

Kinetics of degradation of sulphur mustard on impregnated carbons

G.K. Prasad*, Beer Singh, M.V.S. Suryanarayana, B.S. Batra

Defence Research and Development Establishment, Jhansi Road, Gwalior 474002, Madhya Pradesh, India

Received 12 November 2004; received in revised form 4 February 2005; accepted 6 February 2005

Available online 16 March 2005

Abstract

Kinetics of degradation of sulphur mustard (HD) on the surface of NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C systems has been examined by using gas chromatography technique by extracting and analyzing the residual HD periodically. The carbons were prepared by impregnating activated carbon with 4% sodium hydroxide plus 3% Cr(VI) as CrO₃ with and without 5% ethylene diamine (EDA) and 5% ruthenium chloride by using their aqueous solutions. Obtained carbons were characterized for surface area analysis by BET conventional method. Kinetic plots reveal that the observed reactions are fast at the initial stages, slow at the later stages and progress to a steady state indicating the first order behavior. Effect of moisture on kinetic rate is also observed. In the case of NaOH/CrO₃/C system the rate constant is decreased from 13.36 to $5.53 \times 10^{-2} \text{ h}^{-1}$ and half life is increased from 5.2 to 12.54 h while moisture content is increased from 1.9% to 11.2%. Whereas, the rate constant of HD degradation reaction is decreased from 10.4 to $4.14 \times 10^{-2} \text{ h}^{-1}$ and half life is increased from 6.7 to 16.72 h while moisture content is increased from 2.1% to 10.8% on NaOH/CrO₃/EDA/C. Reaction on RuCl₃/C system also behaves in the similar manner. Extracted reaction products were characterized by GC/MS and it is found that on NaOH/CrO₃/C, HD degrades to hemisulphur mustard, thiodiglycol and 1,4-oxathiane. Whereas, on NaOH/CrO₃/EDA/C, HD is degraded to 1,4-thiazane and it is degraded to divinyl sulphone on RuCl₃/C. All these investigations reveal that above mentioned carbons can be used in nuclear, biological and chemical (NBC) filtration systems for protection against sulphur mustard.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Activated carbon; Adsorption; Chemical warfare agent; Impregnation; Sulphur mustard

1. Introduction

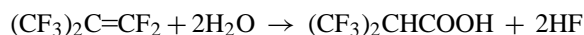
Disposal of carbon based filtration systems [1–4] after their use is of great concern due to several reasons. Of them, cross contamination of the environment due to desorption of adsorbed agents is considered to be the important aspect which should be taken care off due to the possible threat after the disposal of filtration systems. Such task is performed efficiently by the filtration system containing reactive carbons and they are prepared by impregnating activated carbon with various metal salts. ASC whetlerite [5] is one such im-

pregnated carbon which is used in NBC filtration systems for the reactive removal of hydrogen cyanide, cyanogen chloride and phosgene [6–21]. Activity of such impregnated carbons to degrade the above agents is quite dependent on ingredients present on the surface of active carbon. However, it was found to be deteriorating due to weathering, aging, exposure to high temperatures and storage for long time. This deactivation of the active catalyst is caused owing to the change in oxidation state of the ingredient and also due to drastic reduction in surface area. This reduction of surface area arises due to the formation of large crystallites within the pores owing to the dissolution of active species in water present on the surface of the adsorbent. On the other hand, reactions [22] of many gases on impregnated carbons were reported to be strongly influenced by the presence of water. In this regard, Hall et al. [23] studied the hydrolysis reaction of perfluoro isobutene on charcoal (PFIB). PFIB [24] was hydrolyzed as

* Corresponding author. Present address: Center for Crystal Science and Technology, Faculty of Engineering, Yamanashi University, Miyamae 7, Kofu, Yamanashi 4008511, Japan. Tel.: +81 552541094; fax: +81 298587190.

E-mail address: gkprasad@lycos.com (G.K. Prasad).

per the following reaction to hexafluoro isobutyric acid and hydrofluoric acid:



Moreover, Gall et al. [25] reported the detoxification reactions of thioether (mustard analogue) with poly oxo metallate on carbon supports and Prasad and coworkers [26a] have studied the reaction of thiodiglycol (a hydrolysis product of sulphur mustard) on impregnated carbon. Such type of carbons can be used suitably in NBC filtration systems for irreversible adsorption and in situ degradation of sulphur mustard leaving no scope for cross contamination due to desorption [26b]. Hence, it was thought to obtain the information regarding the kinetics of degradation and the extent of degradation of sulphur mustard on various impregnated carbons which will be helpful to predict their behavior in real conditions. Further, it will also give information regarding the time needed for complete degradation of the adsorbed HD after the disposal of the filter cartridge and also regarding the scope of desorption of the agent in to the environment which is indispensable for the safety of the user of filter cartridge and the personnel living in the premises.

For this purpose, we have studied the kinetics of degradation of sulphur mustard and the effect of moisture content on the rate of degradation on reactive carbon systems such as NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C. Kinetic parameters are reckoned by first order rate equation and reaction products were characterized by GC/MS.

2. Experimental

2.1. Materials

Activated carbon of surface area 1100 m²/g of coconut shell origin, with a particle size of 12 × 30 of British sieve size was procured from Active Carbon (India) Ltd., Hyderabad. Pure sulphur mustard (99%) was obtained from the Process Technology Development Division of our establishment. Dichloromethane, acetonitrile, NaOH, RuCl₃·3H₂O, CrO₃ and EDA were obtained from E Merck (India) Pvt. Ltd.

2.2. Impregnated carbons

Activated carbon was impregnated with aqueous solutions of NaOH (4%), Cr(VI) oxide (3% Cr(VI)), EDA (5%) and RuCl₃·3H₂O (5%) (Table 1). Incipient wetness technique [27]

was used for impregnation. These impregnation experiments on active carbon were carried out at room temperature by slowly mixing above solutions and activated carbon. Obtained metal impregnated carbons were dried at 110 °C for 6 h and stored in air tight bottles.

2.3. Estimation of impregnants

Chromium was extracted in basic media from carbons and estimated iodometrically. NaOH was extracted by boiling carbon in distilled water and estimated by titrating with dilute hydrochloric acid. Whereas, RuCl₃ was extracted by using hydrochloric acid and estimated by spectrophotometric method [28].

2.4. Surface area analysis

Impregnated and unimpregnated carbons were characterized for surface area (N₂ BET) using Gemini 2765 surface area analyzer (Micromeritics). Micropore volume was determined by using Dubinin equation [29]. The results were described in Table 1.

2.5. Apparatus used for adsorption of carbons

Adsorption of sulphur mustard has been carried out in the assembly fabricated by us. Fig. 1 shows the outline diagram of adsorption assembly. The system contains sample cell, purge cell to keep the agent (HD) and the circulating pump. The total system volume, consisting of the cell, tubing, fittings and circulating pump is approximately 300–400 ml. The unique feature of the apparatus is that the sample is gently fluidized during adsorption, thus providing uniform contact between the particles and HD vapor. The sample (2.0 gm) was loaded from the top of the cell and once the loading is over, the sample was purged with HD/air mixture at room temperature (36 °C) with valve placed in recycle position (moisture free air was not used for this purpose). After the HD loading on carbons, they were placed in closed glass vials at room temperature. Subsequently, 100 mg of carbon was taken out from the glass vial at kinetic intervals of time and the remaining HD was extracted from it. For this purpose, it was treated with 5.0 ml acetonitrile for five times in order to ensure the complete extraction and the obtained solutions were analyzed by gas chromatograph. Gas chromatograph equipped with flame ionization detector, i.e., Chemito 8610 with BP1 column of 30 ft length was used for the analysis at isothermal conditions. Oven temperature was kept at 120 °C, injection port temper-

Table 1
Recipe of impregnants and systems prepared

Serial no.	Amount of impregnants loaded on carbon	System	Surface area (m ² /g)	Pore volume (ml/g)
1	NaOH (4%), CrO ₃ (3.0%)	NaOH/CrO ₃ /C	912	0.53
2	NaOH (4.0%), CrO ₃ (3.0%), EDA (5%)	NaOH/CrO ₃ /EDA/C	855	0.5
3	RuCl ₃ /C	RuCl ₃ /C	950	0.51
4	Cu(II) (6.0%), Cr(VI) (3.0%), Ag(I) (0.2%), NaOH (2%)	Whetlerite	1050	0.52

Download English Version:

<https://daneshyari.com/en/article/9674277>

Download Persian Version:

<https://daneshyari.com/article/9674277>

[Daneshyari.com](https://daneshyari.com)