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Kinetic Study on Removal of Sulphur Mustard on Granular Activated Carbon from Aqueous Solution

Anuradha Baghel and Beer Singh*

Defence Research and Development Establishment, Gwalior- 474 002, India
**E-mail: beerbs5@rediffmail.com*

ABSTRACT

Sulphur mustard is a powerful blister agent and has been worked as a chemical warfare agent. No specific antidote is available for its wound. Therefore, adsorptive removal is an effective way of removal. Here, adsorptive removal of sulphur mustard from aqueous solution was studied on activated carbon and screened out MeOH : H_2O (1 : 1) solution as a good solvent than others used solvent. Adsorption isotherm of sulphur mustard was compared with its hydrolysis in the same solution. Kinetics of sulphur mustard removal on carbon from aqueous solution was found to be slower than hydrolysis and follow pseudo first order kinetics with the rate constant 5.04 X 10^{-3} min^{-1} and half life 137.5 min. The hydrolysis of sulphur mustard in MeOH : H_2O (1 : 1) solution was found to be following the pseudo first order kinetics with the rate constant 8.68 x10^{-3} min^{-1} and half life 79.8 min.

Keywords: Sulphur mustard, activated carbon, adsorption, kinetic, hydrolysis

1. INTRODUCTION

Sulphur mustard is an organosulphur compound and causes blisters on exposure to skin. Sulphur mustard is used as chemical warfare agent and can also be used to sabotage the water supply. Potable water is, however, important for sustenance of life on earth. Therefore, removal of volatile organic compounds (VOCs) including sulphur mustard from water becomes very important. Various techniques are available for the removal of volatile organic compounds from water; however, adsorption method has many advantages over others[1-3]. For water and waste water treatment, activated carbon has been widely used to remove contaminants with its characteristic features such as high surface area, adsorption capacity, and low cost[4-18].

To develop a carbon column system it is essential to study kinetics of adsorptive removal of contaminant from water. However, direct use of sulphur mustard in adsorption studies from water is a challenge due to its harmful nature and instability in water. It is toxic and requires proper handling and safety. Solubility of sulphur mustard in water is very poor (1mg/mL)[19] but it hydrolyses very fast and hydrolysis products are formed at the water-sulphur mustard interface[20-22]. Thiodiglycol and hydrochloric acid as represented by the Eqn (1) are major products. The rate of decomposition of sulphur mustard depends upon the amount of water and temperature[23]. At 25 °C, its half life in water is 3 min[14].

$$S(CH_2CH_2Cl)_2 + 2H_2O \rightarrow S(CH_2CH_2OH)_2 + 2HCl \quad (1)$$

Tilley[24] also studied the hydrolysis of sulphur mustard in aqueous mixtures at 25 °C while Logan and Sartori[25, 26] studied in D_2O at 22 °C.

Inspite of many challenges, sulphur mustard was directly employed for adsorptive removal study on granular activated carbon to understand the real scenario.

2. MATERIALS AND METHODS

Granular activated carbon from coconut shell origin (M/s Active Carbon India Pvt. Ltd., Hyderabad) was used for the adsorption studies. Methanol (MeOH), dichloromethane, 1, 4 dioxane, acetonitrile, sulphur mustard (provided by schedule-1 chemical DRDE declared facility) were used for kinetic studies.

2.1 Batch Process for Kinetic Study

Many solvents were screened for the kinetic study of sulphur mustard removal on carbon and methanol was found to be suitable solvent as hydrolysis was slow. In order to find the above mentioned, 1000 mg/L of sulphur mustard solution (5 mL) in three different solvent such as methanol, acetonitrile, 1, 4 dioxane were prepared. 0.2 g of activated carbon was added into three different vials of sulphur mustard solution separately and stirred in a thermostat shaker bath at 25 °C for 60 min and analyzed the samples by using GC of M/s Nucon Engineers, India Make equipped with flame ionization detector and BP5 column (30 m length, and 0.5 mm i.d.). Oven, injector port and detector were maintained at 140 °C, 220 °C, and 280 °C, respectively. The GC conditions for quantitative estimation of sulfur mustard were the same throughout the whole study.

Experiments were conducted later in methanolic water (1:1), for which activated carbon (0.1 g) was fixed for each experiment and added into the conical flasks of having 5000 mg/L of sulphur mustard solution prepared in 10 mL. For each

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experiment, a combination of three experiments was carried out simultaneously. First experiment was performed without carbon and stirring treatment, second experiment was carried out only with carbon treatment not with stirring while third experiment was performed with carbon as well as stirring treatment to see the effect of hydrolysis on the adsorption of sulphur mustard on carbon. Conical flasks were agitated at 230 rpm on a thermostat shaker bath at 25 °C and extracted sulphur mustard with dichloromethane. The volume of extractant was used in three parts. The adsorbed amount of sulphur mustard was calculated by the difference with controlled experiment where sulphur mustard was not added but stirred for the same time. Calibration curves were made using standard solution of sulphur mustard in dichloromethane (Fig. 1) and concentration of sulphur mustard in treated samples was determined using this curve.

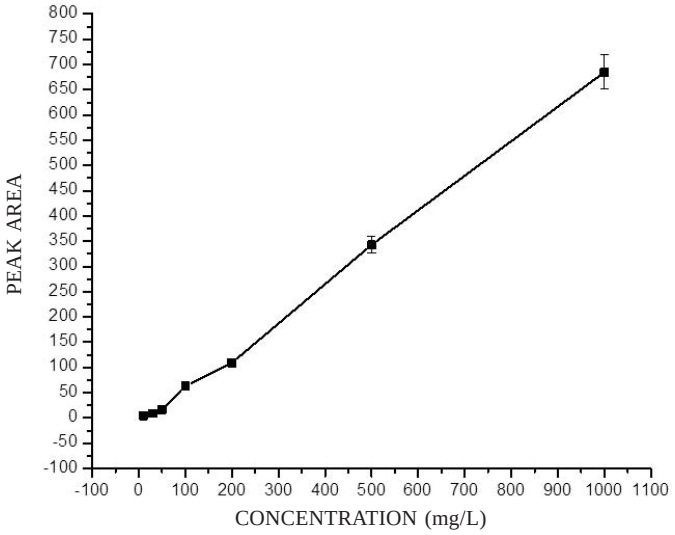

Figure 1. Calibration curve of sulphur mustard.

3. RESULTS AND DISCUSSION

Sulphur mustard is very slightly soluble in water and freely soluble in organic solvents. To study the kinetics of sulphur mustard adsorption from water on granular activated carbon required the sulphur mustard in water. Therefore, a suitable solvent was identified through screening for increasing the solubility of sulphur mustard in aqueous solution which in turn could lead to adsorptive removal of sulphur mustard as shown in Table 1. Table 1 indicates that 53 per cent of sulphur mustard could be removed in methanolic aqueous solution while 1,4 dioxane probably competed with sulphur mustard to get adsorbed on granular activated carbon as no removal of sulphur mustard was observed. Therefore, subsequent experiments were carried out using a solvent mixture of methanol and distilled water in equal volume to prepare sulphur mustard solution.

Out of a combination of three analyses for each experiment first was to nullify hydrolysis effect, second to see the effect of hydrolysis and third to monitor sulphur mustard adsorption on carbon. Adsorption isotherm of sulphur mustard on granular carbon was compared with hydrolysis isotherm of sulphur mustard in aqueous solution and shown in Figs. 2 and 3, respectively. Figures 2 and 3 clearly indicate that hydrolysis of

Table 1. Screening of solvents for sulphur mustard extraction from water

Solvents conc. (g)	Adsorbent (mg/L)	Initial (mg/L)	Final conc.	Stirring time (min)	Removal (per cent)
Methanol	0.2	1000	470	60	53
Acetonitrile	0.2	1000	640	60	36
1,4 dioxane	0.2	1000	1000	60	0

sulphur mustard in solvent always competes with its adsorption on granular activated carbon. Figure 2 shows that inspite of hydrolysis of sulphur mustard in methanolic water, adsorption of sulphur mustard progressed on carbon from it.

After definite time intervals, residual sulphur mustard was extracted with dichloromethane and the solutions were subjected to GC/FID analysis. Obtained data of remaining concentrations of sulphur mustard after treatment with carbon

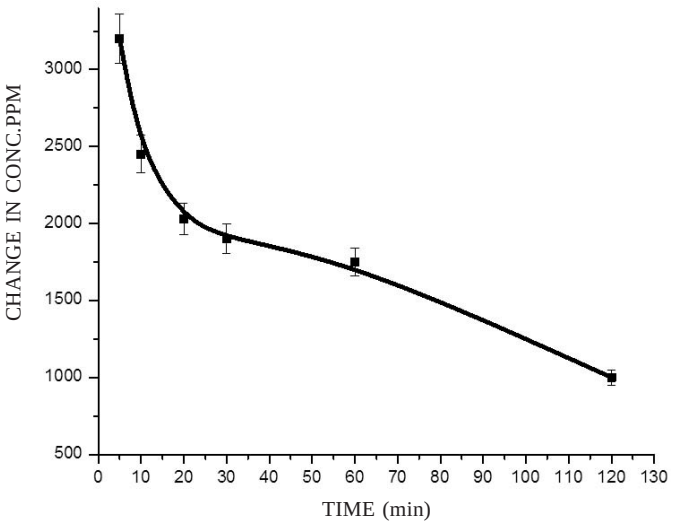

Figure 2. Adsorption isotherm of sulphur mustard on activated carbon from a mixture of solvent (MeOH : H_2O, 1:1).

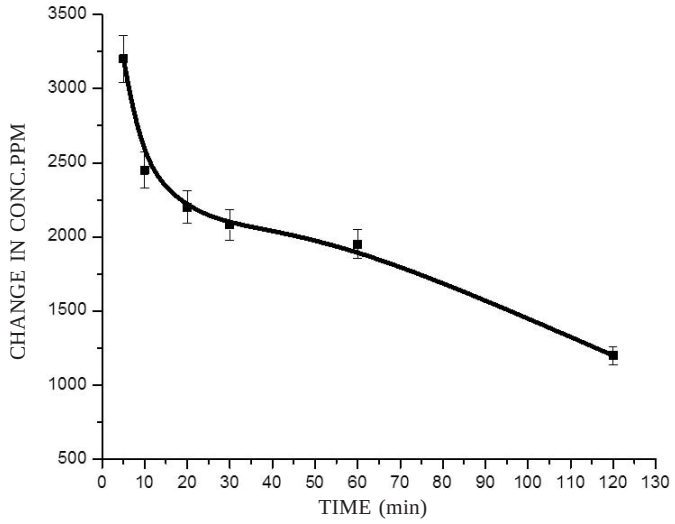

Figure 3. Hydrolysis of sulphur mustard in a mixture of solvent (MeOH : H_2O, 1:1).

with different time intervals were found to be fitting pseudo first order kinetic model as presented in Fig. 4, which shows the plot of log (a-x) against time. Rate constant was calculated using the slope of the straight line drawn. The rate constant value was found to be 5.04 x 10^{-3} min^{-1}. Half life of sulphur mustard adsorption on carbon was calculated from 0.693/k and found to be 137.5 minutes.

Similarly the hydrolysis of sulphur mustard was studied in MeOH : H_2O (1 : 1) solution and it was also found to be following the pseudo first order kinetics with the rate constant 8.68 x 10^{-3} min^{-1} and half life 79.8 min, and the kinetics plot is described.

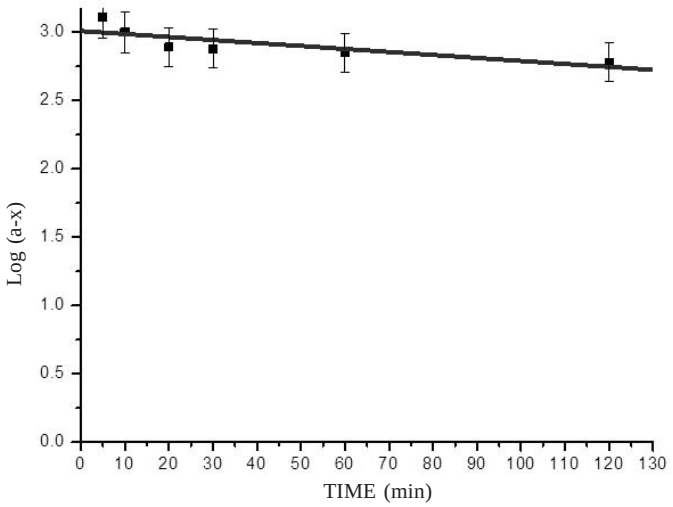

Figure 4. Pseudo first-order kinetic of sulphur mustard adsorption on granular carbon from (MeOH : H_2O, 1:1).

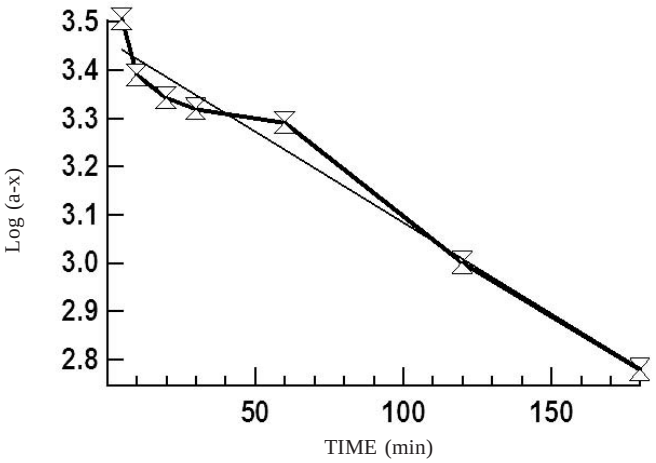

Figure 5. Pseudo first-order kinetics of sulphur mustard hydrolysis in (MeOH : H_2O, 1:1).

4. CONCLUSIONS

Sulphur mustard is slightly soluble in water, as a result, a mixture of two solvent viz water and methanol (MeOH : H_2O, 1 : 1) was used to solubilise it for kinetic study. However, hydrolysis of sulphur mustard in methanolic water competes, its adsorption on granular activated carbon and it was studied by simultaneous experiments of sulphur mustard adsorption from a solvent mixture. Kinetics of sulphur mustard adsorptive removal on carbon from methanolic water was found to follow pseudo first order however slower than hydrolysis. The rate constant of sulphur mustard adsorption from methanol-water mixture on granular activated carbon was 5.04 x 10^{-3} min^{-1} and half life of adsorption reaction was 137.5 min. The hydrolysis of sulphur mustard in MeOH : H_2O (1 : 1) solution was found to be following the pseudo first order kinetics with the rate constant 8.68 x 10^{-3} min^{-1} and half life 79.8 min.

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CONTRIBUTORS

Dr Beer Singh received his MPhil and PhD in chemistry from Delhi University. Presently working as a scientist 'G' in DRDE, Gwalior. He has 125 research papers and 24 patents to his credit. He has received many prestigious awards including of DRDO Scientist of the year in 2008. He has over 36 years of research experience in the multi-disciplinary branch of chemistry.

Dr Anuradha Baghel received her PhD from Jiwaji University, Gwalior in chemistry. Presently working as a scientist 'C' in DRDE, Gwalior. Her research interests are in the water analysis and development of novel adsorbents including carbon, molecularly imprinting polymers and metal organic framework.