Decontamination of Sulfur Mustard and Sarin on Titania Nanotubes

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Decontamination reactions of sulfur mustard and sarin were studied on the surface of titania nanotubes and the data were compared with that of bulk titania. Before the reaction studies, titania nanotube samples were made by using hydrothermal method and were characterized by scanning electron microscopy, N_2 BET, X-ray diffractometry, and thermogravimetry. Soon after that, titania nanotube samples were exposed to sulfur mustard and sarin separately at room temperature (30°C) and the reactions were monitored by gas chromatography, whereas the reaction products were characterized by GC-MS. The data explore the role of hydrolysis reactions and surface reactions for the decontamination of both sulfur mustard and sarin. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 2957–2963, 2008

Keywords: decontamination, sulfur mustard, sarin, titania nanotubes, hydrothermal method

Introduction

Sulfur mustard and sarin are well-known chemical warfare (CW) agents. They have been abused since the time of world war I and II to incapacitate an enemy.[1] Sulfur mustard acts on DNA and mucous membranes, sarin acts on nervous functions and neurotransmitters thereby causing adverse health effects.[1] Decontamination of these warfare agents becomes a major challenge for the researchers and soldiers. Although several liquid decontamination formulations have been developed so far, there are inherent limitations of their application due to low solubility of the CW agents, toxicity, and corrosive properties. As an alternative, researchers have been using solid adsorbents such as Fuller's earth, XE-555, bleaching powder, and modified resins for the decontamination applications. Although these adsorbents remove the agents from contaminated surfaces physically, they do not neutralize or detoxify the agents even after several days due to lack of reactivity and hence warrant the development of more effective and reactive solid adsorbent materials for the decontamination applications.[2] Nanosized particles of MgO, Al_2O_3, and CaO are promising potential reactive sorbent materials owing to their high surface area, strong adsorbability, and potential reactivity toward chemical warfare agents. They remove the agent rapidly from the contaminated surfaces and degrade them in situ and render them nontoxic.[3–11] These nanosized particles have a tendency to get aggregated, thereby making the most of their surface inaccessible to the adsorbate molecules.[12] However, nanotubes of metal oxides orient typically and randomly to keep their charge, steric balances, and pore connectivity intact thereby providing large surface area and promising wider adsorption and decontamination related applications.[13–15]

Recently Ma et al.,[16] Kasuga et al.,[17,18] and Chen et al.[19] have prepared nanotubes of TiO_2, MnO_2, $Ca_3Nb_3O_{10}$, and $K_{4-x}H_xNb_6O_{17}$ by soft chemical and hydrothermal methods. Among them, TiO_2 nanotubes have got immense importance because of their exceptional photocatalytic and CW agent decontamination properties.[20] They have been successfully used in the decontamination of 2-chloro ethyl ethyl sulfide (CEES), a well-known surrogate of sulfur mustard.[21] These nanotubes were formed when the material was treated with dilute HCl after the hydrothermal treatment of titania and possess inner diameter of ~5 nm and outer diameter of

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~10 nm as per the TEM data.[18] Prasad et al.[22,23] have recently reported the decontamination of sulfur mustard and its surrogate CEES by manganese oxide nanostructures. He explained that, intrinsic active sites within the nanostructures participate in the hydrolysis reactions and decontaminate the above said warfare agents. However, there are no reports so far on the decontamination of sulfur mustard or sarin on the surface of titania nanotubes to assess their efficacy. In this report, we have evaluated the decontamination of sulfur mustard and sarin on the surface of titania nanotubes, which were synthesized and well characterized by XRD, SEM, N_2 BET, and TG.

Experimental

Materials

Titanium dioxide of anatase phase was obtained from Alfa Aeaser, UK. Sodium hydroxide, HCl, dichloromethane, methanol, chloroform, *N*-hexane, and acetonitrile were obtained from E. Merck India. Sulfur mustard (HD) and Sarin (of more than 99% purity) were obtained from synthetic chemistry division of our establishment (*Caution:* These agents are toxic, hence to be handled by trained personnel only).

Synthesis of reactive sorbent composed of titania nanotubes

Titania nanotube samples were synthesized by treating titania (anatase phase) with 10 M sodium hydroxide. After mixing the above materials along with 90 mL ultra pure water, the suspension was transferred into a Teflon lined autoclave and heated at 130 °C for 5 days. Later, the material was sonicated, washed with dilute hydrochloric acid, and filtered until the material becomes neutral (pH 7.0). Thereafter, the material was dried at 50°C for 3 h before the reaction studies.[18]

Characterization of titania nanotubes

XRD patterns were obtained in an X Pert Pro Diffractometer (Panalytical, Netherlands) using Cu Kα radiation. SEM measurements were done on a Philips instrument. N_2 BET measurements were done on Autosorb of Micrometrics, USA. Subsequently, thermograms were recorded on TGA-2950 (TA instruments, USA) and the Nucon 5765 gas chromatograph equipped with FID detector and BP5 column (30 m length, 0.5 mm i.d.) was used for monitoring the degradation kinetics of HD and sarin. Agilent GC-MS system (5973 Inert) was used for the characterization of reaction products.

Reaction and sorption procedures

The reaction of sulfur mustard or sarin on the surface of titania nanotubes in the powder form was studied by treating 100 μL of dichloromethane solution having 5 μL of HD or sarin with 200 mg of the titania nanotube samples. The remaining HD or sarin were extracted by acetonitrile at periodic interval of time until 24 h to study the kinetics of degradation. For each time interval, the residual HD or sarin were extracted using 5.0 mL of acetonitrile for five times to (each time 1 mL) ensure the complete extraction. Extracted solutions were quantitatively analyzed by gas chromatograph equipped with flame ionization detector under isothermal conditions at 110°C for HD and under a temperature programme from 50 to 150°C at a rate of 10°C/min for sarin. The injection port was kept at 220°C and the detector port was kept at 230°C. Above mentioned column was used for this analysis also.

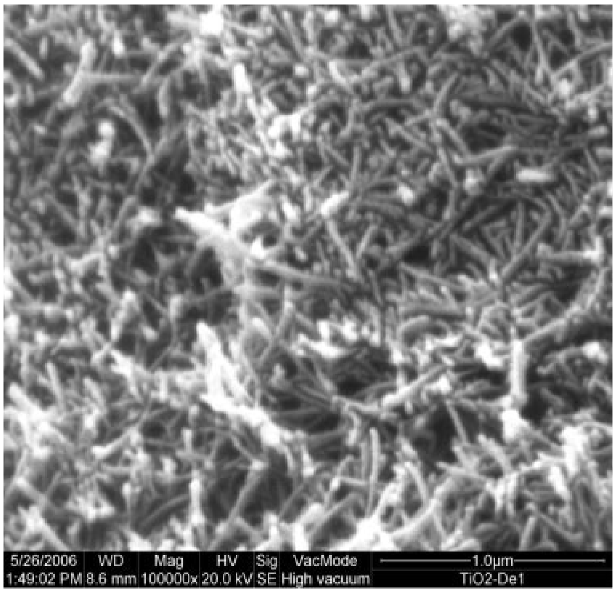


Figure 1. Scanning electron micrograph of titania nanotubes.

Results and Discussion

Before the reaction studies, the titania nanotubes were synthesized by hydrothermal method and characterized by scanning electron microscopy. Figure 1 shows the scanning electron micrograph of the aggregates of needle like titania nanomaterials (having dimensions <100 nm) with the porous structure. These materials are nothing but nanotubes and were seemed to orient randomly in irregular fashion to minimize the steric and electric charge repulsions generated within them thus yielding the porous structure and the same is consistent with previously reported results.[18] N_2 BET investigations on the titania nanotubes revealed the type IV adsorption isotherm with a hysterisis typical of mesoporosity as per IUPAC nomenclature and the same is illustrated in Figure 2a. Although bulk sized titania did not show any hysterisis in the adsorption isotherm, the pore size distribution of the same revealed the minute amount of mesopores with a pore maxima at ~3.5 nm and this can be attributed to the random aggregation of anatase particles thus yielding the mesoporous structure. Whereas the titania nanotubes exhibited the pore size distribution with the pore maxima at 5.0 nm (Figure 2b). The values of surface area and pore volume of titania nanotubes were found to be 271 m^2/g and 0.4 mL/g, where 40 m^2/g and 0.07 mL/g for bulk titania. This considerable amount of surface area in the case of nanotubes can be ascribed to their random orientation without losing the pore connectivity at their tips and smaller size. Later, obtained material was characterized by X-ray diffraction

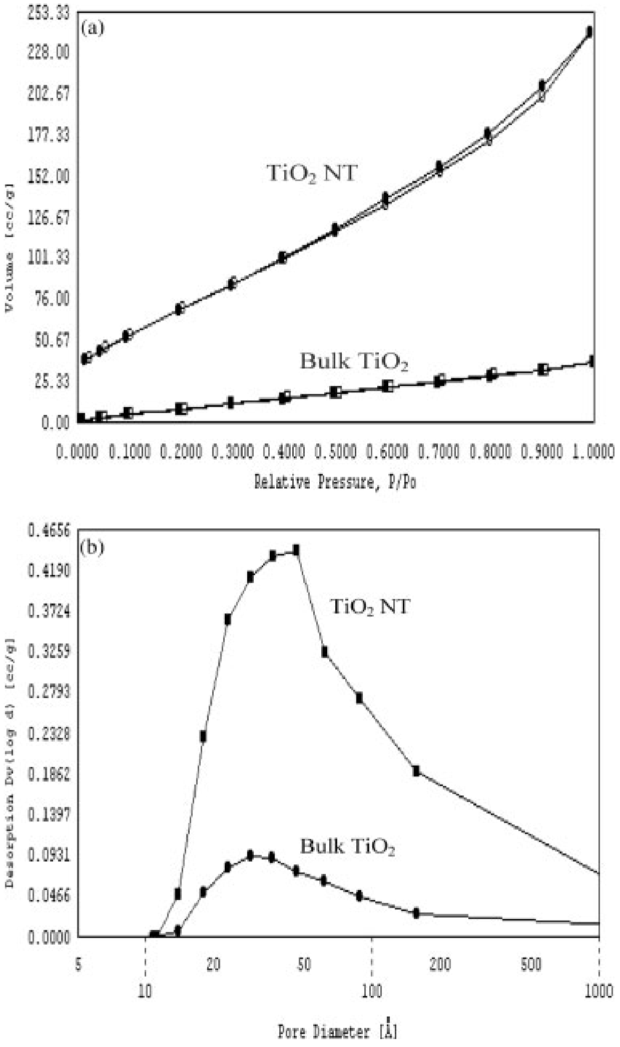


Figure 2. (a) Nitrogen adsorption isotherms of titania nanotubes and bulk titania; (b) pore size distributions of titania nanotubes and bulk titania.

technique and the data are shown in Figure 3. It shows broad peaks at 2θ of 9.5, 24.5, 28.4, and 48°, which correspond to 020, 110, 130, and 200 reflections of lepidocrocite titanate phase and the peak at 9.5° illustrate a d-spacing of 0.93 nm. The data were compared with that of the bulk titania and it exhibited anatase like XRD pattern. Formation of nanotubes can be attributed to the ion exchange process, perhaps, due to the hydrothermal treatment of titania with NaOH, certain Ti—O—Ti bonds were broken and new Ti—O—Na/Ti—OH bonds were formed. Subsequently, on treatment with very dilute HCl solutions some of Na^+ ions were expected to be exchanged with H^+ ions, and at this stage the layered sheets were expected to scroll and form nanotubes to avoid electrostatic repulsions within the charges and to minimize the steric repulsions between the sheet edges.

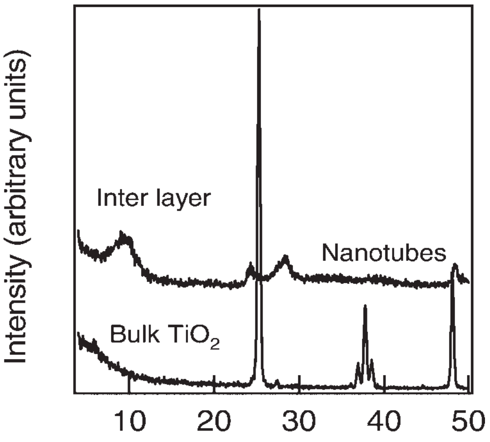


Figure 3. XRD data of titania nanotubes and bulk titania.

Thereafter, obtained mesoporous adsorbent composed of titania nanotubes in powder form was exposed to dichloromethane solution of sulfur mustard or sarin to study the reactions with them at room temperature (30°C) and the data were compared with that of the bulk titania. As per GC data, sulfur mustard was eluted at 3.2 min (at isothermal conditions) and sarin eluted at 3.32 min under temperature program and all the reaction mixtures extracted from the HD or sarin exposed titania nanotubes or bulk titania at kinetic intervals of time were quantitatively analyzed by calibrating the concentrations. Subsequently, obtained kinetic data were plotted by taking log $(a - x)$ ($(a - x)$ is HD/sarin concentration at time t h) on Y-axis and time on X-axis and the graph showing the kinetics of decontamination reaction of HD is depicted in Figure 4. The figure depicts the linear curve with fast initial reaction and a steady state at later stages of the reaction with a rate constant of 0.1156 h^{-1} and half life of 5.99 h thus indicating the pseudo first order behavior of decontamination reaction of HD on TiO_2 nanotubes.[24–26] Whereas, bulk TiO_2 exhibited a rate constant of 0.0214 h^{-1} and half life of 32.39 h. The rate of decontamination reaction of HD on the surface of titania nanotubes is higher than the rate on the surface of bulk material, where half life of the reaction is smaller for nanotubes relative to bulk material.

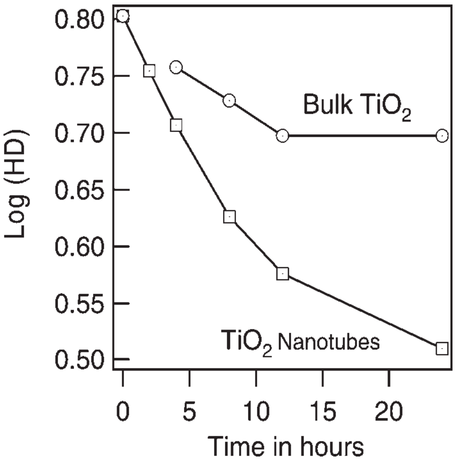


Figure 4. Kinetics of degradation reaction of sulfur mustard on titania nanotubes and bulk titania.

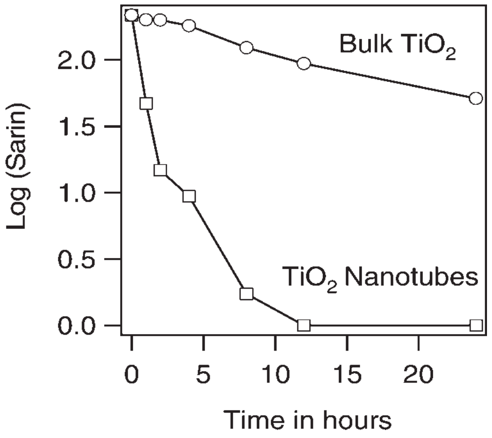


Figure 5. Kinetics of degradation reaction of sarin on titania nanotubes and bulk titania.

Sarin also reacted in a similar fashion, the rate of decontamination reaction (Figure 5) was found to be 0.7536 h^{-1} and half life was found to be 0.92 h and on bulk titania the rate of reaction is 0.0711 h^{-1} and half life of reaction is 9.75 h (Figure 5). The fast initial reaction can be ascribed to the rapid adsorption and distribution of the liquid within the pores and its interaction with the accessible reactive sites. The limited surface reaction occurs when the sites are exhausted, obviously, replacing the initial fast reaction by a steady state reaction. The HD decontamination reaction reaches a steady state in 24 h on titania nanotubes and on bulk titania in 12 h. However, on titania nanotubes 100% sarin was found to be decontaminated within 12 h and on bulk titania steady state was found to reaching at around 24 h. In addition to these studies, we have also conducted some sorption experiments to understand the sorption efficacy of nanotubes and bulk titania toward HD and sarin by dispersing the nanotubes in hexane solutions and following the concentration of respective agents at kinetic intervals of time. We found that, within 6 h of time 82.7% of HD was observed to be adsorbed on titania nanotubes, where 91% was adsorbed in 25 h and on bulk titania only 1.9% HD was found to be adsorbed in 6 h of time and within 25 h 3% was adsorbed. However, 96.5% of sarin was found to be sorbed in 6 h and 100% sorption within 12 h and on bulk titania, only 0.84% sarin was found to be adsorbed even after 25 h. This observation can be attributed to two facts, one is the surface area available on nanotubes, that is, 271 m^2/g which was noticeably higher than the surface area of bulk TiO_2, that is, 40 m^2/g. Apparently, owing to the higher surface area, more amount of HD or sarin was adsorbed on the

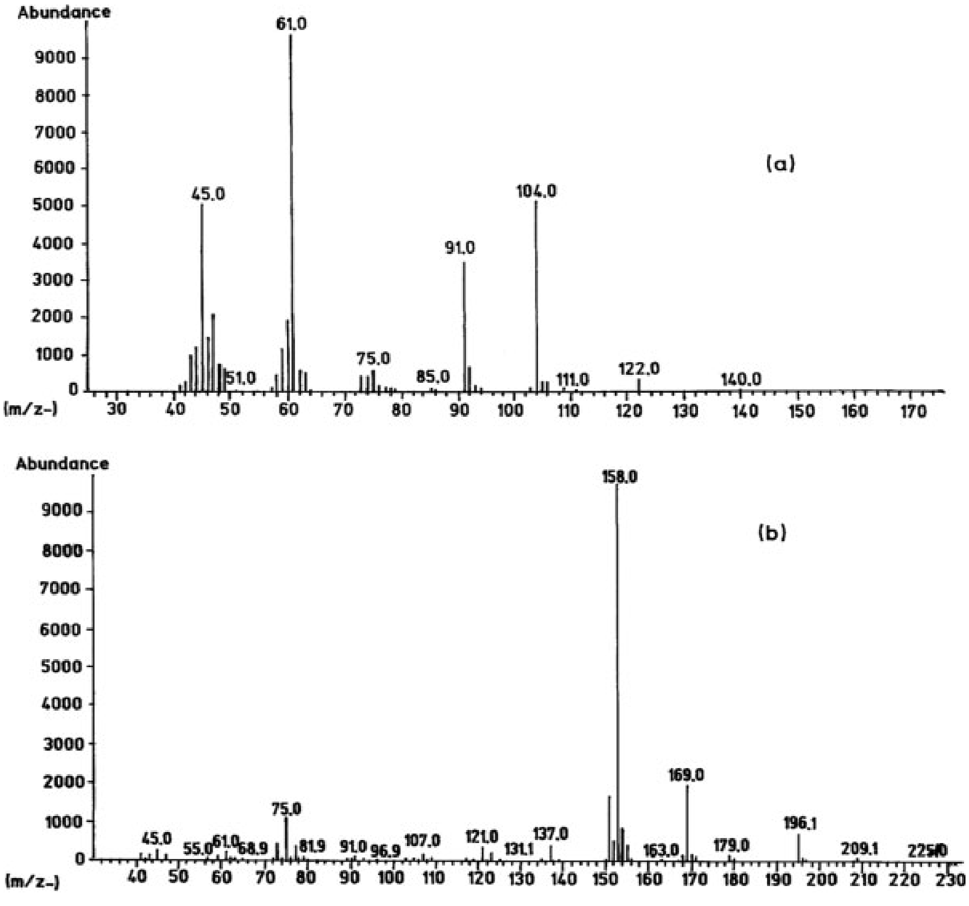


Figure 6. GC MS data of the products extracted from titania nanotubes exposed to HD and GB, (a) thiodiglycol and (b) silylated isopropyl methyl phosphonic acid.

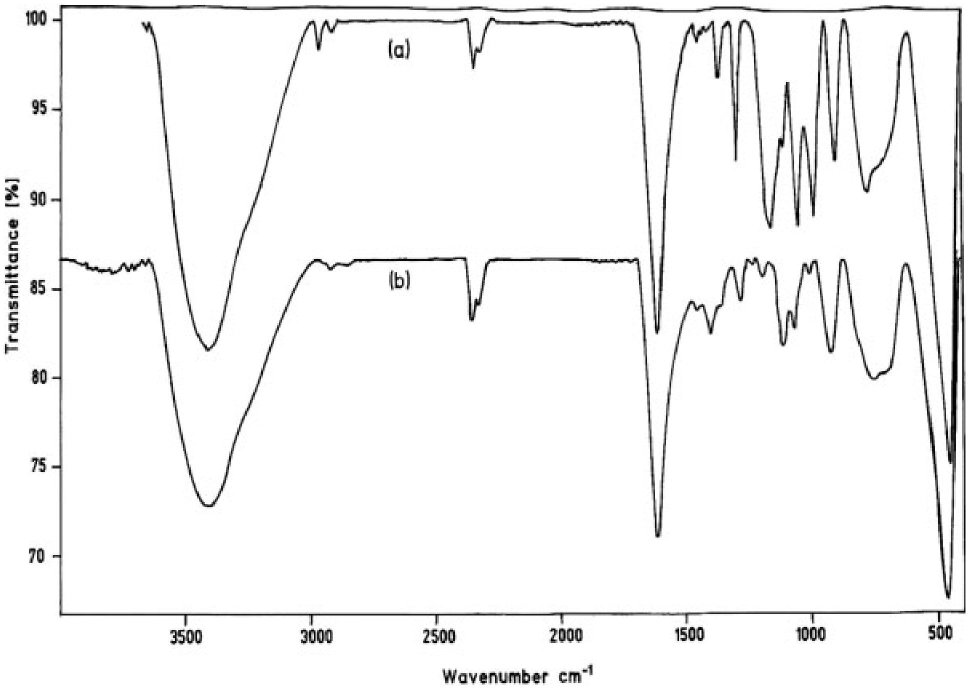
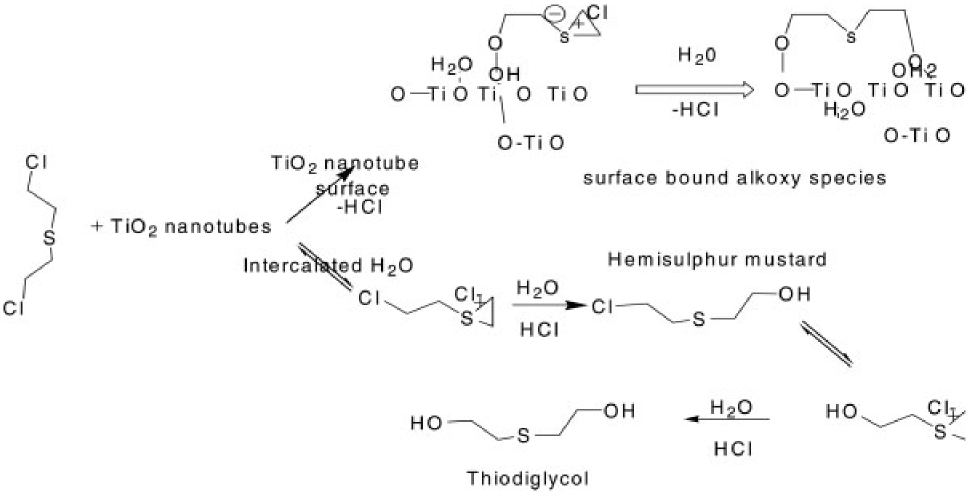


Figure 7. IR data of the titania nanotubes exposed to (a) HD and (b) GB.

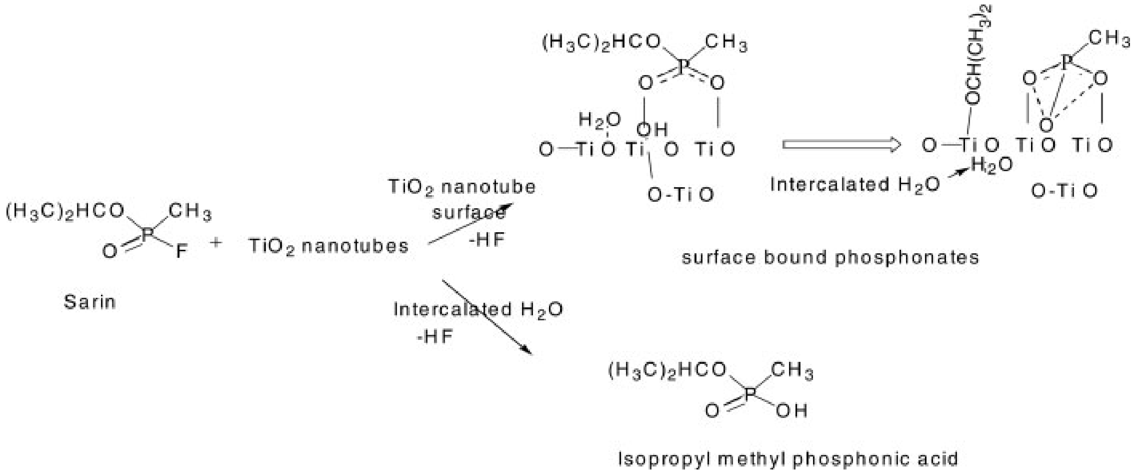
surface and reacted with the relatively larger number of reactive sites available within the nanotubes when compared with the bulk material. Moreover, the experiments were repeated several times to ensure the reproducibility of the kinetic data.

Thereafter, the reaction mixtures extracted from TiO_2 nanotubes and bulk TiO_2 (that areexposed to HD or sarin) were analyzed by GC-MS for the characterization of reaction products. The data were verified for product fragmentation patterns based on matches with the NIH data bases. Data obtained for one of the products formed due to the reaction of HD with titania nanotubes illustrate the m/*z* values at 122, 104, 91, 75, 61, and 45, thus indicating the formation of thiodiglycol (TDG) thus emphasizing the role of hydrolysis reaction in the decontamination of HD to TDG thereby rendering it nontoxic (Figure 6a). In addition to these, residual HD was also identified with the *m*/*z* values at 158, 109, 73, 63, and 45. Moreover, FTIR investigations on the exposed samples revealed the disappearance of band at 700 cm^{-1} (C—Cl), change of peak pattern at around 1440 and 1295 cm^{-1} (CH_2—Cl), slight change in peak intensity at ~3352 cm^{-1} (—O—H) further confirming the hydrolysis of HD to thiodiglycol (Figure 7a).

Based on these observations, a reaction scheme reflecting the decontamination of HD on TiO_2 nanotubes is proposed (Scheme 1). According to this, HD molecules react with TiO_2 nanotubes in two ways, in one way, they react with the



Scheme 1. Decontamination reactions of sulfur mustard.



Scheme 2. Decontamination reactions of sarin.

intercalated or physisorbed water molecules, which are present on the surface of nanotubes to form thiodiglycol. Initially, the cyclic sulfonium ion seemed to be formed which being in the form (non volatile) of salt could not be extracted out and detected by GC.[2,27] In another way, HD molecules react with isolated hydroxyl groups (Ti—OH) and Lewis acid (Ti^{+4}) sites to form surface bound alkoxy species.

Subsequently, reaction products were extracted from sarin exposed titania nanotubes with methanol and were silylated by Bis(trimethylsilyl) trifluoro acetamide and analyzed by GC-MS. The data indicated the formation of silylated hydrolysis product, that is, isopropyl methyl phosphonic acid (m/z values 195, 169, 153, and 75) (Figure 6b). In addition to this, FTIR data revealed that, bands at 1255 cm^{-1} (P=O), 1020 cm^{-1} (C—O—P), and at 840 cm^{-1} (P—F) those are typical of sarin disappeared thus indicating the hydrolysis of sarin (Figure 7b). According to GC-MS and IR data, the reaction scheme reflecting the decontamination of sarin on titania nanotubes is proposed in Scheme 2. As per this, sarin molecules reacted in similar fashion as mustard with nanotubes. They reacted with physisorbed or intercalated water molecules to form nontoxic isopropyl methyl phosphonic acid 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 titania nanotubes and formation surface bound alkoxy species or surface bound phosphonates facilitated the decontamination of sarin or HD and rendered them nontoxic. No excess water was added to the titania nanotube samples, whatever moisture present while the synthesis along with other intrinsic materials seemed to have facilitated the decontamination. To check the amount of water present on the surface of tiania nanotubes and bulk titania, they were subjected to TG analysis. It indicated that, nanotubes showed a weight loss of 18% after heated to 700°C. Where, the bulk TiO_2 exhibited a weight loss of 0.5% when heated up to 700°C which can be attributed to the intercalated water/physisorbed water. Collectively, the nanotubes offer large surface area and facilitate the faster adsorption and encapsulation of the agents, that is, sulfur mustard and sarin and then, the intercalated water, isolated hydroxyl groups and Lewis acid sites reacted with the agent thereby rendering the toxic agent to nontoxic. These results show that, the nanostructures of TiO_2 exhibit promising results on par with the existing solid decontamination systems, such as nanosized MgO, Al_2O_3, etc.[13–15]

Conclusion

Decontamination of sulfur mustard and sarin were studied on the surface of titania nanotubes. The decontamination reactions of these agents followed pseudo first order behavior on the nanotubes. Because of the availability of large surface area, intercalated water, surface hydroxyl groups, and Lewis acid groups titania nanotubes could efficiently decontaminate both the CW agents, sulfur mustard and sarin, thus forming the nontoxic products, thiodiglycol and isopropyl methyl phosphonic acid.

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