Nanomaterials based decontaminants against chemical warfare agents

G K Prasad*, P V R K Ramacharyulu & Beer Singh
Defence Research & Development Establishment, Jhansi Road, Gwalior 474 002, India

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This review deals with history and recent technological advancements in the area of nanomaterials (NMs) and their application in decontamination of chemical warfare agents, which on contact create adverse health symptoms in humans. NMs based decontamination systems are an alternative approach to liquid decontamination media with promising decontamination properties against chemical warfare agents. High surface area and adequate reactivity towards chemical warfare detoxification are key assets of NMs intended for such applications.

Keywords: Chemical warfare agents, Decontamination, Nanomaterials

Introduction
Chemical warfare agent (CWA) contaminated environment causes serious health hazards to exposed human beings. Among CWA, vesicants act as blistering agents and attack skin and mucous membranes. Nerve agents attack central nervous system by reacting with enzyme acetylcholinesterase to cause respiratory collapse, convulsions and death. Blood and choking agents create symptoms like choking of breath, vomiting of blood, etc. These health hazards can be eluded by decontamination of surfaces or environment contaminated by CWA. 1-6

Bleaching powder and potassium permanganate were the first reactive chemical decontaminants employed against CWA. 6 N-chloro compounds (Chloramine-B, trichloroisocyanuric acid, sodium N, N-dichloroisocyanurate, chloramine-T) were found to be promising, but lack of stability hindered their wide spread application. 6 Thereafter, decontamination solution 2 (DS2) was unleashed to replace ineffective bleach solutions in colder climatic conditions. DS2 is a organic formulation that has been found useful against a variety of agents such as 2, 2’ dichloro diethyl sulphide (HD), Isopropyl methyl phosphonofluoridate (GB), O-Pinacolyl methyl phosphonofluoridate (GD), Ethyl N, N-dimethyl phosphoramidocyanidate (GA) and O-ethyl S-[2-(diisopropylamino)ethyl] methyl phosphonothioate (VX). Later, a number of oxidants containing peroxygen (m-chloro peroxy benzoic acid, magnesium monoperoxyphthalate, potassium persulfate, oxone, sodium perborate, sodium 2 nitro -5 iodoxybenzonate, o-iodosobenzoic acid, sodium hypochlorite) were examined as active components along with surfactants in microemulsions for CWA decontamination. 7-15 Formulations composed of hydrogen peroxide (H2O2) & molybdenum salts, peroxy bicarbonate based aqueous decontaminants, H2O2 aerosols have also been tested as reactive decontaminants for neutralization of CWA. 16-17 Certain disadvantages exist with the use of bleach based decontaminants and N-chloro decontaminants. Another option to liquid decontamination media is the use of nanomaterials (NMs) for decontamination of CWA. Due to large surface area, NMs have enhanced capacity to strongly adsorb CWA from affected surfaces and make them safe to operate. Once trapped in pores of sorbent, CWA undergo reactions facilitated by reactive sites integrated with NMs, which could neutralize hazardous properties. Although, metal oxide particles of silica, alumina, a-Fe2O3, MgO, La2O3 of larger size could convert toxic CWA into non toxic products, reactions are slow and major quantities of agents are found to remain in metal oxide matrix even after several hours of use. 18 Because of this, nano-sized metal oxides with enhanced sorption and reaction capacities towards CWA have been investigated.

*Author for correspondence
Tel: +91-751-2341960, Fax: +91-751-2341148
E-mail: gkprasad@lycos.com
Multitude of properties depends on particle size of materials. In spherical nanoparticles (NPs, ~3 nm size), 50% of atoms or ions are found on external surface indicating enhanced stoichiometric reaction chemistry towards adsorbates or CWA. In addition, number of surface, edge, corner, kink like defects increase with the decrease in size. Subsequently, electronic environment on surface also changes prompting surface chemistry to change. Also, NCs possess unusual lattice planes, which help in stereochemical reactions with CWA like dimethyl methyl phosphonate or sarin. Plane of nanocrystalline MgO (111) shows peculiar and interesting interaction with CWA that assist formation of surface bound non toxic phosphonates on their surface. Amounts of Lewis, Bronsted acid sites, residual or isolated hydroxyl (–OH) groups become more in number in NC materials, thereby promising better reactivity towards adsorbate CWA and hence work as destructive adsorbents or reactive adsorbents.

This review deals with history and recent technological advancements in the area of NMs and their application in decontamination of CWAs.

Properties that Facilitate Chemical Warfare Decontamination

Hydrolysis, elimination, nucleophilic substitution and oxidation reactions involving C-X or P-X bond or H-X (X=Cl, F and CN), -C-S- or -P-OR bond and surface complexation reactions assist decontamination of CWA. Decontamination efficiency, speed of decontamination, eco friendliness, equipment friendliness, versatility, (ability to decontaminate wide range of CWA) are some of the key requirements of a decontaminant.

In the case of sorbent decontaminants based on NMs, high reactivity and high surface area impart potential to neutralize CWA. Extremely porous solids or fine powders composed of NPs usually have high surface area and pore volume, which assist strong adsorption due to inherent large adsorption capacity towards CWA. Active sites become more in number in NMs relative to bulk materials and as and when size decreases for a material, surface chemistry changes. If NP is a cube with corners cleaved off, edge ions are 20% to total surface ions, whereas in larger hexagonal microcrystal, edge ions to surface ions are 0.5%. Thus there is higher portion of edge sites in NCs. Moreover, NC metal oxides exist with numerous surface sites and enhanced surface reactivity as crystal corners, edges, or ion vacancies, etc. High-resolution TEM imaging of a single crystalline MgO indicated presence of high concentration of edge/corner sites, more defects, and various exposed crystal planes on the surface. Defects could be of Frenkel or Schottky type vacancies also. The (111) plane of MgO is particularly reactive, trigonal symmetry of the (111) face particularly provide space for methyl phosphonic acid (MPA), which is also tridentate. Such sites that possess proper geometry to hydrolyze bound bidentate species [GB or GD or dimethyl methyl phosphonate (DMMP)] actually facilitate MPA formation.

Residual surface –OH sites also add to rich surface chemistry exhibited by metal oxides (MgO, CaO, SrO, BaO, Al₂O₃, TiO₂, Fe₂O₃, ZnO, etc.). It has been observed that 7-9 surface –OH groups are present on 1 nm² surface of a NC, however concentration of surface –OH groups decrease on heating. –OH groups on NCs (AP-MgO) are concentrated more on edge and corner sites and are more isolated, whereas on relatively larger particles, they are found to be on flat planes in closer proximity to each other. If surface –OH groups on NCs are situated on edge/corner sites, then it might be expected that Bronsted acidity would be lower since O₂⁻ would be of lower coordination and therefore have more basic character. The same was confirmed by chemisorption of benzene and xylene on Bronsted sites as evidence by shift of δO-H to lower frequency. Lewis acid sites also impart reactivity to surface of NC metal oxides. In the case of alumina, adsorption of pyridine showed that dominant mode of adsorption involves Lewis acidic surface Al³⁺ sites, an infra red (IR) band at 1450 cm⁻¹ due to the mode of ligated pyridine becoming a doublet after evacuation at 423K, suggesting that there are at least two types of Lewis acidic site on the surface. However, NMR studies showed two types of coordinated pyridine and indicated presence of octahedral and tetrahedral co-ordinatively unsaturated Al³⁺ sites.

In addition to Lewis acid sites, there have been reports on IR bands due to pyridinium ions resulting from Bronsted acidity of –OH groups on alumina, although this is exception rather than rule for relatively weak base pyridine, which most IR studies have shown is non protonated on alumina surfaces. In addition to alumina, NC metal oxides (MgO, Al₂O₃, CaO, BaO, SrO, Fe₂O₃, ZnO, TiO₂, etc.) exhibit unusual destructive chemisorption capability towards acid gases, polar organics, and CWA due to Lewis acid, Lewis base, and Bronsted acid sites of varying coordination (M³⁺), that is, metal cations, oxide anions. IR spectroscopy technique has been widely used...
to explore interaction and reaction mechanisms which facilitate decontamination of chemical warfare simulant (DMMP) with above sites. Templeton & Weinberg found that DMMP initially adsorbs at both Bronsted and Lewis acid sites through phosphoryl oxygen. At room temperature (RT), interaction at Bronsted acid sites resulted in molecular adsorption. Dissociative adsorption at Lewis acid sites led to formation of an adsorbed methyl methylyphosphonate (MMP). Second methoxy group is presumably converted into methanol either directly through reaction with a surface –OH group, or via a two-step process (Fig. 1) with a surface methoxy group as an intermediate.

IR spectra also indicate that initial interaction of DMMP with surface of AlO₃ clearly involves an interaction with –OH groups, since spectra show a loss in concentration of –OH groups, relative to oxide before DMMP adsorption. Frequency of –OH groups involved in initial binding indicates that they correspond to the most acidic protons, which are not hydrogen bonded. Interaction of DMMP with MgO surfaces using IR photoacoustic techniques indicated initial chemisorptions involved Lewis acid Mg surface sites binding to phosphoryl oxygen, similar to observations by Templeton and Weinberg with alumina. Kuipers et al. showed that nerve gas (sarin) closely related to DMMP, underwent initial molecular adsorption on AlO₃ at coordinately unsaturated Al sites followed by slow hydrolysis at RT. As temperature increases to 200°C, a clear loss of intensity is displayed by bands, which correspond to methoxy methyl groups. Intensities of methoxy group methyl stretching vibrations at 2956 cm⁻¹ and 2853 cm⁻¹, have decreased by 50% on heating to 200°C, while intensities of methyl modes associated with phosphorous bound methyl groups at 2996 cm⁻¹ and 2930 cm⁻¹ remain constant. This is consistent with loss of one methoxy group forming DMMP molecules and formation of surface bound MMP. Frequency of P=O adsorptions shift to lower side and is consistent with an interaction between phosphoryl oxygen and Lewis acid aluminium sites on the surface. As temperature increases, an Al-O bond is formed at 200°C with P=O bond breaking and taking on more single bond character, the frequency of P-O stretch adsorption decreases by 60 cm⁻¹, and finally band is observed at 1185 cm⁻¹, which can be associated with a surface bound MMP. However, under DMMP destruction on Fe₃O₄ surface, this surface oxidises P-CH₃ bond between 200-300°C under vacuum, whereas other three oxides could not accomplish this oxidation even upon heating to higher temperatures or adding oxygen. Complementary to the behavior of Fe₃O₄, DMMP decomposes on AlO₃, MgO, and La₂O₃ by nucleophilic displacement reaction. Surface –OH or oxide groups act as nucleophile and displace H₂CO-groups from DMMP molecules. Due to the availability of multiple oxidation states for iron atom, Fe(II) and Fe(III), iron oxide surface can act as an oxidation catalyst via Mars and Van Krevelen mechanism. Lattice oxygen from surface oxidizes adsorbed DMMP to form the products. Gas-phase oxygen is reduced at surface and replaces lattice oxygen. In this way, Fe₃O₄ surface provides a low energy path way, which is not available on AlO₃, MgO, and La₂O₃ surfaces. Although, there are chances that reactive sites on oxides could be poisoned by H₂O and CO₂ in air, conserved acid and base sites over oxides might act as reaction center for degradation of CWA molecules like HD. Degradation activity and product distribution are strongly determined by strength and density of acid-base sites and adsorbed water over oxides.

Reactions of CWAs and Decontamination Mechanisms on Nanosized Metal Oxides
Reactions of VX, GD, GB and HD with nanosized AP-MgO, AP-AlO₃ and AP-CaO

Wagner et al. have extensively studied decontamination reactions of VX, GD, GB and HD on the surface of aero gel produced MgO (Fig. 2), AlO₃ and CaO nano-sized oxide materials using solid-state MAS NMR. Elimination of HCl from sulphur mustard and hydrolysis ratio was observed on AP-MgO (50:50), AP-AlO₃ (17: 83) and AP-CaO (80:20); GD, GB and
VX were observed to simply hydrolyze on AP-MgO, AP-CaO and AP-Al₂O₃. Hydrolysis reactions observed for GD, VX, and HD are attributed to basic MgO or CaO or Al₂O₃ surface and are strictly analogous to the known solution chemistry of agents. For VX and GD, broad ³¹P NMR lines observed for their products are consistent with the formation of surface-bound magnesium phosphonates or calcium phosphonates or aluminium phosphonates. MgO, Al₂O₃ and CaO surfaces surely contain surface hydroxyl groups, as understood by IR spectroscopy.

In the case of HD, NMR studies indicated formation of thiodiglycol (TDG) along with magnesium alkoxide on the surface. HD on AP-MgO displayed same kinetic behavior as exhibited by GD and VX. Same behavior is observed for HD on wet or dried AP-CaO and wet CaO. AP-Al₂O₃, AP-MgO and AP-CaO exhibited promising RT reactivity for VX, GB, GD, and HD and can be used as decontaminants on battle field, where CWA deposited on personnel, equipment, vehicles, and perhaps even strategic locations could be quickly removed, adsorbed, and subsequently detoxified. Finally, these materials can consume large quantities of CWA and are promising for use in large-scale decontamination of CWA stockpiles.

Detoxification Reactions of Sulphur Mustard on Surface of Zinc Oxide Nanosized Rods

Prasad et al. explored decontamination properties of ZnO NMs against chemical warfare sulphur mustard. ZnO nanorods (size, 100-500 nm) have been used as materials for decontamination attributed to the presence of more number of reactive sites in ZnO nanorods when compared to bulk ZnO materials. Sulphur mustard molecules interact instantaneously with unreacted active sites of ZnO nanorods due to high reactivity of ZnO.
Typical IR absorption at 1222 cm\(^{-1}\), 905 cm\(^{-1}\) and 720 cm\(^{-1}\) indicated formation of surface complexes\(^{64}\). GC-MS data indicated formation of TDG, hemi sulphur mustard thus emphasizing role of hydrolysis reaction, and divinyl sulphide, vinyl chloro ethyl sulphide, and vinyl hydroxyl ethyl sulphide confirming the role of elimination reactions in decontamination of HD.

Sulphur mustard reacts with ZnO surface by elimination reaction and releases hydrochloric acid (HCl) and further yields divinyl sulphide, vinyl chloro ethyl sulphide and vinyl hydroxyl ethyl sulphide (Fig. 4). Released HCl may react with ZnO surface and can form minute amounts of zinc chloride species thereby poisoning active surface. X-ray diffraction data has confirmed formation of \(\text{Zn}_x(\text{OH})_y\text{Cl}_z\text{H}_2\text{O}\) on the surface of ZnO nanorods due to the reaction of HCl released while HD reacted with ZnO nanorod surface. Precisely, ZnO nanorods offer enough surface area and facilitate adsorption and encapsulation of HD molecules on reactive sites present on the surface, most probably surface hydroxyls will react with it rendering hazardous agent to non-toxic one. These results show that ZnO nanorods aggregates exhibit promising results on par with existing solid decontamination systems (nanosized MgO, Al\(_2\)O\(_3\), etc.) and further emphasize potentiality of ZnO nanorod for decontamination of CWAs.

**Fig. 3—Hydrolysis reactions of sulphur mustard occurring on the surface of ZnO nanorods**

**Fig. 4—Elimination and hydrolysis reactions of sulphur mustard occurring on the surface of ZnO nanorods**

**Fig. 5—Kinetics of decontamination reactions of sarin on ZnO nanomaterials and bulk ZnO**

Nanocrystalline ZnO for Decontamination of Sarin and DMMP

DMMP molecules bind with ZnO surface through P=O bond; gas phase P=O stretching frequency 1276 cm\(^{-1}\) red shifts to 1242 cm\(^{-1}\) when adsorbed on ZnO, subsequently to 1210 cm\(^{-1}\) when P=O bond interacts with hydroxyls present over the surface of metal oxides. Similar shift of phosphoryl frequency was reported\(^{47}\) for dimethyl phosphate due to interaction with ZnO.

Sarin decontamination reactions on the surface of ZnO nanosized particles have been studied by GC\(^{68}\). Rate constant of detoxification reaction of sarin on bulk ZnO was observed to be 0.1017 h\(^{-1}\) and half-life was estimated to be 6.81h (Fig. 5). However, nanocrystalline ZnO exhibited a rate constant of 4.12h\(^{-1}\) and half-life of 0.16h. Rate of decontamination reaction of sarin on the surface of ZnO NMs is higher than the rate observed on the surface of bulk materials, whereas half-life is smaller for NMs relative to bulk material. The data is consistent.
with reported data. Relatively, NMs exhibited better reactivity than bulk ZnO, attributed to the presence of more number of reactive sites in ZnO NC. FT-IR data revealed bands at 1255 cm\(^{-1}\) (P-O), 1020 cm\(^{-1}\) (C–O–P) and at 840 cm\(^{-1}\) (P–F), indicating hydrolysis of sarin. Surface hydroxyls present in ZnO NMs attack P–F bond and GB was converted to isopropyl methyl phosphonic acid (IMPA) and then it was converted to methyl phosphonic acid (MPA) in bound or free form (Fig. 6). Degradation of GB and accumulation of free MPA were experimentally detected. Rate of GB degradation was seemed to be higher than the rate of accumulation of free MPA. It means that degraded GB was collected as either IMPA or MPA. Accumulation rate of free MPA was limited by either transformation rate of IMPA into MPA or desorption rate of MPA. Final product MPA exists both in surface bound and free states as per IR and GC-MS data. Formed MPA seemed to bind with basic groups existing on ZnO.

NMs offer enough surface area and facilitate adsorption of sarin and then, surface hydroxyls and other basic reactive sites (edge defects, etc.), reacted with agent thereby rendering toxic agent to non-toxic product. Thus NMs of ZnO exhibited promising results on par with existing decontamination systems (nano-sized MgO, Al\(_2\)O\(_3\), etc.)\(^{54-66}\). Moreover, NMs of ZnO possess interesting photo-catalytic properties emphasizing their potentiality for photo-catalytic decontamination of persistent CWAs\(^{68}\).

Decontamination of Sulphur Mustard and Sarin on Titania Nanotubes (NTs)

NTs of metal oxides orient randomly to keep their charge, steric balances and pore connectivity intact, thereby providing large surface area and promising wider adsorption and decontamination related applications. TiO\(_2\) NTs were successfully used for decontamination of 2-chloroethyl ethyl sulphide (2-CEES), a well-known surrogate of deadly CWA HD\(^{69}\). Prasad et al\(^70\) studied reactions of HD and GB on TiO\(_2\) NTs in powder form. On TiO\(_2\) NTs, HD exhibited a rate constant of 0.1156 h\(^{-1}\) and half life of 5.99 h. On bulk TiO\(_2\), it exhibited a rate constant of 0.0214 h\(^{-1}\) and half life of 32.39 h. Rate of decontamination reaction of HD on surface of TiO\(_2\) NTs is higher than rate on the surface of bulk material, whereas, half life of the reaction is smaller for NTs relative to bulk material. Sarin also reacted in a similar fashion; rate of decontamination reaction was found to be 0.7536 h\(^{-1}\) and half life was 0.92 h and on bulk TiO\(_2\), rate of reaction is 0.0711 h\(^{-1}\) and half life of reaction is 9.75 h. HD decontamination reaction reaches a steady state in 24 hours on TiO\(_2\) NTs and on bulk TiO\(_2\) in 12 h. However, on TiO\(_2\) NTs 100% sarin was found to be decontaminated within 12 h and on bulk TiO\(_2\) steady state was found to reaching at around 24 h, attributed to surface area available on TiO\(_2\) NTs (271 m\(^2\)/g), which was noticeably higher than surface area of bulk TiO\(_2\) (40 m\(^2\)/g). Apparently, owing to the higher surface area, more amount of HD or sarin were adsorbed on the surface.
and reacted with relatively larger number of reactive sites available within TiO$_2$ NTs when compared with bulk material.

Data obtained for one of the products formed due to the reaction of HD with TiO$_2$ NTs, illustrated m/z values at 122, 104, 91, 75, 61 and 45, indicating formation of TDG and emphasizing role of hydrolysis reaction in decontamination of HD to TDG, thereby rendering it non-toxic. FT-IR studies on exposed samples revealed disappearance of band at 700 cm$^{-1}$ (C-Cl), change of peak pattern at around 1440 and 1295 cm$^{-1}$ (CH$_2$-Cl), and slight change in peak intensity at ~ 3352 cm$^{-1}$ (-O-H), further confirming hydrolysis of HD to TDG. Based on these observations, HD molecules react with TiO$_2$ NTs in two ways: i) HD molecules react with intercalated or physisorbed water molecules, which are present on the surface of NTs to form TDG (Scheme 1); and ii) HD molecules react with isolated hydroxyl groups (Ti-OH) and Lewis acid (Ti$^{4+}$) sites to form surface bound alkoxy species (Scheme 2). In the case of reaction of GB on TiO$_2$ NTs, GC-MS data indicated formation of IMPA. FT-IR data revealed that, bands at 1255 cm$^{-1}$ (P=O), 1020 cm$^{-1}$ (C-O-P) and at 840 cm$^{-1}$ (P-F) are typical of sarin disappeared, thus indicating hydrolysis of sarin.

According to GC-MS and IR data, reaction scheme reflecting decontamination of sarin on TiO$_2$ NTs is proposed (Scheme 2). Sarin molecules reacted with
physisorbed or intercalated water molecules to form non-toxic IMPA in one way and in other they reacted with isolated hydroxyl groups (Ti-OH) groups and Lewis acid (Ti$^{4+}$) sites to form surface bound phosphonates.

Occurrence of hydrolysis reactions on the surface of TiO$_2$ NTs and formation surface bound alkoxy species or surface bound phosphonates facilitated decontamination of sarin or HD and rendered them non-toxic. No excess water was added to TiO$_2$ NTs samples, whatever moisture present during synthesis along with other intrinsic materials seemed to have facilitated decontamination$^{70}$. NTs offer large surface area and facilitate faster adsorption and encapsulation of agents (sulphur mustard and sarin), and then intercalated water, isolated hydroxyl groups and Lewis acid sites reacted with agent, thereby rendering toxic agent to non-toxic$^{69}$. These results show that nanostructures of TiO$_2$ exhibit promising results on par with existing solid decontamination systems such as nanosized MgO, Al$_2$O$_3$, etc.$^{64-66}$.

Modified Titania Nanotubes for Decontamination of Sulphur Mustard

Certain metal ions (Cu$^{2+}$, Ce$^{3+}$, Mn$^{2+}$, Ag$^+$ and Hg$^{2+}$) were found to catalyze hydrolysis reactions of CWAs (sarin and HD) in aqueous solutions$^{71}$. Wagner reported catalytic hydrolysis of VX on Ag$^+$ exchanged zeolites$^{72}$. Value of rate constant of 0.1156 h$^{-1}$ and half life of 5.99 h were observed in case of original TiO$_2$ NTs at initial stage of the reaction. Rate constant and half life at initial stages of the reaction were found to be 0.0186 h$^{-1}$, 0.0760 h$^{-1}$, 0.049 h$^{-1}$, 0.179 h$^{-1}$, 0.0875 h$^{-1}$, 0.0621 h$^{-1}$, 0.179 h$^{-1}$ and 37.26 h, 9.12 h, 14.14 h, 3.87 h, 7.92 h, 11.16 h respectively for Ru$^{3+}$, Ni$^{2+}$, Cu$^{2+}$, Ag$^+$, Mn$^{2+}$, Co$^{2+}$ modified TiO$_2$ NTs. Rate constant of decontamination reaction of HD on the surface of Ag$^+$-TiO$_2$ NTs was found higher even than the rate exhibited by original NT sample. Whereas, half life of reaction was smaller, attributed to enhancement of reaction rate by Ag$^+$ on TiO$_2$ NTs with HD indicating catalysis by Ag$^+$. 

Scheme 3—Decontamination pathways of sulphur mustard on metal exchanged titania nanotubes
Based on these observations, HD molecules react with TiO$_2$ NTs in three ways: i) HD molecules react with intercalated or physisorbed water molecules, which are present on surface of nanotubes to form TDG; ii) HD molecules reacted with isolated hydroxyl groups (Ti–OH) and Lewis acid (Ti$^{4+}$) sites to form surface bound alkoxy species; and iii) either metal ion (that was present on ion exchanged NTs) could have abstracted chloride ion or oxidized sulphur atom of HD (Scheme 3). Moisture present at the time of synthesis along with other intrinsic materials seemed to have facilitated decontamination. Collectively, NTs offer large surface area and facilitate faster adsorption and encapsulation of agents, (sulphur mustard) and then, intercalated water, isolated hydroxyl groups and Lewis acid sites reacted with agent, thereby rendering toxic agent to non-toxic. In addition to these, metal ions that were exchanged with surface of TiO$_2$ NTs such as Ag$^+$ facilitated accelerated catalytic hydrolysis of HD by abstraction of chloride ion. Other materials (Cu$^{2+}$, Ru$^{3+}$, Co$^{2+}$, Mn$^{2+}$, Ni$^{2+}$- TiO$_2$ NTs) exhibited lower values of rate constants than even original TiO$_2$ NTs indicating negligible role in abstraction of chloride ion. These results show that Ag$^{+}$- TiO$_2$ NTs exhibited promising results on par with existing solid decontamination systems such as nanosized MgO, Al$_2$O$_3$, etc., and original untreated NTs.$^{64-66}$.

**Reactions of Sulphur Mustard and Sarin on V$_{1.02}$O$_{2.98}$ Nanotubes**

Vanadia NTs$^{74}$ also possesses superior decontamination properties against CWA. Rate constant and half life were calculated to be 0.11$h^{-1}$ and 6.30$h$. For GB, rate constant of decontamination reaction was found to be 0.1$h^{-1}$ and half life was 6.93$h$, indicating reactivity of V$_{1.02}$O$_{2.98}$ NTs towards HD or GB with first order behaviour. Thus HD molecules react with V$_{1.02}$O$_{2.98}$ NTs in three ways: i) HD molecules react with intercalated or physisorbed water molecules, which are present on the surface of NTs to form TDG; ii) HD molecules react in the presence of oxygen with V$^{4+}$ sites to form sulphoxide of HD; and iii) HD molecules react with V-OH (surface hydroxyls), V$^{4+}$ groups (Lewis acid) to form surface alkoxy species (Scheme 4).

Reaction products were extracted from GB exposed V$_{1.02}$O$_{2.98}$ NTs with methanol and were silylated by bis (trimethylsilyl) trifluoro acetamide and analyzed by GC–MS. The data indicated formation of IMPA ($m/z$ at 195, 169, 153, 75). FT-IR data revealed that bands at
1255 cm\(^{-1}\) (P– O), 1020 cm\(^{-1}\) (C-O-P) and at 840 cm\(^{-1}\) (P-F) are typical of GB disappeared thus indicating hydrolysis. Based on GC–MS and IR data, reaction scheme reflecting decontamination of GB on V\(_{1.02}O_{2.98}\) NTs is proposed (Scheme 4).

GB molecules reacted with physisorbed or intercalated water molecules to form non-toxic IMPA in one way and in other they reacted with isolated hydroxyl groups (V—OH) groups and Lewis acid (V\(^{4+}\)) sites to form surface bound phosphonates. Occurrence of hydrolysis reactions on the surface of V\(_{1.02}O_{2.98}\) NTs and formation of surface bound alkoxy species or surface bound phosphonates facilitated decontamination of GB or HD and rendered them non-toxic. Based on these results, Scheme 4 proposed by these authors shows the reaction mechanism for decontamination of GB on V\(_{1.02}O_{2.98}\) NTs. These observations are consistent with reported data 76.

Mesoporous Manganese Oxide Nanobelts for Decontamination of Sarin, Sulphur Mustard and Chloro Ethyl Ethyl Sulphide (CEES)

Functional mesoporous manganese oxide nanobelts demonstrate intriguing adsorption and reactive properties against environmental pollutants. It is exemplified by outcome of reactions of chemical warfare (sarin, sulphur mustard and sarin) and then, intercalated water and V\(^{4+}\) sites reacted with agent, thereby rendering toxic agent to non-toxic. These results show that nanostructures of V\(_{1.02}O_{2.98}\) exhibit promising oxidative and hydrolysis reaction on par with existing solid decontamination systems such as nanosized MgO, Al\(_2\)O\(_3\), etc 64-66.

Reactions were repeated several times in order to test reproducibility of kinetic behavior. Rate constant and half life, respectively, were found as follows: GB, 0.43 h\(^{-1}\) & 1.6 h; 2-CEES, 0.02 h\(^{-1}\) & 34.6 h; and HD, 0.01 h\(^{-1}\) & 69.32 h. In addition, 100% GB was found to be decontaminated within 7 h, where HD and CEES were not completely decontaminated. Faster decontamination reaction of GB has been attributed to rapid adsorption and distribution of liquid within the pores and its interaction with accessible reactive sites. High surface area available on adsorbent could have facilitated faster adsorption and enabled GB molecules to reach reactive acid base sites 50 at a faster rate and finally GB molecules get decontaminated. However, surface had become poisoned thus forming strongly bound products on the surface and as a result, spreading of liquid stopped. This observation was supported by high vapour pressure of GB (2.9 mm Hg), due to which rate of evaporation is high, resulting in GB diffuse very fast to fresh reactive sites and was found to get decontaminated at a faster rate with nanobelts. Whereas, HD has very low vapour pressure (0.07 mm Hg), resulting reactions relatively slow. On the contrary, 2-CEES with high vapour pressure (3.4 mm Hg) could not exhibit faster reaction rates, may be poisoning of active sites due to release of HCl and results are consistent with reported data 64.

Phosphonic acid, expected degradation product of GB, is difficult to be analyzed by GC-MS, and hence extracted by acidic methanol and silylated by Bis (trimethylsilyl) trifluoro acetamide and then analyzed. The data indicated formation of silylated hydrolysis products, MPA (m/z at 240, 225, 195, 147, 133, and 73). In addition, FT-IR data revealed that bands at 1255 cm\(^{-1}\) (P=O), 1020 cm\(^{-1}\) (C-O-P) and at 840 cm\(^{-1}\) (P-F) are typical of GB disappeared, thus indicating hydrolysis. According to GC-MS and IR data, reaction scheme reflecting decontamination of GB on manganese oxide nanobelts is proposed (Scheme 5). Thus, GB molecules reacted with physisorbed or intercalated water molecules to form non toxic MPA in one way and in other they reacted with isolated hydroxyl groups (Mn-OH) and Lewis acid (Mn\(^{4+}\)) sites to form surface bound phosphonates. These observations are consistent with reported data 76.

Formation of TDG (m/z at 122, 104, 91, 75, 61 and 45) and HEES (m/z at 106, 75, 61, 47 and 29) emphasized role of hydrolysis reaction in decontamination
of HD to TDG and 2-CEES to HEES, thereby rendering
them to non-toxic products. FT-IR on exposed samples
revealed reduced band intensity at 700 cm\(^{-1}\) (C-Cl),
change of peak pattern at 1440 and 1295 cm\(^{-1}\) (CH\(_2\)-Cl),
and slight change in peak intensity at \(~ 3352\) cm\(^{-1}\) (-O-H),
confirming hydrolysis of HD and 2-CEES. Thus, HD or
CEES molecules reacted with MnO\(_2\) nanobelts in two ways:
i) they reacted with intercalated or physisorbed water molecules,
which were present on the surface of nanobelts to form thiodiglycol
or HEES; and ii) HD or 2-CEES molecules reacted with
isolated hydroxyl groups (Mn-OH) and Lewis acid
(Mn\(^{4+}\)) sites to form surface bound alkoxy species\(^{77-79}\).

Occurrence of hydrolysis reactions on the surface
of manganese oxide nanobelts and formation of surface
bound phosphonates or surface bound alkoxy species
facilitated decontamination of GB, HD and 2-CEES
and rendered them non-toxic (Scheme 6). Manganese oxide
nanobelts offer large surface area and facilitate faster
adsorption and encapsulation of GB, HD and 2-CEES
and then, intercalated water, isolated hydroxyl groups
and Lewis acid sites reacted with toxic agents, thereby
rendering them non-toxic. On comparing current results
of decontamination reactions of GB, HD and 2-CEES
on manganese oxide nanobelts, with those prepared
and studied earlier with 2-CEES, HD and GB on mesoporous
aggregates, showed that in the case of 2-CEES and HD,
mesoporous aggregates (rate constants, 0.02 h\(^{-1}\) and
0.01h\(^{-1}\)) exhibited better reactivities than present nanobelts
(rate constants, 0.148 h\(^{-1}\) and 0.076 h\(^{-1}\)). Whereas, in the
case of GB, presently synthesized nanobelts exhibited
better reaction rate (rate constant 0.43 h\(^{-1}\)) than earlier
synthesized mesoporous aggregates (0.12 h\(^{-1}\)). These
results also showed that manganese oxide nanobelts
would exhibit promising results on par with existing solid
decontamination systems such as nanosized MgO, Al\(_2\)O\(_3\),
etc. and titania nanotubes\(^{64-66,69,70}\).

Al\(_2\)O\(_3\) Nanoparticles Impregnated with Polyoxometalates as
Reactive Sorbents for Removal of Sulphur Mustard

AP-Al\(_2\)O\(_3\) NPs were synthesized using sol-gel
(bottom-up wet chemical) method. Thereafter, these NPs
were impregnated with polyoxometalates (synthesized /
commercial) and other reactive chemicals. Adsorptive
removal followed pseudo first order reaction kinetics.
9-Molybdo-3-vanadophosphoric acid [MoVPA (V3)] and
dodeca tungstophosphoric acid (PTA) (10%, w/w)
impregnated AP-Al\(_2\)O\(_3\) NPs were found to be most
reactive among synthesized and commercial
polyoxometalates impregnated systems respectively.
Aluminium oxide NPs impregnated with MoVPA (V3)
degraded sulphur mustard via hydrolysis and elimination
reactions to hemimustard, thiodiglycol, 2-chloroethylvinyl
sulfide, 2-hydroxyethylvinyl sulfide and 1,4-oxathiane.
In addition, formation of HD-sulfoxide was also observed\(^{80}\).

Adsorption, Desorption and Thermal Oxidation of 2-CEES on
Nanocrystalline Zeolites

FTIR spectroscopy was used to investigate adsorption,
desorption and thermal oxidation of 2-CEES
on NC zeolites. NaZSM-5 was found more reactive
toward 2-CEES compared to silicate. Total 2-CEES
adsorption capacity increases as NC particle size
decreases, suggesting that adsorption occurs on external
surface as well as in internal pores of zeolite. Both zeolites
effectively adsorb 2-CEES, suggesting that 2-CEES
adsorption and subsequent thermal oxidation may be a
viable method for decontamination of mustard gas\(^{81}\).
Future Directions

Promising reactivity of NMs towards hazardous CWAs is a gift for hasty battle field decontamination of surfaces adversely affected with CWAs. Materials alike can also find applications in filtration systems, and building materials, thereby providing protection to occupants. Due to large surface area to volume ratio and enhanced reactivity, NMs can consume large quantities of CWAs, promising their use in decontamination of stockpiles or munitions. NMs can also be used as catalyst material in continuous reactors, which can be easily regenerated and can effectively neutralize CWA. It is also a direction to add stable reactive impregnants in optimum quantities on the surface of neutral nano-sized metal oxides and can be used for decontamination of surfaces with a speed of decontamination on par or better than liquid decontaminants. NMs can be employed on the surfaces either by spraying or as powders or as pellets to facilitate adsorptive removal of contaminants. Photo-responsive materials can be self assembled or coated on to the surfaces as paints on buildings, equipments, vehicles, armoured vehicles, etc., for incorporating surfaces the self decontamination or self cleaning capabilities.

References


