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MnO₂-AgX Zeolite Nanocomposite as an Adsorbent Catalyst for the Decontamination against Sulfur Mustard Simulants

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Abstract:

The our main goal of the present research is evaluating the performance of MnO₂ nanoparticles-AgX zeolite composite as a novel adsorbent catalyst for the decontamination reactions of two most known sulfur mustard simulants; 2-chloroethyl phenyl sulfide (2-CEPS), 2-chloroethyl ethyl sulfide (2-CEES) at room temperature and monitoring by Gas chromatography flame ionization detector (GC-FID) and Gas chromatography-mass spectrometry (GC-MS) analyses subsequently. Prior to the experiment reactions of MnO₂ nanoparticles-AgX zeolite composite with sulfur mustard simulants, this composite was prepared through three steps; first NaX zeolite was prepared under hydrothermal method. In the next step, silver ions were loaded in the NaX zeolite structure via ion exchange procedure and silver nitrate solution as silver precursor for the preparation of the AgX zeolite. Finally, MnO₂ nanoparticles as an 18.4 wt % of unit were dispersed and deposited on the external surface of AgX zeolite through insitu impregnation method. The formation, morphology, crystalline phase, particle size and elemental component of the as-prepared simples were characterized by employing Scanning electron microscopy (SEM), Atomic adsorption spectrometry (AAS), X-ray fluorescence (XRF) spectroscopy, X-ray diffraction (XRD) spectroscopy and Fourier transform infrared spectroscopy (FT-IR) techniques. The GC-FID results denoted that both sulfur mustard simulants were decontaminated (adsorbed and destructed) completely on the surface of the composite in n-hexane solvent after 12 h. The hydrolysis and elimination products; 2-hydroxyl ethyl phenyl sulfide (2-HEPS) and phenyl vinyl sulfide (PVS) from 2-CEPS and 2hydroxyl ethyl ethyl sulfide (2-HEES) and ethyl vinyl sulfide (EVS) from 2-CEES molecules were also identified by GC-MS, respectively.

Key words: MnO_2 nanoparticles-AgX zeolite, composite, sulfur mustard stimulants, decontamination, hydrolysis, elimination.

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1. Introduction

Despite elapsing two decades since the end of Cold War superpower confrontation, the threats of weapons of mass destruction have been posed renewed concerns to global society [1, 2]. At present, neutralization and decontamination of chemical warfare agents (CWAs) is intended for nonproliferation programs due to their devastating effects manifested in case of military actions, large worldwide stock of ammunition and certainly on the specter of terrorist attack [3,4]. Vexing reports from Middle East and Syria during the last year have shown the crisis of CWAs such as sulfur mustard and phosphorus nerve agents used by terrorist organization as they are cheap and easy to manufacture. Sulfur mustard (bis(chloroethyl)sulfide with molecular formula of (ClCH₂CH₂)₂S, commonly abbreviated as H for munition grade and HD for distilled) has been long considered as a persistent and potential CWA which is of great importance for military defense and encountering terrorism [5]. The use of HD was started from World Wars I and II and continued up to Iran-Iraq war of 1980s [6]. HD can be degraded through the cleavage of Cl-Cl and Cl-S bonds [7, 8].

Since highly persistent CWAs are extremely toxic, research studies have been generally performed with less toxic analogues (simulants) with physicochemical characteristics similar to those kinds of agents. The most famous sulfur mustard simulants are 2-chloroethyl phenyl sulfide (2-CEPS) and 2-chloroethyl ethyl sulfide (2-CEPS) and 2-chloroethyl ethyl sulfide (2-CEES). Exposure to these compounds, blistering of the skin and mucous membranes is very common. Hence, they are so-called vesicants or blistering agents. According to Talmage et al [9], and Devereaux et al [10], 2-CEPS and 2-CEES molecules act as cytotoxin or mutatoxin via an intermediate form that binds to DNA, especially in the bone marrow.

This would lead to aplastic anemia (decrease in blood cells) or pancytopenia (red and white blood cells and platelets) [11], Vorontsov et al [12], suggested that high toxicity of these molecules is also associated with the ability of the SCH₂CH₂Cl group to alkylate proteins. 2-CEPS and 2-CEES are considered as a HD simulants because they contain a single chlorine atom on the β carbon atom relative to HD as illustrated in Scheme 1.



Scheme 1. The chemical structures of: (a) HD, (b) 2-CEPS and (c) 2-CEES.

Many advances have been made so far to design methodologies and strategies to neutralize harmful CWAs. The very first and long-term methods were traditionally high aggressive chemicals like bleaching powder, potassium permanganate, mchloro peroxybenzoic acid. magnesium monoperoxyphthalate, potassium persulfate, oxon, sodium hypochlorite and hydrogen peroxide (H_2O_2) [13,14]. However, due to the disadvantages associated with liquid detoxification, investigation for new decontaminants with no hazardous side effects has been started. Lately, reports have revealed that there is a great interest to use of solid sorbent decontaminants such as aluminumcontaining X- and Y-type zeolites [15-19]. Among these two zeolites, X-type faujasite molecular sieve zeolite has attracted more attention because of the higher aluminum content within its crystalline structure [20, 21]. Zeolites are often referred to as molecular sieves which are considered as hydrated crystalline solid structures consisted of silicon, aluminum and oxygen species together form a framework inside which cavities and channels let cations, water and small molecules reside. Baerlocher et al [22], defined zeolites as crystalline aluminosilicates with open 3D framework structures built of SiO₄ and AlO₄ tetrahedral linked to each other by sharing all the oxygen atoms to form regular intra-crystalline cavities and channels of molecular dimensions. Sodalite cages consisted frameworks connected to each other through hexagonal prisms are known as faujasite. X-type zeolite is a large-pore synthetic form of zeolite with the same structural framework as faujasite that possesses a Si/Al ratio between 1 and 1.5 [23, 24]. Moreover, As in the recent years, interests have been inverted toward the application of nanomaterials and nanotechnology, more nanocrystalline inorganics such as metals and metal oxides with adsorptive and catalytic properties have been assayed as solid catalysts to decontaminate toxic chemical agents. Due to the large surface area, high chemical activity and adsorption capacity, nanomaterials are regarded as promising nonaggressive reagents useable for the treatment of sensitive materials contaminated with lethally CWAs, so-called HD and its surrogates through hydrolysis, hydrodehalogenation and/or hydrodesulfurization processes [25, 26]. The detoxification capability of those highly dispersed nanosized metal oxides e.g. V2O, CaO, MgO,

Al₂O₃, ZnO, CuO, TeO₂, SnO₂, and TiO₂ has been

extensively studied and reported [5, 27-33]. In another study done via Howard H. Patterson,

Fe₂O₃/AgY composite were used to investigate the

rapid decontamination for nerve chemical warfare

agents [34]. 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 increase the efficiency of the catalytic process [35].

The methods for modifying zeolites are usually by impregnation [36] and ion-exchange [37]. Also, the dispersion of metal oxide nanoparticles onto zeolite depends on the type of metal precursor used and its action during the preparation method. In this research, we have utilized the combination of AgX zeolite as host and MnO2 nanoparticles as guest materials to synthesize an adsorbent catalyst in which the high surface area of nanoparticles and the absorbent capacity provided by the zeolite cooperation to increase the efficiency of the catalytic process of sulfur mustard simulants. Ag⁺ is the only noble mono-positive cation that forms mononuclear species with appreciable stability in aqueous solution. Besides, silver is known to have strong influence on the absorption properties of zeolites. As an important functional metal oxide, manganese dioxide (MnO_2) is of the most attractive representations of inorganic materials exhibiting such a rich physical and chemical properties and wide applications in various fields such as catalysis, ion exchange, molecular adsorption, biosensor, and energy storage. MnO₂ is a very interesting material because of the diversity in its crystalline structure and high manganese valence [38-40]. To the best of our knowledge, there are no papers reporting the application of MnO_2 nanoparticles-AgX zeolite composite catalyst used for the decontamination of 2-CEPS and 2-CEES.

2. Experimental

2.1. Materials and Reagents

Sodium aluminate, sodium silicate, aluminum sulfate, tetramethyl ammonium chloride, silver

nitrate (AgNO₃), manganese nitrate hexahydrate (Mn(NO₃)₂.6H₂O), potassium permanganate (KMnO₄), n-hexane and toluene all were purchased from Merck Co (Merck, Darmstadt, Germany). 2-chloroethyl phenyl sulfide (2-CEPS) and 2-chloroethyl ethyl sulfide (2-CEES) were obtained commercially from Sigma-Aldrich Co. (USA). All the chemicals were used as received and were of chemical grade. Deionized water was used for the preparation of all the solutions.

2.2. Instrumentation

Different characterization techniques were used to elucidate the physicochemical properties of the produced catalysts. The morphology and size of the prepared adsorbent catalyst were performed via SEM micrographs using a scanning electron microscope (SEM, LEO-1530VP). Weight percentages of the elements (silver and manganese) were measured by atomic adsorption spectrometry (AAS, PerkinElmer, USA) coupled to a HGA 400 programmer hybrid system and equipped with a hollow cathode lamp at respective wavelength using an acetylene-air flame.

The quantitative determination of major elemental compositions as percentages of metal oxides within NaX zeolite was investigated using X-ray fluorescence (XRF) spectroscopy (Bruker, S4 Pioneer, USA) equipped with an array of up to 8 analyzing crystals and fitted with an Rh X-ray tube target. Vacuum was used as the medium of analyses to avoid interaction of X-rays with air particles.

The powder X-ray diffraction (XRD) patterns were recorded at room temperature using a Philips X'pert Pro diffractometer equipped with CuK α radiation and a wavelength of 1.54056 Å (30 mA and 40 kV). Data were collected over the range 4– 90° in 2 θ 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 to 4000 cm⁻¹ using KBr pellets. A Varian Star 3400CX series gas chromatograph equipped with flame ionization detector (FID) and an OV-101CWHP 80/100 silica capillary column (30 m×0.25 mm inner diameter (i.d.), 0.25 µm film thickness) was used to monitor the decontamination reactions of the sulfur mustard simulants, 2-CEPS and 2-CEES. 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). The GC conditions used were as follows: the column temperature was initially hold at 60 °C for 6 min and programmed at 20 °C min⁻¹ to 200 °C to reach the final temperature which was then held for 13 min. The injector, MS quad and source temperatures were fixed at 60 °C, 200 °C and 230 °C, respectively. Helium (99.999% purity) was selected as the carrier gas with the flow rate of 1 mL min⁻¹.

2.3. Synthesis of NaX Zeolite by Hydrothermal Method

In a typical preparation procedure, 20 g of sodium aluminate was dissolved in 30 ml deionized water and slowly heated up to 80 °C under vigorous stirring and maintained at this temperature. Afterward, 55 g of sodium silicate was slowly added to the sodium aluminate solution and together stirred for 2 h. After that, the heating stirrer was turned off and the mixture aged at 25 °C for 48 h (solution A). 78 g of sodium silicate was dissolved in 120 ml deionized water, 16 g of aluminum sulfate added and the mixture stirred continuously for 2 h (solution B). 10 g of sodium aluminate was diluted with 10 ml deionized water, then added drop wise and mixed with a sodium silicate and aluminate precursors under continuous stirring until the complete grain growth was achieved (seed). Subsequently, 2.5 g of nucleation seed was added to solutions A and B. In the next step, 8 g of tetramethylammonium chloride was dissolved in 10 ml of deionized water and added drop wise to the above components. The final mixture was placed in a Teflon-lined stainless steel autoclave, gradually heated to 100 °C and kept for 72 h until a gray gel was derived. The obtained gel was then filtered in a Buckner funnel and washed with double dionized water until pH of the filtrate was equal to 9 (pH=9). Finally, the residue was dried at 110 °C for time interval of more than an overnight [41].

2.4. Preparation of AgX Zeolite by Ion Exchange Method

For promoting the practicality of X-type zeolite, often ionic exchange substitution of Na⁺ by other cations such as Ag^+ is preceded. Ag^+ as a significant reagent is applied in many catalytic procedures [42-44]. To prepare the AgX zeolite, 2.2 g of the synthesized NaX zeolite before ionic exchange was calcined at 400 °C for 3 h in a furnace for excluding moister and impurities from the surface.

The calcined NaX zeolite was then added to a 50 mL of 0.15 M silver nitrate (AgNO₃) solution and the mixture was stirred magnetically at 60 °C for 5 h to allow Ag⁺ ions replace Na⁺ ions and perform ion exchange process. The synthesized product (AgX zeolite) was then filtered and washed with deionized water and 0.1 M HCl solution to remove the excess and unreacted silver ions from the zeolite framework, sequentially and then dried at 110 °C for 16 h.

At last, the clean and dry AgX zeolite was calcined at 400 °C for 4 h [45]. It is reported elsewhere that usually there are some ion exchange sites (about 10–20% of total exchangeable sites) that are occupied with hydrogen and are not exchangeable with Ag cations.

2.5. Preparation of MnO₂NPs Loaded onto AgX Zeolite by Impregnation Method

The incorporation of MnO₂NPs loaded into AgX zeolite was accomplished by the impregnation method. For the preparation of MnO₂NPs-AgX zeolite composite, first 1.5 g of AgX zeolite was poured into a 20 mL of 1 M Mn(NO₃)₂ aqueous solution and stirred for 5 h. Under continuous stirring, 50 mL of a 0.2 M KMnO₄ solution was added suddenly. KMnO₄ has been known among the strong oxidizing agents [46], so that, the color of the solution immediately turned to dark brown immediately, indicating the formation and precipitation of MnO₂NPs through oxidation with KMnO₄. The obtained sample was then dried at 100 °C for more than an overnight. In the final step, the calcination of the product was performed at 550 °C for 4 h. The ionic equation of the reaction is as follows (1) [47, 48]:

 $3Mn^{2+} + 2MnO_4^- + 2 H_2O \rightarrow 5MnO_2 + 4H^+$ (1)

2.6. Decontamination Procedure of the Sulfur Mustard Simulants by MnO₂NPs-AgX Zeolite Composite

For investigation of the decontamination reactions of 2-CEPS and 2-CEES on the surface of MnO₂NPs-AgX zeolite composite, the samples were prepared according to the following procedure; 5 mL of n-hexane as the solvent, 10 μ L of a 5:1 (v/v) ratio of each sulfur mustard simulant samples (2-CEPS/H₂O and 2-CEES/H₂O) and 10 μ L of toluene as the internal standard were added to two 10 mL Erlenmeyer flasks which were sealed to prevent the vaporization of the solvents. All samples were vortexed for 1 min to give blank samples. Then, 0.3 g of MnO₂NPs-AgX zeolite composite was added to above solutions. No efforts were made to control ambient light or humidity. To achieve a perfect adsorption and a complete reaction between adsorbent catalyst and sulfur mustard simulants through optimizing various shaking times intervals, the samples were shaken on a wrist-action shaker for 5 and 12 h under N_2 atmosphere and room temperature, respectively. At last, 10 μ L of each solution samples were extracted by a micro syringe and injected to GC and GC-MS instruments for quantitative analysis.



Figure 1. SEM images of the catalyst samples: (a) and (b) NaX zeolite, (c) and (d) AgX zeolite, and (e) 18.4 wt % MnO₂NPs-AgX zeolite composite.

3. Results and discussion

3.1. SEM Analysis

The crystalline size and morphology of the assynthesized NaX and AgX zeolites and 18.4 wt % MnO₂NPs-AgX zeolite composite were surveyed through magnification by SEM images as depicted in figure 1. The SEM images demonstrate homogenous morphology of the structures, approximately cubic shape of NaX and AgX zeolites and production of quasi-spherical MnO₂ crystals dispersed and deposited on the external surface of AgX zeolite and also denote that these morphologies and the crystallinity of the structures are retained with silver ion exchange and MnO₂NPs loading processes which are indicated by SEM images in Figures 1a to 1e. Also, SEM image obviously show that MnO₂NPs have been dispersed and deposited on the external surface of zeolite AgX (Figure 1e). The crystalline sizes of MnO₂ NPs were demonstrated to have nanometric dimensions (less than 100 nm). The presence of some bigger particles in the micrographs is attributed to the aggregation or overlapping of particles some smaller during composite preparation.

3.2. AAS Analysis

The amounts of silver and manganese elements in the adsorbent catalyst were determined through elemental analysis by atomic absorption spectrometry (AAS). The results revealed that the amounts of silver and manganese were 10.3 wt % and 18.4 wt %, respectively.

3.3. X-ray Fluorescence (XRF) Analysis

The chemical element compositions (metal oxides) contained in the initial NaX zeolite was investigated using the wavelength dispersive X-ray fluorescence (XRF) spectroscopy as summarized in table 1. As can be seen from XRF analysis, SiO₂, Al_2O_3 and Na_2O species are the main components and sources of silicon (Si), aluminum (Al) and sodium (Na) for the zeolite, respectively. The existence of heavy metals was not observed in the structure of the zeolite. Meanwhile, the loss on ignition (LOI) parameter was determined due to the giving off the structural hydroxyl water and volatile organic components.

3.4. X-ray Diffraction (XRD) Patterns

In Figure 2, XRD patterns of the understudy NaX and AgX zeolites and the 18.4 wt % MnO₂NPs-AgX zeolite composite are displayed, respectively. As seen from the patterns, the sharp peaks referring to NaX zeolite occurred at scattering angles (2 θ) of 5.940°-48.685° corresponded to miller indexes of 111-955 respectively (Figure 2a) that have been crystallized in the cubic system (Fd–3m with lattice size of 24.9600 Å and are in good agreement with those of the NaX zeolite with molecular formula of C₅H₄O₂.Na₂O.Al₂O₃.3.3SiO₂.7H₂O, Reference code: 00-041-0118). NaX zeolite structure was retained even after silver cation exchange in AgX zeolite (Figure 2b).

Meantime, synthesized MnO_2NPs (as guest material) loaded as a 18.4 wt % of unit onto AgX zeolite as the host material, possesses a series of new peaks which were obtained at 20 of 35.752°-64.565° corresponded to miller indexes of 131-421, respectively (Figure 2c). No characteristic peaks related to the presence of impurities were observed in the patterns during manganese (IV) oxide loading.

 Table 1. XRF analysis results for the Initial NaX zeolite

Compounds	Concentration (wt ^a %)		
SiO ₂	47.04		
Al_2O_3	30.55		
Na ₂ O	9.51		
SO_3	0.673		
K_2O	0.574		
Fe_2O_3	0.509		
CaO	0.128		
TiO ₂	0.035		
Cl	0.034		
CuO	0.015		
LOI^b	10.77		
Total	99.84		

^a Weight percentage amount. ^b The loss on ignition parameter.



Figure 2. XRD patterns of the catalyst samples: (a) NaX zeolite, (b) AgX zeolite and (c) 18.4 wt% MnO₂NPs-AgX zeolite composite. The black points show the diffraction peaks of MnO₂ crystal.

These peaks which are illustrated as black points in Figure 2c, reveal that MnO₂ crystals have been dispersed and deposited onto AgX zeolite and also indicate a host-guest interaction between AgX framework and MnO₂. A definite line broadening of the scattering pattern in Figure 2c is a demonstration upon which the synthesized MnO₂ particles are in nanoscale range. However, a small loss of crystallinity is observed in Figures 2b and 2c associated with the lower intensity of the peaks at 20 of 9.890°, 11.630°, 18.318°, and 19.975°. This may be because of the dealumination process of AgX zeolite and MnO2NPs-AgX zeolite composite and associated with the location of substituted silver and impregnated manganese cations. The Mn^{4+} ions within the zeolite framework can interact with the aluminate sites

Totally, it can be concluded that with silver ion exchange in NaX zeolite and subsequent loading of MnO₂NPs onto AgX zeolite, the structure of the zeolites did not changed. On the other hand, the capacity of the X-type zeolite to keep the guest species is limited. Consequently, the adsorption of the host cations (Si, Al and Na) will stop if the capacity is filled. In contrast, the amount of the host species in the AgX zeolite increases with increasing the manganese dioxide content. The introduced MnO₂NPs were dispersed and deposited on the external surface of AgX zeolite; however, due to the relative aggregation during processing of the composite, some particles are too large to perch inside the structure. Hence, high MnO₂NPs loading will cause structural damage to the zeolite. Similar

more strongly strongly than that of Na⁺ or Ag⁺ ions.

results were also observed by other researchers in several studies [49-52]. The crystalline size of MnO_2NPs was also investigated via XRD measurement and line broadening of the peak using Debye-Scherrer equation (2) [53]:

$$d = \frac{0.94\lambda}{\beta\cos\theta}$$
(2)

Where *d* is the crystal size, 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 size is estimated to be 13.2 nm. The crystalline sizes obtained from XRD measurement are consistent with the results from the SEM study.

3.5. FTIR Study

The characterization of the prepared adsorbent catalyst along with the X-type zeolite precursors was further surveyed by FT-IR spectra as plotted in Figure 3.



Figure 3. FTIR spectra of the catalyst samples: (a) NaX⁴ zeolite, (b) AgX zeolite and (c) 18.4 wt % MnO₂NPs-AgX zeolite composite.

Peak positions are nearly identical for three samples. All of the three as-synthesized typical samples, namely NaX zeolite, AgX zeolite and 18.4 wt % MnO₂NPs-AgX zeolite composite have peaks around 456 cm⁻¹ and 562 cm⁻¹ which are assigned to the bending vibrations of the insensitive internal TO₄ (T=Si or Al) tetrahedral units and double six rings (D6R) external linkage within the X-type zeolite structure, respectively. The peaks around 674 cm⁻¹ and 754 cm⁻¹ are attributed to the external linkage and internal tetrahedral symmetrical stretching vibrations, respectively. Furthermore, the peaks around 984 cm⁻¹ are corresponded to the linkage and internal external tetrahedral asymmetrical stretching vibrations, and the peaks around 1643 cm⁻¹ and 3459 cm⁻¹ are assigned to H-O-H bending and O-H bonding (hydroxyl groups) vibrations of the X-type zeolite structure, respectively. Surveying Figures 3a and 3b confirms that no changes has occurred in the bands of AgX zeolite compared with the original NaX zeolite, which tends to lend further support to the idea that the ion exchange modification of NaX zeolite by silver ion has a very little influence on the chemical structure of the zeolite framework. On the other hand, Figure 3c illustrates three new peaks related to the synthesized loaded MnO₂NPs. The absorption peak at 577 cm⁻¹ is corresponded to Mn–O bond. The peaks around 1474 cm⁻¹ and 3347

cm⁻¹ are attributed to H–O–H bending and O–H bonding (hydroxyl groups) vibrations of the nanoparticles, respectively.

3.6. GC Analysis

In order to study the decontamination chemistry of sulfur mustard simulants, the catalytic performance of MnO₂NPs-AgX zeolite composite with 18.4 wt % MnO₂ nanoparticles content was evaluated in nhexane solvent at room temperature and those progresses were monitored by GC-FID analysis as a rapid and suitable analytical technique. The GC chromatograms are shown in Figures 4 and 5. It is observed from GC chromatograms that 2-CEPS and 2-CEES have retention times at approximately 10.6 min. In order to calculate the amounts of destructed sulfur mustard simulants, the integrated AUC data of 2-CEPS and 2-CEES samples and toluene as the internal standard have been given for three different points (0, 5 and 12 h) in the reaction time intervals. Subsequently, the ratio of the integrated data (integrated AUC of 2-CEPS and 2-CEES/integrated AUC of toluene) was determined and with increasing the reaction time, the intensity of the AUC data of simulants was decreased respect to that of toluene and higher amounts of these molecules were neutralized. Area under curve (AUC) data and the results under different shaking times are summarized in Table 2.

Table 2. GC analysis results for sulfur mustard simulants in different reaction time intervals

Simulant	Reaction Time	AUC ^a of	AUC of	Ratio	Decontamination
Туре	(h)	Simulant (1)	Toluene (2)	(AUC 1/AUC 2)	(%)
2-CEPS ^b	0	351786	483222	0.7280	00.00
	5	54433	866779	0.0628	91.37
	12	000000	631890	0.0000	100.00
2-CEES ^c	0	245557	547663	0.4502	00.00
	5	10026	864322	0.0116	96.69
	12	000000	863598	0.0000	100.00

^aArea under curve. ^b2-chloroethyl phenyl sulfide. ^c2-chloroethyl ethyl sulfide.



Figure 4. GC chromatograms of decontamination reactions of 2-CEPS by MnO_2NPs -AgX zeolite composite in n-hexane solvent and different reaction time intervals: (a) 0 h, (b) 5 h and (c) 12 h.

This is illustrated by the new peaks in Figures 4c and 5c, occurred at retention times of 9 and 12.6 min assigned to 2-CEPS decontamination products and 8.2 and 12.3 min assigned to 2-CEES decontamination products, respectively. Subsequently, a complete decontamination (100%) was observed after 12 h. Due to the n-hexane is an

inert solvent, there is no competition between this solvent and 2-CEPS and 2-CEES molecules to occupy the reactive sites presented on the surface of the catalyst including Bronsted and Lewis acid sites, so that they can be easily adsorbed and destructed by the composite.



Figure 5. GC chromatograms of the decontamination reactions of 2-CEES by MnO_2NPs -AgX zeolite composite in n-hexane solvent and different reaction time intervals: (a) 0 h, (b) 5 h and (c) 12 h.

3.7. GC-MS Analysis

Once the sulfur mustard simulants reacted on the surface of 18.4 wt % MnO₂NPs-AgX zeolite composite, the identification and quantification of

the decontamination products was followed by GC-MS analysis. Figures 6 and 7 depict mass spectra for 2-CEPS (m/z values 28, 45, 69, 84, 109, 123 and 172), 2-CEES (m/z values 28, 47, 61, 75, 91,

109 and 123) and their products including 2hydroxyl ethyl phenyl sulfide (2-HEPS) (m/z values 28, 43, 59, 85, 131, 155, 166 and 193) and phenyl vinyl sulfide (PVS) (m/z values 28, 43, 58, 75, 91, 137 and 165) for 2-CEPS and 2-hydroxyl ethyl ethyl sulfide (2-HEES) (m/z values 28, 47, 61, 75, 89 and 106) and ethyl vinyl sulfide (EVS) (m/z values 27, 47, 61, 71 and 88) for 2-CEES, respectively. The formation of the above less-toxic products emphasizes the role of hydrolysis and elimination reactions in the decontamination of the sulfur mustard simulants.



Figure 6. The GC-MS analysis and mass spectra of 2-CEPS-18.4 wt % MnO₂NPs-AgX zeolite composite sample: (a) 2-CEPS, (b) 2-HEPS, and (c) PVS.

3.8. Mechanism of the Decontamination Procedure

Based on the observations provided by GC and GC-MS analyses, the mechanism schemes reflecting the neutralization chemistry (adsorption and destruction) of the sulfur mustard simulants on the adsorbent catalyst along with the formation of destruction products are proposed (Schemes 2 and 3) in which the decontamination reactions through both manganese dioxide and silver species have been reviewed. It is worth noting that both of the proposed routes are possible and may proceed simultaneously.

In route (a) adsorption reactions of sulfur mustard simulants occur through nucleophillic attack of the Bronsted (hydroxyl groups (Mn-OH)) acid sites presented on the MnO₂ nanoparticles of the external surface of the composite to chlorine and sulfur atoms of 2-CEPS and 2-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 2-CEPS and 2-CEES will be molecules removed through the dehalogenation reaction. In the presence and

absence of H_2O molecule, different reactions may proceed and hydrolysis and elimination products on the surfaces of manganese species (Mn⁴⁺) as Lewis acid sites will be revealed. Both hydrolysis and elimination processes take place to yield 2hydroxyl ethyl phenyl sulfide (2-HEPS) and phenyl vinyl sulfide (PVS) as decontamination products of 2-CEPS and 2-hydroxyl ethyl ethyl sulfide (2-HEES) and ethyl vinyl sulfide (EVS) as decontamination products of 2-CEES, respectively [54-57]. On the other hand, in route (b) the electrophillic attack of positive silver (Ag⁺) of the zeolite structure to chlorine and sulfur atoms of sulfur mustard simulants, makes 2-CEPS and 2CEES molecules adsorb on the surface and pores of the catalyst. Transition states for the formation of $S-Ag^+-Cl$ bonds will further lead to the formation of cyclic sulfonium ions which act as intermediate. These are unstable intermediates and subsequently, in the presence and absence of water, turn into 2hydroxyl ethyl phenyl sulfide (2-HEPS) and 2hydroxyl ethyl phenyl sulfide (2-HEES) as hydrolysis products and phenyl vinyl sulfide (PVS) and ethyl vinyl sulfide (EVS) as elimination products of 2-CEPS and 2-CEES molecules on the surfaces of silver species (Ag⁺) as Lewis acid sites of the adsorbent catalyst, respectively [58, 59].



Figure 7. The GC-MS analysis and mass spectra of 2-CEES-18.4 wt % MnO_2NPs -AgX zeolite composite sample: (a) 2-CEES, (b) 2-HEES, and (c) EVS.





2-HEPS



Scheme 3. Reaction mechanisms for the decontamination of 2-CEES on the surface of the 18.4 wt % MnO_2NPs -AgX zeolite composite catalyst: (a) manganese and (b) silver as Bronsted and Lewis acid sites.

In this scientific research, we have produced 18.4 wt % MnO_2NPs -AgX zeolite composite as a novel adsorbent catalyst with the goal to decontaminate and convert the sulfur mustard simulants such as 2-

CEPS, 2-CEES to much less-toxic products. The Characterization of the samples was carried out by SEM, AAS, XRF, XRD and FT-IR techniques which showed crystallinity and homogenous morphology of the zeolites and adsorbent catalyst, elemental weight percentages of silver and manganese species, chemical element compositions (metal oxides) within the initial X-type zeolite, silver ion exchange and manganese dioxide loading processes and nanometric range of MnO₂ particles, functional groups and partial molecular structure of the synthesized zeolites and final composite, respectively. Based on the observations obtained by GC analysis, the utilized adsorbent catalyst possesses such a high performance and potential for the decontamination of the mentioned pollutants. The obtained results revealed that the above simulants were decontaminated (adsorbed and destructed) completely (100%) on the surface of this composite in n-hexane solvent after 12 h at room temperature. On the other hand, GC-MS analysis has provided valuable information about the reaction products of sulfur mustard simulants, namely, 2-HEPS and 2-HEES as the hydrolysis and PVS and EVS as the elimination products.

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