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Decontamination of 2-chloro ethyl ethyl sulphide and dimethyl methyl phosphonate from aqueous solutions using manganese oxide nanostructures

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ABSTRACT

Current study investigates the efficiency of reactive adsorbent composed of MnO_2 nanoparticles and nanorods for the detoxification of 2-chloro ethyl ethyl sulphide (CEES) and dimethyl methyl phosphonate (DMMP), well-known simulants of sulphur mustard and sarin, respectively. The MnO_2 nanoparticles and nanorods were synthesised using novel reactive magnetron sputtering technique and then characterised by powder XRD, Raman spectroscopy, FE-SEM, TEM, BET, FT-IR and Thermogravimetry (TG) analysis. Powder XRD and Raman results confirm the formation of pure tetragonal phase of MnO_2 nanostructure material. The FE-SEM and TEM analysis exhibited the formation of aggregate MnO_2 nanoparticles and nanorods. The surface area of the synthesised aggregate MnO_2 nanoparticles and nanorods (164.28 m^2/g) was found to be enhanced significantly in comparison with what was reported in the literature. Decontamination reactions of synthesised nanostructure material were examined by GC equipped with FID and the products obtained after reaction were analysed by GC–MS and FT-IR techniques. It was observed that the currently synthesised MnO_2 nanoparticles and nanorods exhibit much better decontamination results towards CEES as well as DMMP in comparison to or as per existing solid decontaminants. The reactions exhibited pseudo first order kinetic behaviour with rate constant and half life value 0.267 h^{-1} and 2.58 h for CEES and 0.068 h^{-1} and 10.10 h for DMMP, respectively. The data exhibits the formation of non-toxic hydrolysis products in the detoxification of CEES as well as DMMP.

1. Introduction

Reactive sorbent systems composed of inorganic oxide nanoparticles are currently under consideration as potential adsorbent materials for the detoxification of worldwide chemical warfare agents (CWA) and their well-known simulants. These materials possess interesting physisorption and chemisorption properties which encourage their use as reactive sorbents for the actual time decontamination of CWA [1–5]. Some reactive adsorbents composed of nanocrystalline oxides such as CaO, ZnO, Al_2O_3 and WO_3 were established as favourable materials for the decontamination of CWA [6–9]. They have greater reactivity towards CWA due to their higher surface area to volume ratio, large amount of highly reactive edges and corner defect sites, and unexpected lattice planes in comparison to bulk materials [10–12]. The reactions to decontaminate the CWA with the above stated materials were analysed using solid state MAS NMR and GC techniques at 25 °C temperature and observed that the reaction kinetics were fast in the initial phase and steady state at the later phase of the reaction with pseudo first order kinetic behaviour. These metal oxide nanostructures degrade the CWA through hydrolysis and elimination reactions [13]. Also, the catalytic reaction plays an important role in the CWA degradation [14–18]. Besides that, nanoparticles have a proclivity to aggregate, due to some of the existing reactive sites on the surface which are not available to the adsorbate molecules. However, other variants of these materials such as nanosheets, nanotubes or nanobelts combined to each other without losing their surface area and due to which encouraging accessibility to occur for sorbate molecules towards the surface active sites. This characteristic interaction in the aggregated nanotubes or nanobelt materials occurs to minimize the electrostatic and steric repulsion of remaining charges which exist on their surface.

Recently, TiO_2, $V_{1.02}O_{2.98}$, MnO_2 nanotubes and nanosheets and ZnO nanorods have been synthesised using different methods for the decontamination of deadly CWA such as HD, GB and their simulants [19–22]. Prasad and Ramacharlu et al. reported that the TiO_2 nanotubes were synthesised using sol–gel and hydrothermal process for the decontamination of HD and GB [23,24]. Of the above, titania nanotubes exhibit huge importance because of their effective decontamination properties towards photocatalytic, chemical biological warfare (CBW) agents and

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Table 1
Sputtering parameters for the synthesis of aggregates of MnO_2 nanoparticles and nanorods.

Target	Base pressure	Working pressure	Gas used	Deposition time	Distance (d)	Power (Watt)	Substrate temperature
Mn	$6.4 * 10^{-7}$ Torr	30 mTorr	$Ar:O_2::40:10$	18 h	5 Cm	60 W	− 194 °C

d = Distance between target and substrate.

were used in the detoxification of 2-chloro ethyl ethyl sulphide (CEES), a simulant of well-known sulphur mustard (HD) agent. Also, Prasad and Mahato et al. reported the detoxification of sarin (GB), HD and CEES over the surface of MnO_2 nanobelts and nanotubes, prepared using flocculation and exfoliation methods, respectively [25,26]. The detoxification of the above agents within the MnO_2 nanotube and nanobeltsurfaces occur through hydrolysis reactions. Moreover, these MnO_2 nanotubes and nanobelts displayed better decontamination properties in comparison to the TiO_2 nanotubes. Inspired by these results, we have synthesised MnO_2 in the form of aggregates composed of nanoparticles and nanorods (nanostructures) using reactive magnetron sputtering technique under highly controlled conditions and investigated their decontamination properties against CEES and dimethyl methyl phosphonate (DMMP). This novel technique provides some important advantages such as high purity, uniformity and reproducibility over chemical synthetic routes [27–30]. Recently, our group reported superior decontamination results of CEES and DMMP on the surface of magnetron sputtered CuO and WO_3 nanoparticles through hydrolysis reactions [5,9]. To the best of our knowledge, nobody has reported the synthesis of aggregates composed of MnO_2 nanostructures using magnetron sputtering technique and their use for the degradation of CWA or their simulants. Thereafter, characterisation was done using XRD, FE-SEM, TGA, TEM, and N_2-BET, then the progress of reactions was examined by a gas chromatograph and the degradation products were confirmed by GC equipped with MS and FT-IR analysis.

Sulphur mustard and sarin are highly toxic CWA, and are not proposed in the research laboratory. Hence, CEES and DMMP which are less toxic and well-known simulants of sulphur mustard and sarin, respectively are widely used in the research. Therefore, in the current study, we present the synthesis of aggregate MnO_2 nanostructures and their use as a reactive adsorbent for the adsorptive removal kinetics of these simulants i.e. CEES and DMMP.

2. Experimental

2.1. Synthesis of reactive sorbent composed of MnO_2 nanoparticles and nanorods

The aggregates of MnO_2 nanostructures were synthesised using reactive magnetron sputtering technique in custom designed vacuum chamber (Excel Instrument, Mumbai). A turbo molecular pump and a rotatory pump were attached with the chamber to create the required high vacuum. Sputtering was carried out using high purity (99.98%) manganese target of 2 in. diameter and 5 mm thickness. Initially, the vacuum (lower than 10^{-7} Torr) was created in the chamber. The high purity argon and oxygen gases were introduced into the chamber during sputtering. The standard mass flow controller (MFC) and manometers were used to control and measure the flow of the gases respectively. During sputtering, the copper cold finger becomes cooled up to − 194 °C using Liq-N_2 and it was continuously filled up to make constant temperature. Lower temperature stopped the grain growth in the plane of the film on the substrate to produce nanostructure materials. Also, low temperature minimized the impurity due to diffusion of atoms from the substrate to the synthesised materials. During sputtering, Mn atoms reacted with O_2 atoms in the chamber during transit or on the substrate surface to form aggregates of MnO_2 nanostructures. After deposition, the samples were collected carefully at room temperature. The sputtering parameters for the preparation of MnO_2 nanostructures are listed in Table 1.

2.2. Characterisation

The crystallographic information of the synthesised aggregate MnO_2 nanostructures were investigated using X-ray Diffractometer (XRD), D8 advance, Bruker AXS Germany with Cu K_α radiation ($\lambda = 1.541$ Å). The measurements were conducted using a voltage of 40 kV, a current setting of 30 mA, scanning rate 1 s/step and step size 0.02° at room temperature in the range of 25–90°. Raman spectra were obtained on an inVia Raman analyser (Renishaw, United Kingdom) with 514 nm laser as an excitation wavelength. The surface morphology occurred using a field emission scanning electron microscope (FE-SEM), Zeiss Ultra Plus 55. Elemental composition of the synthesised MnO_2 nanostructures was measured with energy dispersive X-ray spectroscopy (EDS) attached to FE-SEM. The morphologies and structures of the synthesised MnO_2 were further examined by transmission electron microscope (TEM), selected area electron diffraction pattern (SAED) and high resolution transmission electron microscopy (HR-TEM), FEI TECNAI G^2, Nederland Company, operating at 200 k voltage. N_2 adsorption–desorption isotherm was collected at liquid nitrogen temperature (− 196 °C) using Autosorb 1C of Quantachrome analyzer, USA. Brunauer–Emmet–Teller (BET) and Barret–Joyner–Halenda (BJH) methods were used to determine the surface area and cumulative desorption pore volume, respectively. Thermogravimetry (TG) analysis was carried out on EXSTAR 6300, thermogravimetric analyzer in the flow of air with a heating rate of 10 °C/min up to 500 °C. The Chemito 8610n gas chromatograph (GC) equipped with flame ionization detector (FID) and BP5 column (30 m length and 0.5 mm inner diameter) was used to examine the reaction kinetics of CEES and DMMP. Whereas, HP Agilent gas chromatograph attached with mass spectrometer (5973 inert) was used to characterise the reaction products. The reaction products were also characterised using Fourier-transform infrared (FT-IR), spectroscopy, Nicolet NEXUS Aligent 1100 spectrometer in the frequency range of 4000–500 cm^{-1} using KBr pellets that contain the samples.

2.3. Reaction procedure

The reactions of CEES and DMMP with aggregate MnO_2 nanostructures were studied by treating 100 μl of dichloromethane (DCM)

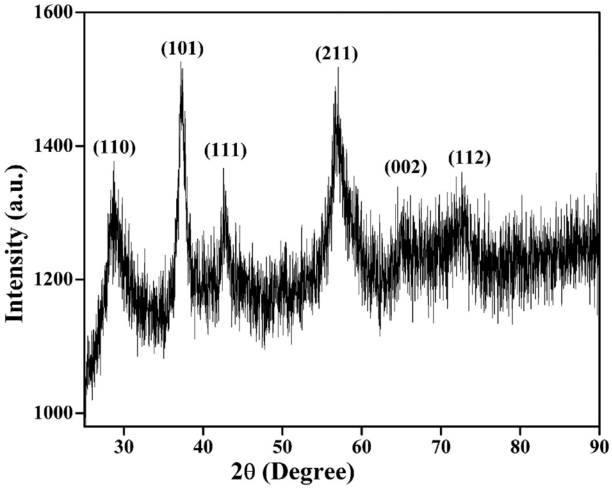

Fig. 1. Powder XRD pattern of reactive sorbent based on MnO_2 nanoparticles and nanorods.