Removal of sulphur mustard, sarin and simulants on impregnated silica nanoparticles

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ABSTRACT

Silica nanoparticles of diameter, 24–75 nm and surface area, 875 m^2/g were synthesized using aerogel route. Thereafter, nanoparticles were impregnated with reactive chemicals, and used as reactive adsorbent to study the removal of toxic nerve and blister chemical warfare agents and their simulants from solutions. Trichloroisocyanuric acid impregnated silica nanoparticles showed the best performance and indicated physisorption followed by chemisorption/degradation of toxicants. This indicated their suitability as universal decontaminant for nerve and blister agents. This system showed a decrease in $t_{1/2}$ from 1210 to 2.8 min for the removal of king of chemical warfare agents, i.e., sulphur mustard. Hydrolysis, dehydrohalogenation and oxidation reactions were found to be the route of degradation of toxicants over impregnated silica nanoparticles.

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1. Introduction

In recent years, the scientific community has expressed great concern about the possibilities of use of toxic chemical warfare agents (CWAs) by terrorists and highly ambitious Nations. Thousand tons of CWAs exist with Nations, which have the production capabilities. Spills of these toxic chemicals can create extreme environmental hazards and must be effectively cleaned up and controlled. For that, investigations are underway to find safe and effective measures to detoxify CWAs without endangering the human life or the environment [1–19]. This can be achieved with the development of suitable real-time decontamination materials, which can perform in situ degradation (physisorption followed by chemisorption) of CWAs [1–5,7,8,11–13].

Recently, highly porous multifunctional metal oxide/hydroxide nanoparticles have received enormous interest because of their unique physical and chemical properties, and are in use as destructive adsorbent against CWAs [1–3,11,12,20]. Koper and Klabunde [3] have discussed the use of metal oxide nanoparticles as destructive adsorbents for biological and chemical contamination. Her preferred metal oxides include MgO, CaO, TiO$_2$, ZrO$_2$, FeO, V$_2$O$_3$, Mn$_2$O$_3$, Fe$_2$O$_3$, NiO, CuO, Al$_2$O$_3$, ZnO, and their mixtures thereof. Silica nanoparticles have been used for sensing of CWAs [21,22]. But these have never been used as such for the degradation of CWAs; this is because of the inert nature of silica.

Literature [1–3,11,12,15,16,20] suggest that single metal oxide nanoparticles show promising results, but these nano-adsorbents can further be modified for second generation nano-adsorbents by loading/impregnating with those reactive compounds [4–8,13,23], which have already been proven to be active against CWAs. Hydrated chloroisocyanuric acid salt has been used as active ingredient in the development of broad spectrum decontamination formulation against CWA [6]. Okun and Hill [9] have prepared the compositions of polyoxometalate/cationic silica material, copper salts and combinations thereof to decontaminate 2-chloroethylethyl sulphide (2-CEES). Moreover, scarcity of literature is available for loading of reactive chemicals on metal oxide nanoparticles, especially silica, to degrade CWAs. This attracts the attention to explore the opportunity. If reactive nanoparticles (alumina, magnesium or calcium oxide, etc.) have been impregnated with reactive chemicals, then the chances of cross reaction do exist and this may destroy the reactivity of both. Therefore, the use of inert and high surface silica nanoparticles as support to reactive chemicals will stabilize reactive chemicals over it, and could be the best way to remove and detoxify CWAs. Here, high surface area of silica can bring an increase in physisorption efficiency and loaded reactive chemicals can impart chemical degradation capability to the system. In our own efforts, we have first reported the use of impregnated silica nanoparticles against HD [bis-(2-chloroethyl)sulphide, sulphur mustard, a cytotoxic alkylating vesicant] and 2-CEES [7,8].

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Reactive adsorbents can degrade CWAs by variety of reactions such as oxidation, hydrolysis, elimination, addition and dealkylation [1,2,11]. Wagner et al. has investigated room temperature destruction of GB (isopropylmethylphosphonofluoridate, sarin) and HD on nanoparticles of magnesium oxide [1] and aluminum oxide [2] using solid state MAS-NMR (magic angle spin-nuclear magnetic resonance) technique. He has indicated half life of 6.3 and 17.8 h for the degradation of HD over Al_2O_3 and MgO respectively. Moreover, study indicated that the hydrolysis and dehydrohalogenation of these agents take place on the surface of metal oxide nanocrystals, and thereby, HD degraded to thiodiglycol, 2-chloroethylvinyl sulphide and divinyl sulphide.

Inspired by this, SiO_2 nanoparticles have been synthesized by aero-gel process [24] and subsequently characterized. Thereafter, to increase their reactivity and give them a permanent self-decontaminating feature, these have been impregnated with reactive chemicals using incipient wetness technique [5,7]. Trichloroisocyanuric acid (TCCUA), camphorylsulphonyl oxaziridine and ruthenium trichloride were taken as choice of impregnants because of their proven potential against CWAs [6,7]. Sodium hydroxide was also taken as impregnant due to its potential to hydrolyze nerve agents. Later, prepared systems were used to study the adsorptive removal kinetics of HD, 2-HEES [(2-hydroxyethyl)ethyl sulphide], 2-CEES, GB and DECIP (diethylchlorophosphate) from solutions [11]. The aim of the present study was to develop indigenous sorbent system, which can be used in decontamination devices and filtration systems with suitable modifications (converting impregnated nanoparticles to granules by mechanical compression technique) to remove and detoxify CWAs effectively in less time.

2. Experimental

2.1. Synthesis of SiO₂ nanoparticles

SiO_2 nanoparticles were synthesized using "bottom-up" wet chemical method (aero-gel process). For that 83.2 g of tetraethoxysilane was taken in a 1000-mL round-bottom flask having 500 mL of ethanol. To this 500 mL of toluene was added and the solution was stirred for 30 min under inert atmosphere of nitrogen gas. Thereafter, a solution of stoichiometric amount, i.e., 28.8 mL of triple distilled and deionized water in 240 mL of ethanol and 735 mL of toluene was prepared. This solution was slowly added to the solution prepared in first step with vigorous stirring in 3.0 L round-bottom flask. The solution was covered with aluminum foil and stirred for 24 h. This resulted in to opaque liquid like-gel.

600 mL of thus produced gel was transferred to 1000 mL capacity Parr autoclave. The gel in autoclave was flushed with nitrogen gas and pressurized to 100 psi. The reactor was slowly heated from room temperature to 265 °C at the rate of 1.0 °C/min and the time of heating was 4 h. The reactor was maintained at 265 °C for 10 min. During heating the pressure inside the autoclave increased to 800 psi. The system was quickly vented to the atmosphere for over a period of 1 min. The furnace was taken off and the produced powder was flushed with nitrogen gas for 15 min to remove the remaining solvent vapours. The autoclave was allowed to cool to room temperature over approximately 3 h. After that thus produced material was thermally treated. For that, 25 g of thus produced powder was placed in 500 mL capacity thermal reactor. This was evacuated for 30 min at room temperature. Later, it was slowly heated for 6 h from room temperature to 500 °C under dynamic vacuum of 10^{-2} Torr and kept under this condition for 10 h. Finally, the material was cooled to room temperature under vacuum, flushed with nitrogen gas and stored in air tight bottles till further use.
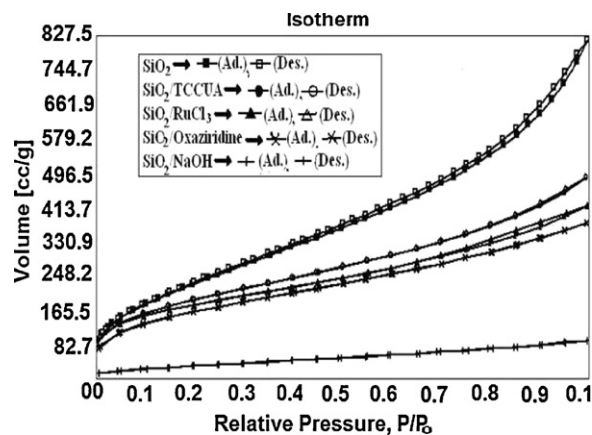

Fig. 1. Adsorption isotherms of SiO_2 with and without impregnants.

2.2. Loading of impregnants on SiO₂ nanoparticles

In order to prepare impregnated silica nanoparticles, first the impregnant (10%, w/w) was dissolved in aqueous or organic solvent (corresponding to incipient volume of silica nanoparticles, i.e., 10 mL/g). The solution of trichloroisocyanuric acid in acetone, camphorylsulphonyl oxaziridine in dichloromethane and the rest (ruthenium trichloride and sodium hydroxide) in water were prepared. Thereafter, silica nanoparticles were separately impregnated with impregnant solution using incipient wetness technique [5]. This technique allows the impregnant solution to just wet the adsorbent and get completely adsorbed on solid adsorbent. Thus prepared material was dried at 110 °C for 4 h, cooled in desiccators under dried calcium chloride, and finally stored in airtight bottles till further use.

2.3. Characterization of prepared SiO₂ nanoparticles based samples

Prior to use, silica nanoparticles with and without impregnants were characterized for porosity and surface characteristics using various techniques such as surface area analysis, scanning electron microscopy, transmission electron microscopy, etc. The material was also characterized for bulk density and moisture content (Table 1).

2.3.1. Surface area and porosity

Surface area and pore size distribution of SiO_2 with and without impregnants were determined using Autosorb-1-C from Quantachrome, USA. The samples were first outgassed under dynamic vacuum (10^{-2} Torr) for 8 h at 200 °C and then allowed to cool to room temperature. After that, the N_2 adsorption–desorption isotherms were obtained at liquid nitrogen temperature, i.e., 77 K. Surface area and micropore volume were determined using Brunauer–Emmett–Teller (BET) and Dubinin–Radushkevich (DR) methods respectively. Cumulative desorption pore volume was determined using Barrett–Joyner–Halenda (BJH) method. Pore maxima for micropores (<2 nm) and mesopores (2–50 nm) were determined considering BJH and DFT (density functional theory) methods. Surface area, micropore volume, cumulative desorption pore volume and pore maxima for micropores and mesopores have been given in Table 1. Figs. 1 and 2 represent the adsorption–desorption isotherms and BJH pore size distributions of prepared samples.

Table 1
Surface area, pore size distributions, bulk density and moisture content of prepared adsorbents.

| Adsorbent system	Surface area (N$_2$-BET) (m^2/g)	Micropore volume (N$_2$-DR) (cm^3/g)	Cumulative desorption pore volume (N$_2$-BJH) (cm^3/g)	Pore maxima for micropores and mesopores (Å)		Bulk density (g/mL)	Moisture content (%)
				Micro	Meso		
SiO$_2$	887.3	0.386	1.451	14.6	27.5	0.035	0.8
SiO$_2$ + TCCUA	682.9	0.302	0.839	15.1	24.5	0.048	1.9
SiO$_2$ + RuCl$_3$	625.1	0.282	0.679	14.9	27.2	0.052	2.8
SiO$_2$ + Oxaziridine	582.0	0.251	0.669	14.8	25.2	0.046	2.6
SiO$_2$ + NaOH	120.6	0.049	0.166	15.1	27.5	0.102	1.9
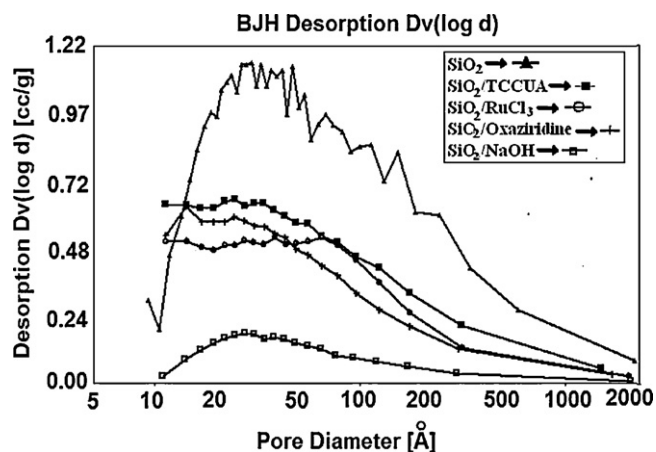
Fig. 2. BJH pore size distributions of SiO$_2$ with and without impregnants.
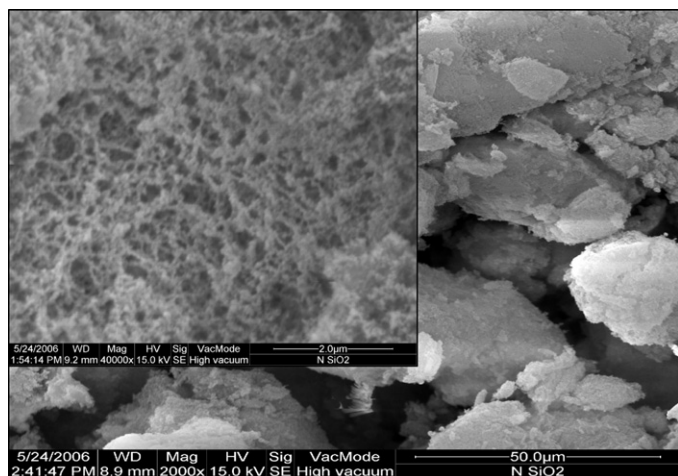

Fig. 3. SEM image of SiO$_2$.

2.3.2. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

For SEM characterization, powder samples were first mounted on brass stubs using double sided adhesive tape and then gold coated for 8 min using ion sputter (JEOL, JFC 1100 coating unit from Tokyo, Japan). The surface texture of silica nanoparticles was observed using FEI ESEM Quanta 400 from Hillsboro, Oregon, USA. Fig. 3 represents the SEM image of SiO$_2$. The image clearly indicated the web/net like structure of nanoparticle aggregates with a quantum of huge porosity, which is confirmed by its surface area value (887.3 m^2/g). TEM studies were performed to find out the particle size of the synthesized materials. For that 10 mg of sample was mixed in 10 mL of pentane and sonicated for 2 h to achieve a better separation of the particles. A drop of supernatant of the solution was placed on copper grid (200 mesh size) followed by

carbon coating. TEM images (Fig. 4) were recorded using JEOL, JEM-1200 Ex from Tokyo, Japan.

2.3.3. Bulk density and moisture content

Bulk density of prepared systems were measured by weighing a known volume (20 mL) of material and expressed in g/mL. The moisture content of the material was determined by heating a known amount (1 g) of sample in oven at 120 °C for 6 h, cooling in desiccators for 1 h and finally weighing. The weight loss in sample per 100 g was taken as moisture content of the material.
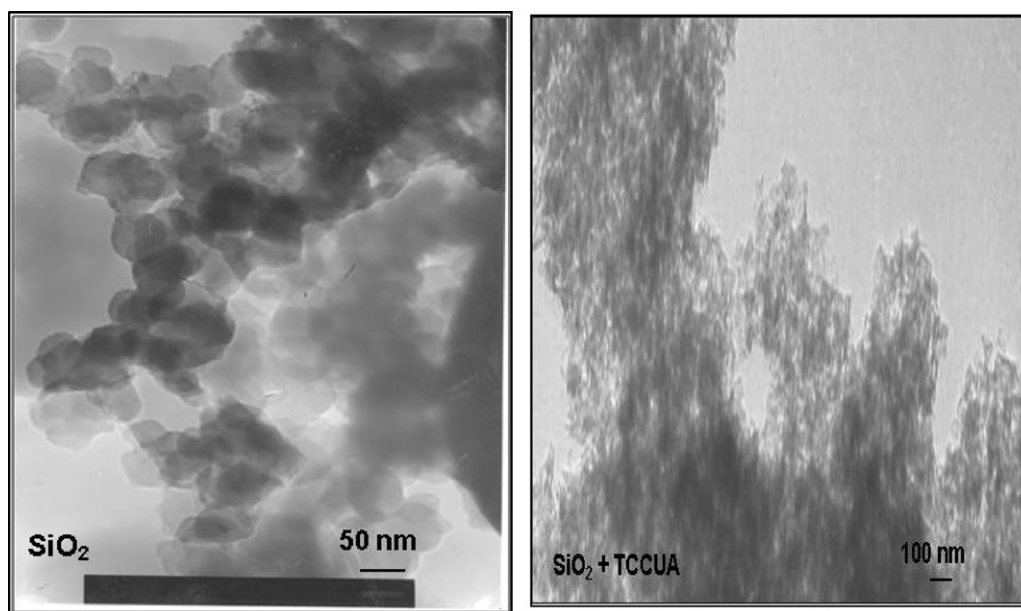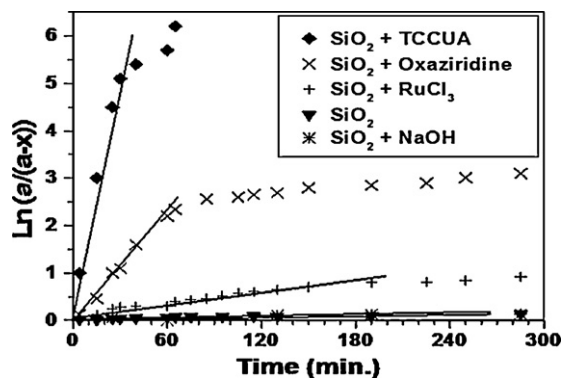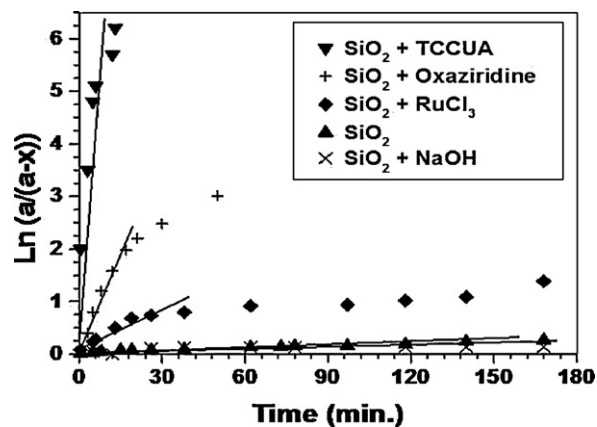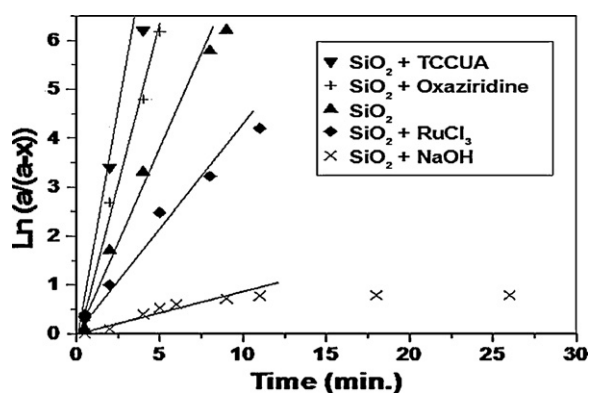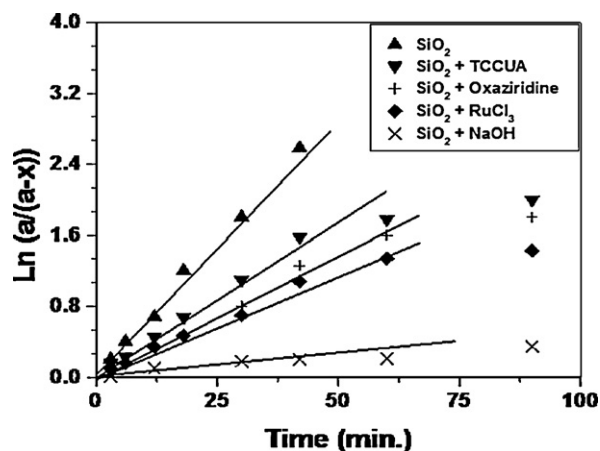
2.4. Kinetics of removal of toxicant

In order to study the kinetics of removal of toxicant, e.g., HD at room temperature (25 ± 1 °C), 2.5 μL of HD was mixed with 4 mL of octane in glass vials (8 mL capacity with Teflon septum caps). Octane was chosen as a solvent for the current work because; it does not react and dissolve the reactive impregnants. This decreases the possibility of leaching of reactive impregnant in octane solution. After that, 50 mg of prepared silica nanoparticles (with and without impregnation) was suspended to the solution and the vials were capped. Vials were rotated at the speed of 50 rpm continuously using Tarsons Rotospin. After definite time intervals, 1 μL of the solution was taken out from glass vials and analyzed for residual amount of toxicant using GC/FID (gas chromatograph coupled with flame ionization detector). The peak area of toxicant peak is compared with the peak area of toxicant peak of control solution, i.e., the solution with similar initial toxicant concentration and without nanoparticles based system. In order to study the kinetics of adsorptive removal, $\ln[a/(a-x)]$ [where, "a" is the initial amount and "$(a-x)$" is the remaining amount of toxicant at time, t] on Y-axis were plotted against reaction time, t on X-axis. Rate constant (K) was calculated using the slope of the straight line and half life ($t_{1/2}$) from 0.693/K. Figs. 5–9 represent the kinetics of removal of toxicants.

2.5. Identification of reaction products

Study on kinetics of adsorptive removal indicated that the toxicant molecules interact with the active sites of silica nanoparticles or impregnants over it and thereby converted into non-toxic reaction products. To study such reaction products, either these have to be investigated directly using the MAS-NMR technique [1,2] or by extracting them into an organic solvent and analyzing using GC/MS (gas chromatograph coupled with mass spectrometer) [6,17,18]. It is difficult to extract reaction products from metal oxide nanoparticles because; as the products are generated, they bind to active sites of the nanoparticles resulting in surface bound reaction products. In the present study, reaction products have been identified using GC/MS analysis of extracts.

In order to investigate the reaction products 10 mg of toxicant exposed nanoparticles were extracted with 2.0 mL of acetonitrile

Fig. 4. TEM image of SiO$_2$ and SiO$_2$ + TCCUA system.

Fig. 5. Kinetics of removal of HD on SiO$_2$ based systems.

Fig. 7. Kinetics of removal of 2-CEES on SiO$_2$ based systems.

Fig. 6. Kinetics of removal of 2-HEES on SiO$_2$ based systems.

Fig. 8. Kinetics of removal of GB on SiO$_2$ based systems.

for 2 h in a well stoppered test tube. Extracts were centrifuged, transferred to another tube, purged with nitrogen gas to concentrate the extracted reaction products and subjected to product identification using GC/MS. GC/MS (6890N GC coupled with 5973 inert MS detector) of Agilent Technologies, USA was used for characterization of reaction products. It was equipped with HP-5 MS column of 30 m × 0.25 mm × 0.25 μm dimensions. Temperature programming [50 (2 min hold) to 280 °C (10 min hold) @ 10 °C/min]

with split injection technique (10:1) was used to perform the study. Injection port and GC/MS interface, MS source and quadrupole analyzer were kept at 280, 230 and 150 °C respectively. The mass spectra of reaction products were compared with the standard
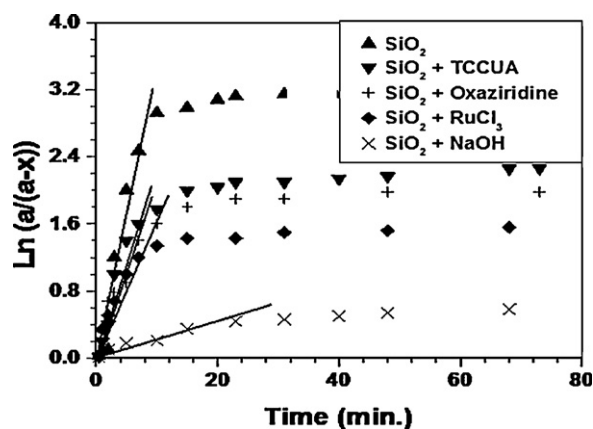
Fig. 9. Kinetics of removal of DECIP on SiO_2 based systems.

mass spectra from existing libraries (Wiley and NIST) in GC/MS instrument.

3. Results and discussion

3.1. Characterization of silica nanoparticles based adsorbents

Silica nanoparticles were synthesized using "bottom-up" wet chemical aero-gel process [7,8,19,24]. Silica nanoparticles showed the maximum uptake of nitrogen gas at liquid nitrogen temperature (-196°C), hence, maximum BET surface area (887.3 m^2/g). Silica nanoparticles exhibited hysteresis loop (Fig. 1), which is the characteristic of adsorption possessing a portion of mesopores. Mesopore maxima were found at 27.5 Å (Fig. 2 and Table 1). Apart from mesoporous characteristics, silica nanoparticles also indicated the presence of micropores with micropore maxima at 14.6 Å. Micropore and cumulative desorption pore volume of silica nanoparticles were found to be 0.386 and 1.451 cm^3/g respectively. When silica nanoparticles were impregnated with trichloroisocyanuric acid [10% (w/w)], surface area decreased from 887.3 to 682.9 m^2/g (Table 1). These decreases was due to impregnants, which during impregnation travel through the macro pores and get deposited in the mesopores or the pore openings of micropores, hence causes the blocking of mesopores and micropores [5]. After impregnation (10%, w/w), a decrease in surface area was found with all samples (Table 1). As expected, silica nanoparticles reacted with NaOH during impregnation and showed maximum reduction in surface area, i.e., from 887.3 to 120.6 m^2/g. All samples showed the similar type of pore size distributions with micropore and mesopore maxima at $\sim$15 and $\sim$25 Å respectively. Micropore (N_2-DR) and cumulative desorption pore volume (N_2-BJH) of silica nanoparticles were also found to be decreased after impregnation.

SEM image (Fig. 3) of silica nanoparticles indicated the web/net like structure of nanoparticle aggregates with a quantum of huge porosity confirmed by its surface area value (887.3 m^2/g). TEM image of silica nanoparticles (Fig. 4) indicated the particles in the size range of 24–75 nm (maximum in the size range of 30–40 nm), whereas XRD pattern indicated particle size of 12–24 nm. Bulk density of silica nanoparticles was found to be $\sim$1/16th (0.035 g/mL) of its counterpart, i.e., commercial silica (0.573 g/mL). For impregnated systems, it was found in the range of 0.046 (SiO_2 + oxaziridine) to 0.102 (SiO_2 + NaOH) g/mL. Moreover, all samples indicated the increase in bulk density after impregnation due to the reason that during impregnation impregnants sit in the mesopores of adsorbent, i.e., the weight increases, whereas the outer surface volume of the material remains same, hence density increases. A three fold increase (from 0.035 to 0.102 g/mL) in bulk density of SiO_2 + NaOH system also indicated the reaction of SiO_2

with NaOH, causing the destruction of pores and decrease in surface area values (Table 1). Moisture content of all prepared systems was found to be in the range of 0.8–2.8% (w/w).

3.2. Kinetics of reactive removal of CWAs

The kinetics of adsorption of CWAs from solutions was found to be following pseudo first order reaction kinetics. Kinetics was initially fast, which gradually slowed down to a steady state at later intervals of time [1,2,7,17]. This can be addressed by having an insight in the adsorption process. When, silica nanoparticles based system is added to the solution of CWA in octane, the physisorption starts, i.e., the CWA molecules approach to the physisorption sites and get physisorbed. Progressively the number of sites decreases due to physisorption of CWA. As a result, physisorption slows down and ends to a steady state.

Generally, physisorption of adsorbate on adsorbent is proportional to surface area of adsorbent, i.e., higher the surface area higher will be the adsorption potential. In order to investigate the same, silica nanoparticles with and without TCCUA/oxaziridine were exposed to HD/2-HEES/2-CEES contaminated octane solution. Results (Table 2) indicated that TCCUA/oxaziridine impregnated silica nanoparticles having lower surface area than unimpregnated silica (Table 1) show increased potential, and the rate constant increased sharply from 0.06×10^{-2} to 24.75×10^{-2} min^{-1} against HD (Table 2). The rate constant, K also increased from 0.63 to 1.38 and 0.002 to 0.693 min^{-1} for the removal 2-HEES and 2-CEES over SiO_2 + TCCUA system respectively. Increase in K values with TCCUA/oxaziridine impregnated silica indicated that either HD/2-HEES/2-CEES is strongly adsorbed (physisorbed or chemisorbed) or chemically degraded. TCCUA/oxaziridine impregnated silica systems with lesser surface area than silica alone should not lead to increased physisorption of HD/2-HEES/2-CEES. Therefore, the HD/2-HEES/2-CEES is either chemisorbed or degraded on TCCUA/oxaziridine impregnated silica nanoparticles. Table 2 also indicated lower values of K for the removal of HD/2-HEES/2-CEES using unimpregnated silica nanoparticles. This was due to its inert surface, which neither chemisorbs nor degrades the toxicant.

Again to address it, we added 2 mL of acetone (polar solvent) to the reaction mixture after kinetics study. The reaction mixture was stirred for 5 min and then subjected to GC/FID. For HD, extracted concentrations were found to be $\pm$5% of values obtained with kinetics of removal study (HD in octane). While in case of 2-HEES and 2-CEES around 80 and 55% of 2-HEES and 2-CEES came out off the systems respectively. This indicated that 2-HEES and 2-CEES are strongly physisorbed on prepared systems, whereas HD is chemisorbed/degraded. Moreover, the order of kinetics of removal based on physisorption was: 2-HEES > 2-CEES > HD. Overall, this indicated that, as the HD/2-HEES/2-CEES molecule is physisorbed on impregnated silica nanoparticles, it starts reacting with the active sites of the adsorbent or impregnant available on their surface. This leads to chemisorptions or destruction of HD/2-HEES/2-CEES, thus gives a self-decontaminating feature to it.

SiO_2 + RuCl$_3$ system showed third rank, whereas SiO_2 + NaOH system showed even less activity than unimpregnated SiO_2 for the removal of HD/2-CEES. This was due to the cross reaction of NaOH with SiO_2 occurred during impregnation. This results to least surface area and least adsorption potential. Overall, the order of reactivity against HD/2-CEES was: SiO_2 + TCCUA > SiO_2 + oxaziridine > SiO_2 + RuCl$_3$ > SiO_2 > SiO_2 + NaOH. Reactivity against 2-HEES was also found similar except for SiO_2, which showed better results than SiO_2 + RuCl$_3$ (Table 2). The suitability of SiO_2 + TCCUA system for decontamination of HD in absence of solvent was also explored by performing direct degradation study. Results indicated 100% degradation of HD

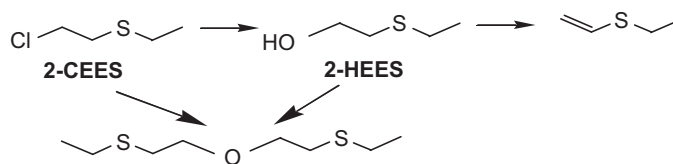**Table 2**
Kinetics parameters for the removal of toxicants.

Adsorbent system	HD		2-HEES		2-CEES		GB		DECIP	
	Half life (min)	Rate constant ($min^{-1}) \times 10^{-2}$	Half life (min)	Rate constant (min^{-1})	Half life (min)	Rate constant (min^{-1})	Half life (min)	Rate constant (min^{-1})	Half life (min)	Rate constant (min^{-1})
SiO_2	1210.0	0.06	1.1	0.63	302	0.0023	12	0.057	2.0	0.346
SiO_2 + TCCUA	2.8	24.75	0.5	1.38	1	0.6931	21	0.033	3.3	0.210
SiO_2 + $RuCl_3$	150.0	0.46	1.6	0.43	23	0.0301	30	0.023	4.5	0.154
SiO_2 + Oxaziridine	14.0	4.95	0.8	0.87	6	0.1155	26	0.026	3.8	0.182
SiO_2 + NaOH	1320.0	0.05	8.0	0.08	328	0.0021	130	0.005	31.0	0.022
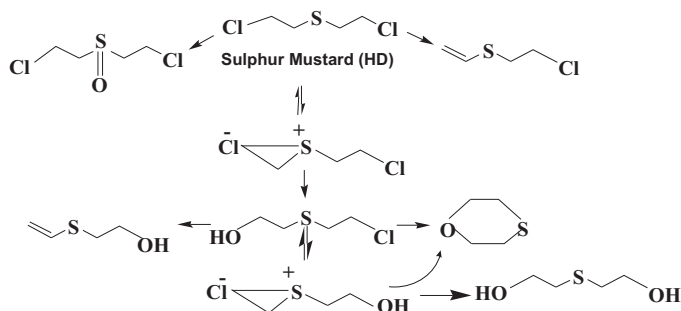
Scheme 1.

Scheme 2.

within 25 min. Our previous work has also indicated the suitability of SiO_2 + TCCUA system against HD and 2-CEES [7,8].

The suitability of silica nanoparticles based adsorbents was also investigated against nerve agent, GB and simulant, DECIP. Study indicated that unimpregnated silica nanoparticles showed the fastest kinetics (12 and 2 min as $t_{1/2}$ values against GB and DECIP respectively). Whereas NaOH impregnated system showed the slowest kinetics (Table 2). SiO_2 + TCCUA, SiO_2 + $RuCl_3$, and SiO_2 + oxaziridine systems did not show much difference in $t_{1/2}$ for GB and DECIP. The kinetics was more or less in accordance with surface area values, favouring physisorption. SiO_2 + NaOH system showed the slowest kinetics, but extraction with acetone indicated 100% degradation of GB and DECIP within 15 min. This was due to the presence of NaOH, which hydrolyze GB and DECIP. Moreover, with respect to extraction with acetone, the order of reactivity against GB/DECIP was: SiO_2 + NaOH > SiO_2 + TCCUA > SiO_2 + oxaziridine > SiO_2 + $RuCl_3$ > SiO_2. SiO_2 + TCCUA got the second rank for the removal of GB and DECIP, silica nanoparticles alone being the first.

Therefore, by considering; (i) unimpregnated silica nanoparticles physisorb CWAs, and does not degrade it, hence non-promising for the reactive removal, (ii) SiO_2 + NaOH system is reactive but has least physisorption capacity, (iii) SiO_2 + TCCUA system got first and second rank against HD/2-HEES/2-CEES and GB/DECIP respectively and (iv) SiO_2 + TCCUA system performs both functions, i.e., physisorption followed by chemisorption/degradation, it can be declared that SiO_2 + TCCUA system is associated with self-decontaminating feature and is the most promising among studied systems against CWAs.

3.3. Identification of reaction products

Reactive adsorbents can degrade CWAs by variety of reactions, such as oxidation, hydrolysis, elimination, addition and dealkylation [1,2,11]. Herein, we report that unimpregnated sil-
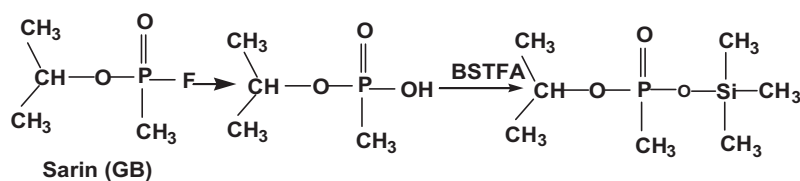
Scheme 3.
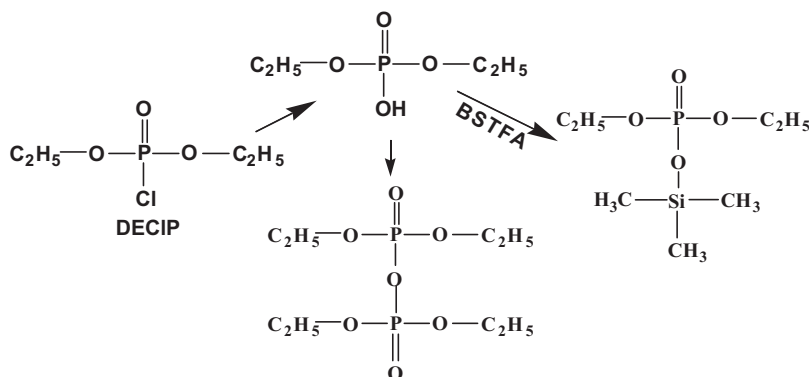
Scheme 4.

ica nanoparticles produce 2-chloroethylvinyl sulphide as the only reaction product of HD. Plausibly, TCCUA reacts with available water on the surface of silica nanoparticles to produce hypochlorous acid, which in turn favours the hydrolysis of CWAs. HD undergoes hydrolysis (Scheme 1) with the formation of intermediate sulphonium ion on SiO_2 + TCCUA system [7,8,17,18]. Sulphonium ion is formed due to the attack of sulphide on the β carbon atom of HD and is considered to be SN^1 reaction. Subsequently, the sulphonium ion undergoes hydrolysis with the water available with nanoparticles under study (no more water is added prior to the reaction), and produces hemimustard. Apart from hydrolysis, dehydrohalogenation reaction was also found to be occurring as a mode of degradation of HD [1,2,6–8,17]. Overall, hemimustard, chloroethylvinyl sulphide, 1,4-oxathiane and O-mustard were observed as reaction products of HD. In addition to that, oxaziridine and $RuCl_3$ impregnated silica nanoparticles indicated the formation of HD-sulfoxide [13,14].

All impregnated systems indicated ethylvinyl sulphide as a reaction product of 2-HEES (Scheme 2). 2-CEES indicated the formation of 2-HEES, ethylvinyl sulphide and bis[2-(ethylthio)ethyl] ether with all systems. The later is formed either via the combination of two 2-HEES molecules with removal of one water molecule or the combination of 2-CEES and 2-HEES (one molecule each) with the removal of HCl.

GB and DEClP indicated the formation of corresponding acids (Schemes 3 and 4) as hydrolysis product [2]. DEClP converted to diethylphosphate, which was detected as diethyltrimethylsilyl phosphate after silylation with BSTFA {N,O-bis-(trimethylsilyl)-trifluoroacetamide}. The formation of tetraethyl pyrophosphate was also observed as degradation product of DEClP. GB detoxified to its corresponding acid, i.e., isopropylmethylphosphonic acid, which was identified as isopropyltrimethylsilylmethylphosphonic acid after silylation with BSTFA.

4. Conclusions

24–75 nm silica nanoparticles were synthesized using aero-gel (bottom-up wet chemical) method. Silica nanoparticles indicated high surface area ($875 \, m^2/g$) and mesoporous characteristics with little microporosity. These were impregnated with reactive chemicals. The reactive removal studies with HD, 2-HEES, 2-CEES, DEClP and GB were found to be following pseudo first order reaction kinetics. SiO_2 + TCCUA system got first and second rank for the reactive removal of HD/2-HEES/2-CEES and GB/DEClP respectively. This system indicated the least $t_{1/2}$ values against simulants and actual blister agent. The order of reactivity against HD/2-CEES was: SiO_2 + TCCUA > SiO_2 + oxaziridine > SiO_2 + $RuCl_3$ > SiO_2 > SiO_2 + NaOH. Reactivity against 2-HEES was also similar except SiO_2, which showed lesser $t_{1/2}$ than SiO_2 + $RuCl_3$. In addition to that, the order of reactivity against GB/DEClP was: SiO_2 + NaOH > SiO_2 + TCCUA > SiO_2 + oxaziridine > SiO_2 + $RuCl_3$ > SiO_2. Overall, study indicated that, as the toxicant molecule is physisorbed on impregnated silica nanoparticles it starts reacting with the active sites of the adsorbent or impregnant available on their surface. This leads to chemisorption or destruction of toxicant to such an extent that the chemical integrity of the toxicant is completely destroyed. HD, 2-HEES, 2-CEES, DEClP and GB were found to be degraded over SiO_2 + TCCUA via hydrolysis, elimination, dehydrohalogenation and oxidation reactions.

In summary, trichloroisocyanuric acid impregnated (10%, w/w) silica nanoparticles based system was found to be the best among prepared systems to remove and detoxify CWAs into non-toxic products effectively in less time. Conclusively, this universal system having self-decontaminating feature and capable of removing blister and nerve agents can promisingly be used in decontamination devices (Handecon, a fire extinguishing type equipment under development at our laboratory) or filtration systems (by mechanical compressing the nanoparticles to granules) to remove CWAs.

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