

In-situ degradation of sulphur mustard and its simulants on the surface of impregnated carbon systems

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Abstract

Bis-2-chloroethyl sulphide (sulphur mustard or HD) is an extremely toxic and persistent chemical warfare agent. For in situ degradation of HD and its analogues (simulants), i.e., dibutyl sulphide (DBS) and ethyl 2-hydroxyethyl sulphide (HEES), different carbon systems such as 11-molybdo-1-vanadophosphoric acid impregnated carbon (V_1/C), ruthenium chloride impregnated carbon (Ru/C) and combination of these two ($V_1/Ru/C$) were prepared. These carbons were characterized for cumulative micropore volume and surface area by N_2 BET. The kinetics of the in situ degradation of HD and its simulants were studied and found to be following the first order kinetics. Kinetic rate constants and $t_{1/2}$ values were determined. Products were characterized using NMR, IR and GC–MS. Reaction products were found to be sulphoxide and sulphone. The combined system, i.e., 11-molybdo-1-vanadophosphoric acid plus ruthenium chloride ($V_1/Ru/C$) was found to be best for in-situ degradation of HD and its simulants. In-situ degradation by polyoxometalate based system was found to be stoichiometry based while Ru/C oxidized HD in presence of chemisorbed oxygen. In combined system of $V_1/Ru/C$ ruthenium worked as a catalyst and polyoxometalate acted as a source of oxygen. Effect of moisture was also studied in combined system. Rate of degradation of HD was found to be increasing with increased percentage of moisture content.

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1. Introduction

Porous activated carbon is an universal adsorbent and widely used for the purification of air and water streams [1–4] using different kinds of air and water filtration systems due to its economical viability, ease of availability and high adsorptive potential. It only physisorbs toxic vapours from contaminated environment but do not degrade them. So there is a chance of cross-contamination due to desorption of physisorbed toxic vapours when these filtration systems containing physisorbed CW agents are thrown carelessly or are not disposed off properly. To achieve the toxic chemical degradation, activated carbon is impregnated with suitable impregnants. Activated carbon impregnated with silver, chromium and copper is used in NBC filtration system and this carbon system is known as ASC whet-

lerite by the name of its researcher. This system removes gases such as hydrogen cyanide, cyanogen chloride, phosgene, etc. [5–13]. All of these gases are highly volatile and fall in the category of non-persistent chemical warfare agents (CW). There is one more category of CW agent, i.e., persistent CW agent which are high boiling liquids and are not degraded over ASC whetlerite, only a little hydrolysis of sulphur mustard (HD) has been reported on it [6]. Therefore, there is a need to develop new adsorbent system which can degrade persistent CW agents in-situ. The aim of persistent study was also the degradation of HD/simulants over suitable adsorbent systems.

In order to degrade HD and its simulants over adsorbent systems different polyoxometalates [14–16] impregnated carbon systems were used by different researchers. Damico et al. (1997) studied the detoxification reactions of thioether (mustard analogue) with carbon-supported polyoxometalate [17]. Heteropolyanion salt ($Na_5PV_2Mo_{10}O_{40}$) was supported on microporous carbons and tested against chloroethyl ethyl sulphide (half sulphur mustard) and tetrahydrothiophene [18]. Polyoxometal-

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lates reactions were also studied with tropical skin protectant cream [19]. Polyoxometalates were not only used for degradation of the half sulphur mustard but also used for detecting the presence of toxic chemical based on color change of the cream. Gall (1996) showed that the oxidation of the HD simulant tetrahydrothiophene (THT) to tetrahydrothiophene oxide (THTO), catalysed by $\text{Na}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ impregnated carbon, is of first order type reaction in substrate and proportional to the concentration of the active sites on the $\text{Na}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ impregnated carbon [20]. Singh et al. studied the reaction of thiodiglycol (a hydrolysis product of sulphur mustard) on impregnated carbon [21]. 1,4-Oxathiane and 1,4-oxathiane, 4-oxide were observed as reaction products. All these studies indicated that the impregnants in the detoxification reactions add reactivity to carbon to make it useful for the reactive removal of CW agents. Inspired by these studies we have prepared and studied the reaction of HD and its simulants on 11-molybdo-1-vanadophosphoric acid impregnated carbon (V_1/C), ruthenium chloride impregnated carbon (Ru/C) and combination of these two impregnants ($\text{V}_1/\text{Ru}/\text{C}$). Degradation products were characterized by NMR, IR and GC–MS techniques.

2. Experimental

2.1. Materials

Activated carbon of surface area $1250 \text{ m}^2/\text{g}$ of coconut shell origin, particle size 12×30 BSS (British sieve size) was procured from M/S Active carbon India Ltd., Hyderabad. Sulphur mustard was obtained from Synthetic Chemistry Division of our establishment. Chloroform (AR grade), ruthenium chloride, sodium molybdate, disodium hydrogen phosphate, sulphuric acid, sodium metavanadate dibutyl sulphide, ethyl 2-hydroxyethyl sulphide were obtained from E-Merck, India Ltd., SD fine, India and Lancaster, UK. 11-Molybdo-1-vanadophosphoric acid was prepared using standard method [22].

2.2. Neutralization of active carbon

Procured active carbon was basic in nature. It was treated with 2% nitric acid and washed with distilled water until the extract did not show pH near 7. Nitric acid washed carbon was dried and surface area was determined that was found to be $1313 \text{ m}^2/\text{g}$.

2.3. Impregnated carbon

Activated carbon was impregnated with aqueous solution of ruthenium chloride (5.0%, w/w) and 11-molybdo-1-vanadophosphoric acid (5.0%, w/w) using incipient wetness technique. Three types of impregnated carbon systems were prepared for the kinetics of degradation of HD. These were 11-molybdo-1-vanadophosphoric acid (V_1/C) impregnated carbon, ruthenium chloride (Ru/C) impregnated carbon and 11-molybdo-1-vanadophosphoric acid plus ruthenium chloride ($\text{V}_1/\text{Ru}/\text{C}$) impregnated carbon. The 11-molybdo-1-vanadophosphoric acid plus ruthenium chloride impregnated

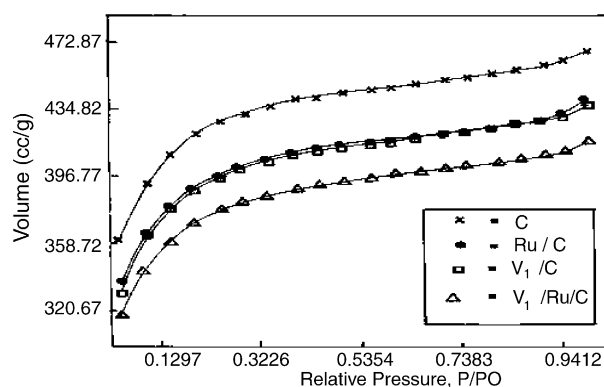


Fig. 1. N_2 adsorption isotherm of carbon systems.

carbon system was prepared by taking 5.0% (w/w) of each impregnants. These systems were dried at 110°C for 6 h.

2.4. Surface area analysis

Surface area of impregnated and unimpregnated carbons were determined by using Autosorb 1C from Quantachrome, USA. Fig. 1 describes the adsorption isotherms. Cumulative micropore volume was determined by using Howarth Kawasaki method.

2.5. Reaction procedure

All the reactions were carried out in glass tubes. One hundred milligrams of impregnated carbon was placed in glass tube with $100 \mu\text{L}$ solution containing $5 \mu\text{L}$ sulphur mustard or dibutyl sulphide or ethyl 2-hydroxyethyl sulphide in chloroform. The tubes containing the reaction mixture were maintained at constant temperature (37°C) in an oven and each tube was taken out for kinetic studies at regular intervals of time. For kinetics of degradation, residual toxicants were extracted in chloroform and the solutions were subjected to GC/FID analysis using splitless injection technique. All gas chromatography analysis was performed on a chemito 8610 gas chromatograph equipped with BP5 column (5% phenyl methyl silicon capillary column of 30 ft. length, 0.3 mm i.d.) and FID detector. Isothermal method was adopted for GC analysis, the oven, injection port and detector were kept at 120, 220 and 250°C , respectively. The experiments were performed carefully using applicable safety procedures. All the experiments were performed in the fume cupboard.

2.6. Effect of moisture

Ninety percent relative humidity was created in a desiccator by using a fixed composition of 90.2 mL water plus 9.8 mL sulphuric acid. One hundred milligrams of carbon samples were taken in Petri dishes and placed in the desiccator for different interval of times to obtain variable moisture content in the adsorbents. In order to study the effect of moisture content, the carbon samples with different moisture contents were subjected for HD degradation.

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