffraction (XRD) pattern of tenorite nanoparticles

Phase purity and crystalline structure have been determined by XRD pattern as shown in Figure 3. The peaks referring to CuO NPs/PVP occurred at scattering angles (2θ) of 37.9379°, 41.5859°, 45.3296°, 57.3058°, 62.9655°, 68.9326°, 72.9516° and 78.8583° corresponding to diffraction planes of (100), (002), (111), (202), (113), (220), (311), and (222), respectively that have been crystallized in the monoclinic phase and are in good agreement with those of CuO NPs with JCPDS=01-072-0629. No characteristic peaks related to impurities were observed in the pattern during synthesis step. A definite line broadening of the scattering pattern in Figure 3 is a demonstration upon which the synthesized CuO NPs are in nanoscale range. The crystalline size of the prepared CuO NPs was investigated via XRD measurement and line broadening of the peak at 2θ=0°-80° using Debye-Scherrer equation (2) [39]:

$$\mathbf{d} = \frac{\mathbf{K\lambda}}{\boldsymbol{\beta}\, \boldsymbol{cos\theta}} \qquad (2)$$

Where d is the crystal size, K is so-called shape factor which usually takes a value of 0.94, λ is the wavelength of X-ray source, β is the full width at half maximum (FWHM) and θ is Bragg diffraction angle. Using this equation, the average crystalline was calculated about 8 nm. The β of the XRD peaks may also contain contributions from lattice microstrain. The average microstrain (ε) of the CuO NPs was calculated using the Stocks-Wlison equation [40]:

$$\varepsilon = \beta/4\tan\theta \qquad (3)$$

Using this equation, the average microstrain was calculated about 0.1.

The size obtained from XRD measurement is consistent with the results from the TEM study.

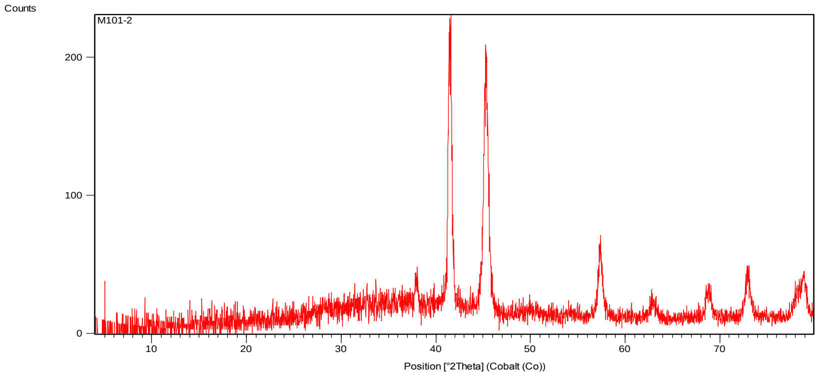


Figure 3. XRD pattern of the synthesized CuO NPs/PVP

GC analysis

In order to evaluate the decontamination reaction of CEES with CuO NPs at ambient temperature, gas chromatography equipped with flame ionization detector (GC-FID) analysis was performed. To accede maximum efficiency, the influencing parameter such as CEES/CuO weight ratio has been investigated. Generally, increasing in weight ratios leads to further decontamination of organo-sulfurous compounds. The GC chromatograms, area under curve (AUC) data and the results under different conditions are summarized in Figure 4 and Table 1. As denoted in the chromatograms, *n*-hexane, toluene and CEES are diagnosed at retention times of 4.5, 5.2 and 10.6 min, respectively. To calculate the amounts of decontaminated sulfur mustard agent stimulant, the integrated area under peak data of two samples, CEES and toluene as the internal standard have been given for all weight ratios. Subsequently, the ratio of the integrated data (integrated AUC of CEES/integrated AUC of toluene) was determined. The results implied that more than 90% of CEES with the weight ratio of 1:40 (CEES: CuO NPs) [38] have been decontaminated in *n*-hexane solvent after 12 h, it refers to the time that contamination occures. The above mentioned time comprared with the results of other similar works is desirable [1, 2]. On the other hand, these amounts decreased with the weight ratios of 1:30, 1:20 and 1:10, respectively.

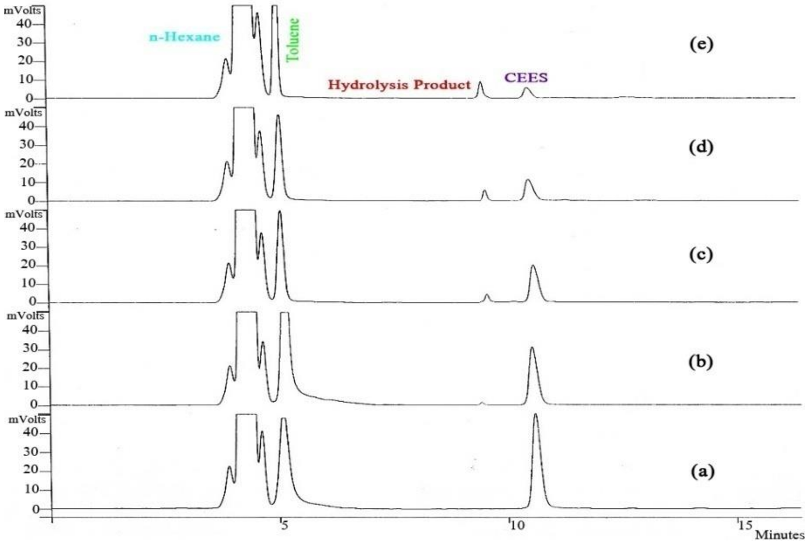


Figure 4. GC chromatograms of the adsorption and decontamination of CEES on the surface of CuO NPs/PVP in *n*-hexane solvent

Table 1. The GC chromatograms results of different weight ratios in *n*-hexane solvent

Sample	Ratio	AUC/Toluene(1)	AUC/CEES(2)	Ratio(AUC 2/AUC 1)	Decontamination%
a	Blank	118747	124954	1.0522	00.00
b	1:10	122533	84256	0.6876	34.66
c	1:20	114799	60512	0.5271	50.09
d	1:30	113258	33520	0.2959	71.88
e	1:40	117692	12261	0.1041	90.10

GC-MS analysis

Once CEES reacted with CuO NPs/PVP catalyst, the identification and quantification of the decontamination product was followed by gas chromatography coupled with a mass spectroscopy (GC-MS) analysis. Figure 5 depicts the mass spectra for CEES (m/z values ranged from 28, 47, 61, 75, 91, 109 and 123) and hydroxyl ethyl ethyl sulfide (HEES) (m/z values ranged from 28, 47, 61, 76, 89 and 106) as hydrolysis product.

The formation of HEES emphasizes the role of hydrolysis reaction in the decontamination of CEES, thereby rendering its non-toxic product.

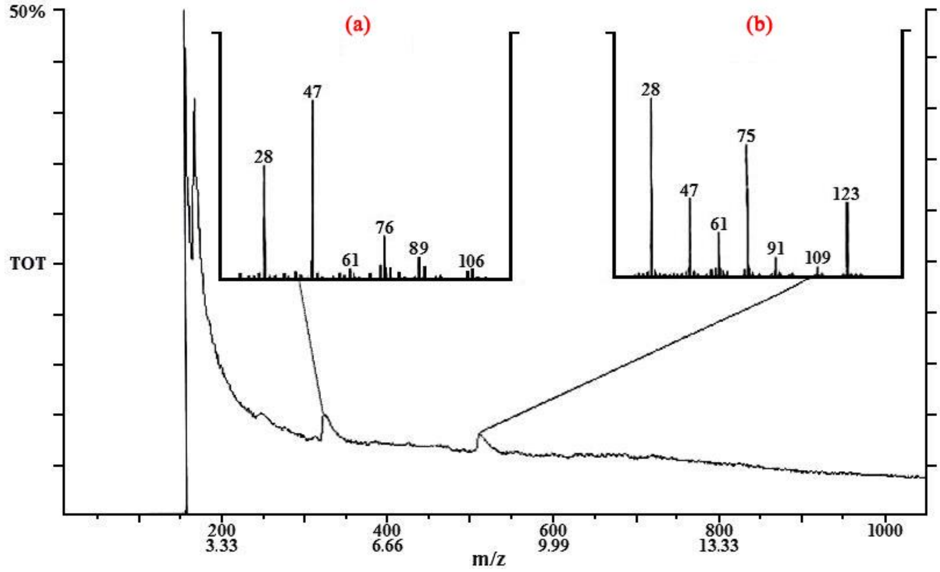
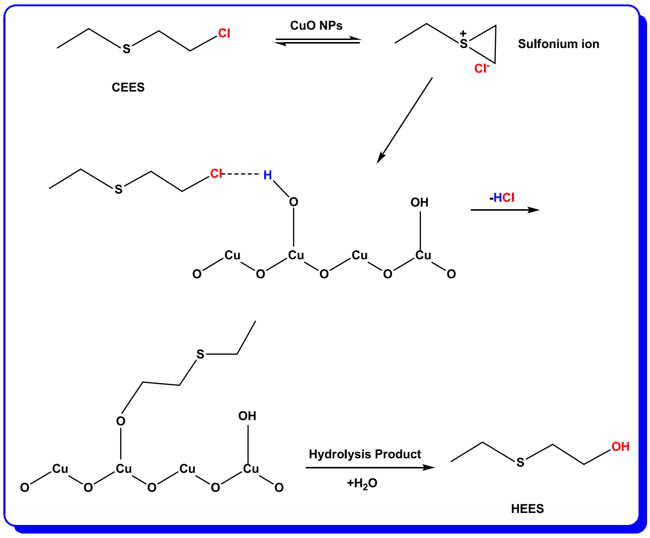


Figure 5. Mass spectra from GC-MS analysis: (a) HEES, (b) CEES

Mechanism of the decontamination procedure

Based on the observations provided by GC and GC-MS analyses, the mechanism scheme reflecting the decontamination chemistry (adsorption and destruction) of the sulfur mustard simulant on the catalyst along with the formation of destruction product is proposed (Scheme 2) in which the decontamination reactions through both CuO nanoparticles have been reviewed. It is worth noting that a proposed route is possible and may proceed simultaneously.

In route adsorption reactions of sulfur mustard simulants occur through nucleophillic attack of the Bronsted (hydroxyl groups (Cu-OH)) acid sites presented on the CuO nanoparticles of the external surface of the nanoparticles to chlorine and sulfur atoms of CEES molecules (initially, cyclic sulfonium ion seems to be formed as an intermediate which is in the nonvolatile form of the related compound so that could not be extracted out and detected by GC). Shortly after that, the chlorine atom in CEES molecule will be removed through the dehalogenation reaction. In the presence of H_2O molecule, different reactions may proceed and hydrolysis product on the surfaces of copper species (Cu^{2+}) as Lewis acid sites will be revealed. Hydrolysis process takes place to yield hydroxyl ethyl ethyl sulfide (HEES) as decontamination product of CEES.



Scheme 2. Proposed mechanism for the decontamination of CEES on the CuO NPs

Conclusion

In this study, CuO nanoparticles were synthesized through precipitation method in the presence of polyvinylpyrrolidone (PVP) as a capping agent characterized by SEM, TEM and XRD techniques. Thereafter, CuO NPs was employed as catalyst in order to investigate the decontamination of chloro ethyl ethyl sulfide (CEES) as sulfur mustard agent simulant. The results obtained by GC and GC-MS analyses demonstrate that CuO NPs have a high catalytic potential to adsorb and destruct the CEES molecules. Higher decontamination (more than 90%) occurred with the weight ratio of 1:40 (CEES:CuO NPs) in *n*-hexane as solvent and the obtained non-toxic product i.e., hydroxyl ethyl ethyl sulfide (HEES) was identified. On the other hand, these amounts decreased with the weight ratios of 1:30, 1:20 and 1:10, respectively.

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