

A NEW METHOD FOR THE SYNTHESIS OF MgO NANOPARTICLES FOR THE DESTRUCTIVE ADSORPTION OF ORGANO-PHOSPHORUS COMPOUNDS

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In this work, a simple and easily available method for the synthesis of MgO particles was introduced and the destroying of the stimulants of chemical warfare agents (CWA) (malathion as VX simulant and DMMP as GB stimulant), by synthesized MgO particles (MS284) was investigated. The specific surface area (SSA) of the synthesized MgO particles and technical grade of MgO powders (MM283) (as received) was determined and compared by BET method. Synthesized MgO particles and technical grade of MgO powders had an average size of up to 75 nm and 20 micrometers, respectively. Results obtained from UV/Vis technique showed that the weight ratios of 1:16 and 1:32 (stimulants: MgO particles) could decompose almost all of the CWA stimulants. It was also shown that the weight ratio of 1:32 could destroy the other destruction products. In comparison with MM283 and NanoActive[®] Magnesium Oxide Plus nanoparticles, MgO particles prepared in this work showed a good performance in the destruction of chemical warfare agents.

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1. Introduction

Some of the chemical compounds such as tabun (GA or ethyl N,N-dimethylphosphoramidocyanidate, CAS 77-81-6), sarin (GB or O-isopropylmethylphosphonofluoridate, CAS 107-44-8), VX (O-ethyl-S-(2-diisopropylaminoethyl)-methylphosphonothiolate, CAS 50782-69-9), and sulfur mustard (H, HT, HD or bis(2-chloroethyl) sulfide, CAS 505-60-2) are used as chemical warfare agents (CWA). The nerve agents GA, GB, and VX are organophosphate esters, which have been developed to cause incapacitation or death in the military use. These agents are among the most potent of all chemical warfare agents and have extraordinarily high levels of acute toxicity. In the vapor or aerosol form, the nerve agents can be inhaled or absorbed through the skin or the eyes. As a liquid, they can be absorbed through the skin, conjunctiva, and upper gastrointestinal tract. The toxicity of agents is related primarily to their ability to the inhibition of producing the acetylcholinesterase, which is a critical enzyme, needed for nerve function [1].

The most important rescue measures after the contamination of instruments or body surface with supertoxic lethal chemical warfare agents are decontamination (detoxification) on the lowest tactical level, i.e. at the individual level [2]. Therefore, the destruction of chemical warfare agents has become an important topic of study over the past decade. For example, the oxidation of sulfur, nucleophilic substitution at the pentavalent phosphorous, and the enzymes have been used to detoxify HD, detoxify the nerve agents, and catalyze the hydrolysis of G agents, respectively [3]. Incineration and hydrolysis by caustic solutions, and certain zeolites (NaY and AgY) have also been used for decomposition of some CWA compounds and found that in some cases, the zeolites did not completely decontaminate these agents [4].

There are many reactions, which have been employed to destroy chemical warfare nerve agents, but only a few are feasible for practical neutralization because the reactions must be simple and reactants must also be stable and cheap with a relatively low molecular weight [5].

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As another Strategy, charcoal filters have been used to adsorb such toxic, and air-borne substances, but activated carbon suffers from the fact that it does not destroy a toxic chemical and merely "holds it" by adsorption forces (i.e., chemisorptions). Moreover, inorganic pollutants such as hydrogen cyanide, cyanogen chloride and acid gases are not adsorbed well by activated carbon. However, better alternatives have been sought for some time, such as Cu-Cr-Ag impregnated charcoal, as well as other impregnated materials, and thermal and catalytic methods. In fact, the development of effective catalysts would be best, but heteroatom-containing pollutants are severe poisons for catalytic sites. Thus, it is of interest to develop alternative reagents that simultaneously adsorb, immobilize, and destroy such pollutants [6-8].

Recently, inorganic oxides have been used for the decontamination of CWA to adsorb destructively these harmful agents. Dry powders are non-toxic, waterless, and they have low logistical burden, easy to handle and storage. [9,10]. Metal oxide crystals exhibit very interesting characteristics and they are attractive for a large variety of applications including catalysis, sensors, (opto)electronic materials, and environmental remediation [11]. They have very high capacities for adsorption of acid gases and polar organics (including CW agents and their mimics) per unit surface area. The ability of the destructively adsorbing of toxic materials makes metal oxide crystals fundamentally different from normal adsorbents such as activated carbon [5].

Conventional metal oxide powders, MgO, CaO and alumina, possess little reactivity toward CWA, but their reactivity is anticipated to be enhanced in micro and especially nanosized particles, due to the larger surface area of smaller particles, and greater amount of highly reactive edge and corner "defect" sites [12-15]. Similarly, nano-MgO, CaO, and Al₂O₃ adsorb polar organics such as aldehydes, alcohols, ketones, and other polar organics in very high capacities, and substantially outperform the activated carbon samples that are normally employed for such purposes [16-18].

Although many metal oxides such as MgO, CaO, TiO₂, ZrO₂, FeO, V₂O₃, V₂O₅, Mn₂O₃, Fe₂O₃, NiO, CuO, Al₂O₃, ZnO and their mixtures may be capable of such surface chemistry, MgO serves as a good model since it possesses a simple crystal structure and because it can be prepared with widely ranging surface areas and methods. Additionally, MgO has exhibited high reactivity in catalytic processes, and its defect sites have been shown to be active sites [7,19].

Nanocrystals of MgO react with organophosphorus compounds at ambient temperatures by dissociative chemisorptions (destructive adsorption). Ultrafine powders of magnesium oxide have unusual crystalline shapes and possess high surface concentrations of reactive edge/corner and defect sites, and thereby display higher surface reactivity, than typical polycrystalline material. This high surface reactivity coupled with high surface area allows their use for effective decontamination of chemical warfare agents and related toxic substances [16]. However, destructive adsorption does not occur on high-surface-area carbon adsorbents, therefore nanocrystalline metal oxides, with their polar nature and high surface reactivities bring a new useful dimension, and this has proven valuable in the quest to find protective measures against chemical and biological warfare [20].

There are several approaches to the synthesis of nanoscale inorganic materials, including metal atom clustering in cold solvents, metal ion reduction or precipitation, reaction in micelle or reverse micelle media, metal cluster oxidation and finally sol-gel process [21].

In this paper, a simple method for the synthesis of MgO particles was performed. The characterization of synthesized MgO particles (their surface reactivity and morphology) and their reactivity toward some organophosphorus compounds were investigated. Furthermore, the performance of synthesized MgO particles (MS284) were compared to the commercial MgO powders (MM283) and NanoActive[®] Magnesium Oxide Plus nanoparticles (this nanoparticles have been introduced as a special product for destruction of CWA agents with the highest defects and specific surface area (SSA), but because of the expensive synthesise method (aerogel) they have high cost).

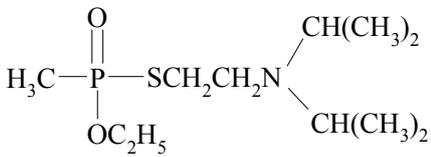
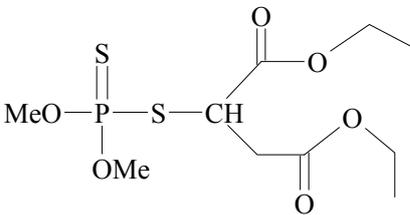
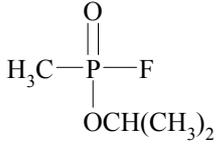
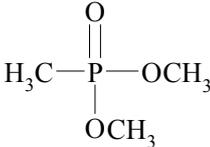
2. Experimental

2.1. Materials

For studying of the most famous nerve agents, malathion and DMMP were used as the stimulants of VX and GB, respectively. Table 1 demonstrates the VX and GB structures in comparison with their stimulants. Malathion was obtained from Riedel-de Haën Chemicals Co. (Germany). DMMP from Sigma-Aldrich Co. (USA) was used as received.

NanoActive[®] Magnesium Oxide Plus nanoparticles was purchased from NanoScale Corporation (USA). Commercial magnesium oxide and n-hexane were obtained from Merck KGaA, Darmstadt, Germany.

Table 1. Nerve agents and their stimulants

Nerve agent	Stimulant
 <p>(VX)</p>	 <p>(Malathion)</p>
 <p>(GB)</p>	 <p>(DMMP)</p>

2.2 Characterization

The absorption spectra of Malathion and DMMP in the presence of different ratios of MgO particles were examined by T70 UV/Vis spectrometer (PG Instruments Corporation, England) in the range of 200–350 nm.

The surface reactivity of particles has been measured by using CHEMBET 3000 BET analyzer (Quantachrome, USA).

The morphology of synthesized MgO particles was examined with a XL30 Philips scanning Electron Microscope (SEM), operating at an acceleration voltage of 20 kV.

X-ray diffraction (XRD) analysis was carried out on a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) using CuK α radiation (40 kV, 40 mA and $\lambda=0.154$ nm). Samples were scanned at 1°/min in the range of $2\theta = 15-90^\circ$.

2.3 Preparation of MgO particles

MgO particles were synthesized according to the following procedure:

- About 200 g of MgCl₂ powders was dissolved in the minimum amount of distilled water (any precipitate was filtered for the separation of impurities from the solution of Mg²⁺ ions).
- There were about 500 mL of a concentrated solution of sodium hydroxide (~10 M) were added to the above solution under vigorous stirring (the milky suspension of the Mg(OH)₂ particles was produced).
- Suspension was boiled for 30 minutes. Then the fine powders of Mg(OH)₂ was filtered.
- The fine precipitates were washed with a plenty of distilled water until the washed solution had not any sign of chloride ions. Testing of the filtrate was performed with a solution of AgNO₃ (1 M). This step had a significant role in the purity of final Mg(OH)₂ powders and consequently MgO particles.
- Mg(OH)₂ powders was placed into atmospheric oven at 400 °C for 4 h to produce MgO particles.
- For preventing the effect of humidity on the synthesized MgO particles, they were placed in a desiccator containing NaOH flakes and kept for subsequent tests.

2.4 Preparation of MgO-CWA samples

To investigate the reaction between MS284 and the simulant of VX (malathion), MgO- malathion samples were prepared according to the following method:

- For each sample, 5 μ L of malathion and 20 mL of n-hexane were added to the 100 mL Erlenmeyer flask.
- Consider to the volume and density of malathion, the weights of particles needed for establishing the different weight ratios of malathion:MgO particles (1:1, 1:2, 1:4, 1:16, and 1:32) were calculated and added to the above solutions.
- To do a complete reaction between particles and malathion, all samples were attached to a shaker and were shaken for about 7 h.
- After that, the presence of the malathion in the samples was investigated by the UV/Vis spectrometer.

For the preparation of MgO- DMMP samples, considering to the density of DMMP, particles weights were calculated and the procedure was performed in the similar conditions.

Due to the accurate study, two kinds of experiments were performed to compare the performance of synthesized MgO particles and the other MgO particles (as received):

- 1) Two samples contained the MM283 (one for malathion and the other for DMMP) were tested (same as the above procedure) to find out the destruction ability of technical grade of MgO powders.
- 2) The performance of “NanoActive® Magnesium Oxide Plus” and synthesized particles were also compared.

3. Results and discussion

X-ray diffraction pattern of synthesized MgO particles (MS284) is shown in Fig.1. The Scherrer equation is used in x-ray diffraction and crystallography to correlate the size of sub-micrometer particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern:

$$d = \frac{0.9 \times \lambda}{\beta \cos \theta} \quad (1)$$

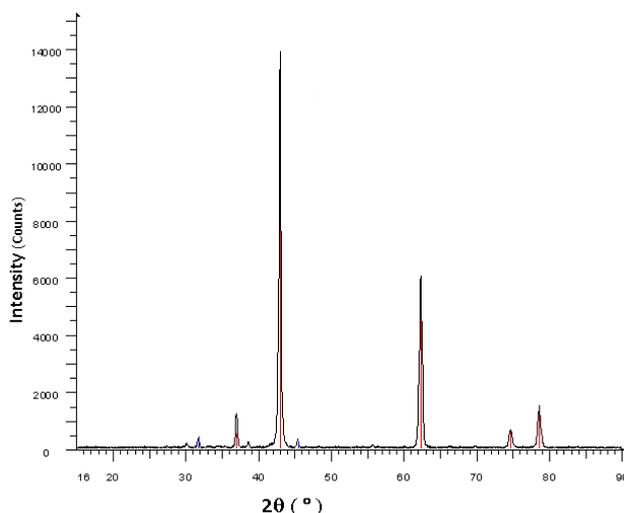


Fig. 1 XRD pattern of the synthesized MgO particles (MS284).

where λ is the x-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. MS284 particles size calculated from Scherrer equation is reported in Table 2.

Table 2. Particle size calculated from XRD data

Obs. Max ($2\theta^\circ$)	Max Int. (Cps)	FWHM ($2\theta^\circ$)	Particle size (nm)
36.92	605	0.309	27.10
42.90	6961	0.348	24.53
62.28	3012	0.420	22.10
74.66	335	0.492	20.31
78.59	748	0.482	21.30

BET results showed that SSA was 30.9641 m²/g and 166.8692 m²/g for MM283 and MS284 particles, respectively. Therefore, the synthesized MgO particles had a SSA more than 5

times than technical grade of MgO powders. Successfully, the surface reactivity of MS284 particles was considerably increased with respect to technical powders. This was confirmed with the results of destructive adsorption tests discussed later.

SEM micrographs were used to indicate the morphology and size distribution of the MgO powders (MM283 and MS284). Fig. 2a and Fig. 2b show the SEM photographs of Technical grade of MgO powders (MM283) and Synthesized MgO particles (MS284) with different resolution, respectively.

According to SEM images, the average size of MS284 particles was considerably smaller than that of MM283 powders. In fact, with a simple and low cost method, fine particles with high performance were synthesized.

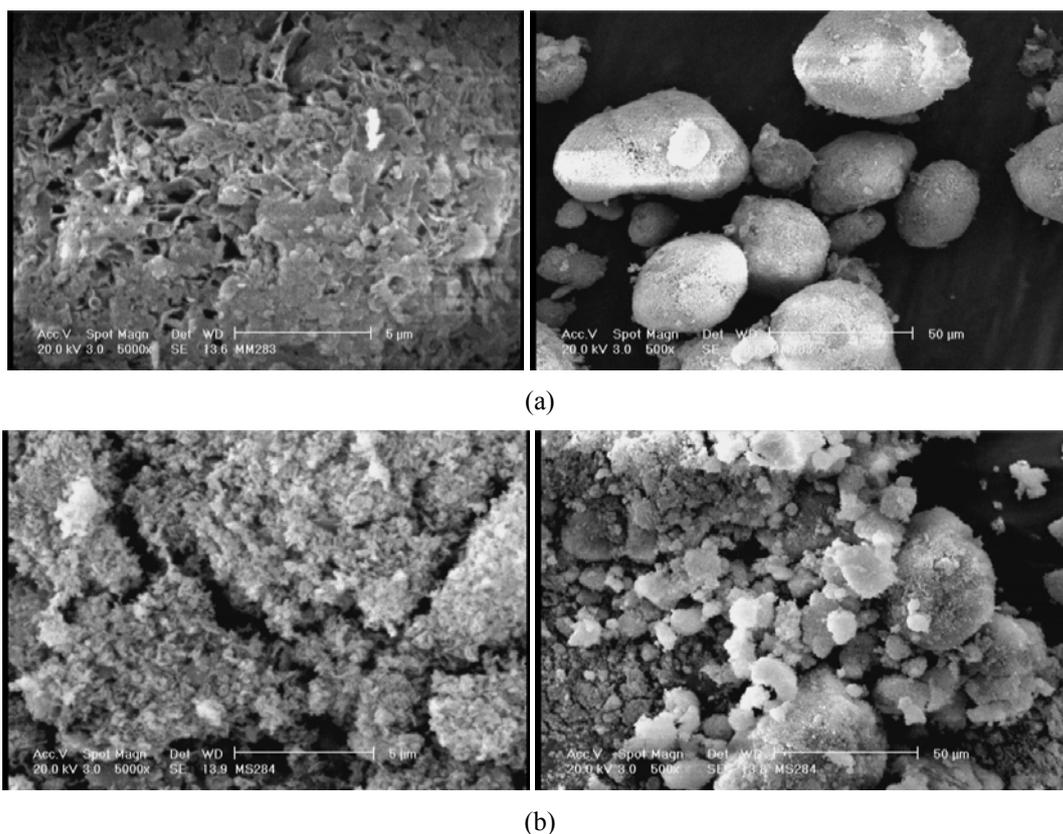
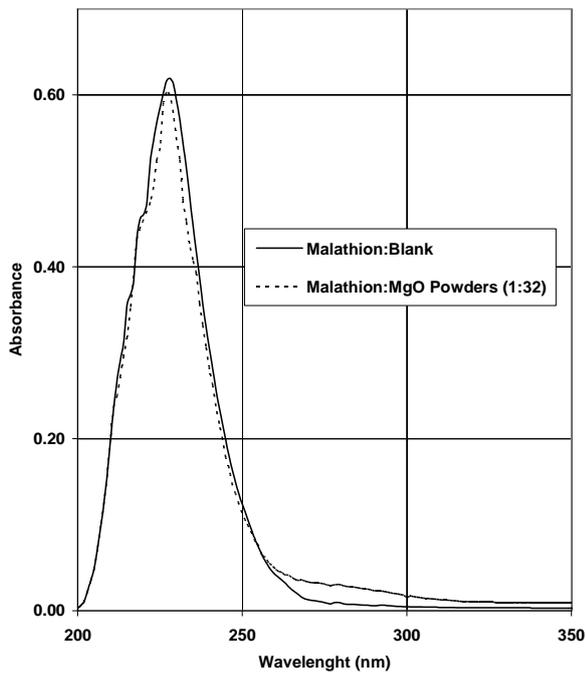


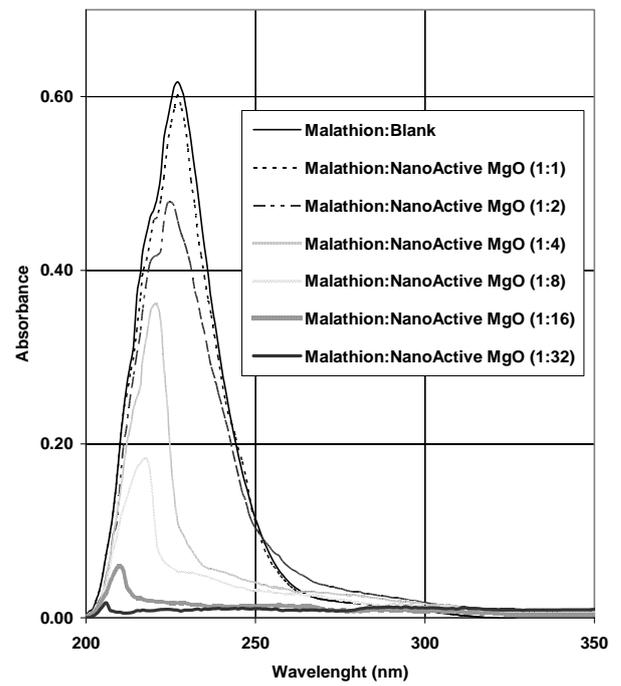
Fig. 2 SEM micrographs of (a) MM283, and (b) MS284.

Due to the investigation of the ability of MgO particles in destruction of organophosphorus compounds, UV/Vis spectrum of each “MgO-CWA” sample was recorded in the range of 200–350 nm. In the other words, both stimulants tend to absorb the UV spectrum and this trait was used for tracing the presence of these agents in the samples.

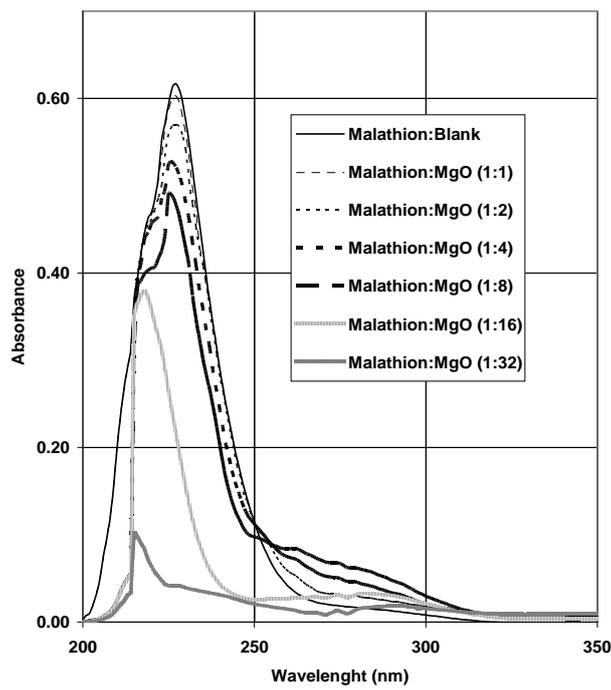
The UV/Vis Spectra of samples contained malathion and DMMP were shown in Fig. 3 and Fig. 4, respectively.



(a)

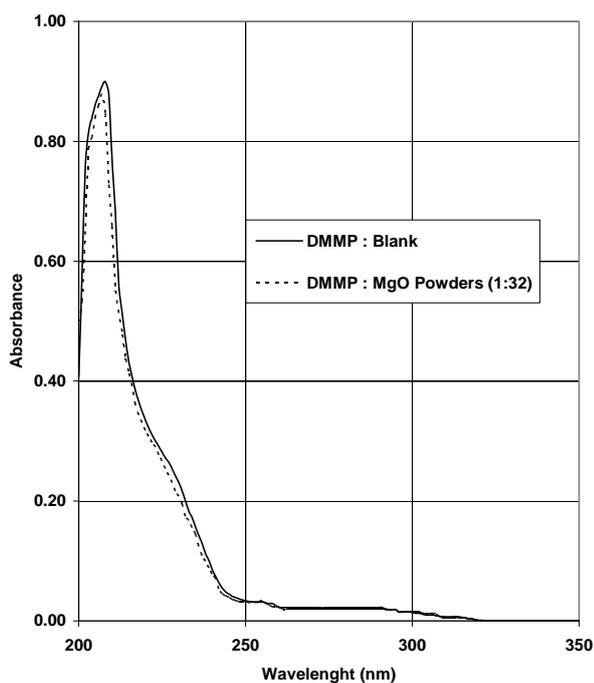


(b)

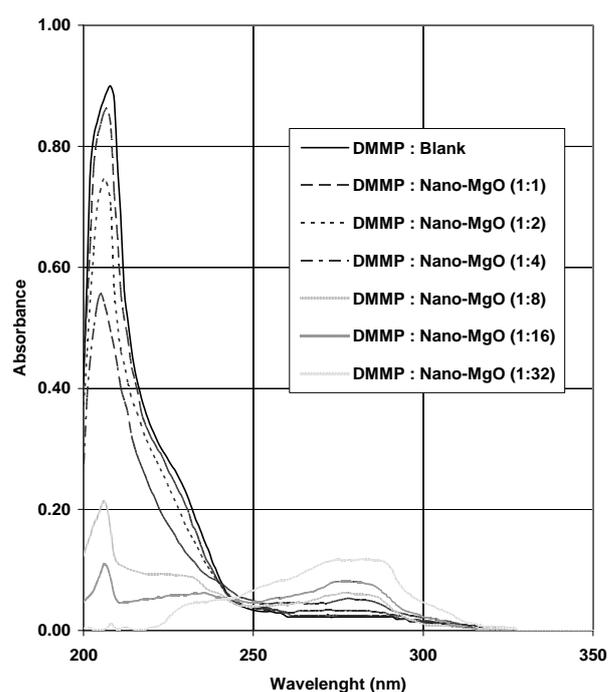


(c)

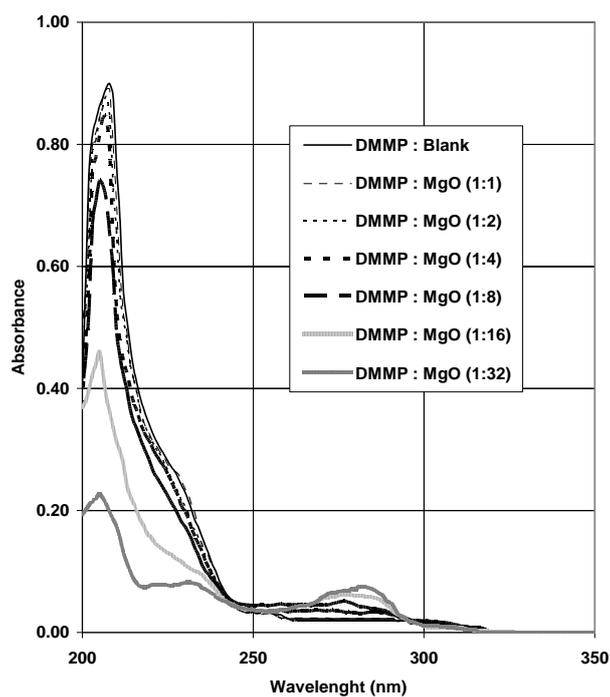
Fig. 3 Absorption spectra for malathion in the presence of different ratios of (a) MM283, (b) NanoActive® Magnesium Oxide Plus, and (c) MS284



(a)



(b)



(c)

Fig. 4 Absorption spectra for DMMP in the presence of different ratios of (a) MM283, (b) NanoActive® Magnesium Oxide Plus, and (c) MS284

It can be concluded that each spectrum divides into two sections: A) The UV adsorption in the range of 200-250 nm (corresponding to malathion or DMMP), and B) The UV adsorption above 250 nm (corresponding to destructed products of these stimulants).

Generally, with increasing the weights of MgO particles with respect to stimulants, higher amount of stimulants can be destroyed. According to Fig. 3a and 4a, MM283 could nowise destroy

malathion and DMMP simulants, in a sealed container, even with the weight ratio of 1:32. In contrast, as expected, in the case of NanoActive MgO nanoparticles, with the weight ratio of 1:8, large amount of stimulants were destroyed (Fig. 3b and 4b). With the increment of weight ratios (1:32), the simulants and destructed products were completely destroyed.

As shown in Fig. 3c and 4c, although very little degradation of stimulants was observed in the weight ratios of 1:1, 1:2, 1:4, and 1:8 of MS284, in the 1:16 and 1:32 weight ratios, the destroying of stimulants was accelerated and the degradation of destruction products was also observed. Also, The ability of MgO particles (synthesized and NanoActive) for the destruction of VX stimulant (malathion) was more than GB stimulant (DMMP). This observation can be related to the malathion and DMMP molecular structures. Malathion has greater polarity with respect to DMMP and, therefore, its adsorption rate to the MgO nanoparticles surface is higher (according to destruction mechanism).

In accordance with BET and SEM analyses, MgO particles prepared via a simple method in this work could show a good performance in the destruction of CWA stimulants in regard of high price NanoActive MgO nanoparticles.

4. Conclusions

The ability of MgO particles (synthesized, technical grade, and NanoActive) for the destruction of CWA stimulants was compared. BET results showed that SSA was 30.9641 m²/g and 166.8692 m²/g for MM283 and MS284 particles, respectively. The average size of MS284 particles was considerably smaller than that of MM283 powders. In fact, with a simple and low cost method, fine particles with high performance were synthesized. Summarily, synthesized MgO particles could destroy CWA stimulants as well as NanoActive® Magnesium Oxide Plus. nevertheless, to see the same results, higher amount of MS284 was needed. However, the economical aspects compensate the greater amount needed for complete destruction.

Acknowledgement

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