Defence Science Journal, Vol. 63, No. 5, September 2013, pp. 473-477, DOI : 10.14429/dsj.63.2512

Adsorption Behaviour of Diisopropyl Flourophosphate on Whetlerite Carbon

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ABSTRACT

Breakthrough behaviour of diisopropyl florophosphate (DFP) vapour on whetlerite carbon has been studied by using modified wheeler equation. The kinetic saturation capacity and pseudo first order rate constant with respect to the effect of various parameters such as bed weight, flow rate, concentration and temperature were correlated. The results of this study indicate that breakthrough time is increased with increase of the bed weight of carbon. Rate constant value increases as flow rate increases, while kinetic saturation capacity value is invariable.

Keywords: Diisopropyl flurophosphate, whetlerite carbon, breakthrough time, service life

1. INTRODUCTION

Vapour breakthrough behaviour of carbon beds challenged with contaminated air streams is of great interest in connection with respiratory protection against hazardous vapour. Carbon beds exhibit relatively better adsorptive properties than the other adsorbents such as silica etc., and make them indispensable for their use in respiratory cartridges[1–7]. Activated Carbon (AC) whetlerite, i.e., active carbon impregnated with salts based on *Cu*(II), *Cr*(VI) and *Ag*(I) ions is one such reactive carbon which has been used in respiratory cartridges for the protection against non-persistent (high volatile and low boiling) chemical warfare agents such as hydrogen cyanide, phosgene and cyanogens chloride[4,8]. Air contaminated by these agents get chemisorbed and detoxified on the surface of above carbon. However, persistent (high boiling and low volatile) chemical warfare agents are mainly removed by physical adsorption. In such a case, active carbon is suffice enough for the physisorption of the persistent chemical warfare (CW) agents such as sulphur mustard[9-12] and nerve agents. Templeton and Weinberg[13] described the adsorption and decomposition of Dimethyl methyl phosphonate (DMMP) on aluminium oxide surface at temperature ranged from 200 K to 673 K. Attempts were also made by Cao[14], *et al.* to study the higher temperature thermo-catalytic decomposition of DMMP on activated carbon to carbon dioxide, methanol and phosphorous pentoxide.

The performance of the carbon bed or the service life of nuclear, biological and chemical (NBC) filtration system depends upon the adsorption capacity of the adsorbent and the rate of adsorption of the contaminants or adsorption kinetics at breakthrough time. In order to understand the adsorption processes and to predict the service life of carbon bed many equations have been derived to correlate the concentration of gas passed into the carbon bed and the quantity of gas adsorbed by measuring the breakthrough time[15–18]. Furthermore, Wheeler[19-21] has proposed a continuity equation which correlates the mass of vapour, that entered the carbon bed and the mass adsorbed and penetrated it to understand the adsorption kinetics and to predict the service life of carbon bed accurately. Consequently, Jonas[22-24], *et al.* have utilized the modified Wheeler equation to predict the service lives of carbon beds accurately.

The equation[15–21] is given below:

$$t_b = [W_e / C_0 Q][W - \rho_b Q \text{ X } \ln(C_o/C_x)]/k_v$$

where t_b is the breakthrough time (min), C_x the exit concentration (g/ml), C_0 the initial concentration (g/ml), Q the volumetric flow rate (LPM), W the weight of adsorbent (g), ρ_b the bulk density of carbon bed (g/ml), W_e the kinetic saturation capacity (g/g) and k_v is the rate constant (min^{-1}).

The values of C_0, W, and Q are established by the experimental test conditions. The value of ρ_b depends upon the weight, particle size and shape of the adsorbent and it can be determined experimentally while C_x/C_0 is preselected. In addition to this, the quantity of gas adsorbed under dynamic conditions depends on parameters such as temperature, concentration, flow rate of gas mixture, particle size and reactivity on the adsorbents surface[25-27]. Of these, flow rate of gas mixture is observed to be one of the important parameters which affects the rate of adsorption prominently. The rate of adsorption increases proportionally with the increase of flow rates of air–gas mixture due to diffusion of vapour molecules and the same was found to be the rate limiting process.

In order to understand this and the effect of above mentioned parameters on adsorption kinetics and to find out the service life of carbon bed against organo-phosphorous compounds, we have selected Diisopropyl fluorophosphate (DFP) vapours as stimulant of nerve agent to study the breakthrough behaviour on whetlerite carbon. In the present study, modified Wheeler equation was used for determination of the adsorption parameters such as kinetic saturation capacity

Received 27 August 2012, revised 27 August 2013, online published 25 September 2013

(W_e), and kinetic rate constant (k_v), and service life of the carbon bed against DFP and same equation was also used to study the effect of various parameters such as flow rate, concentration and temperature on W_e and k_v and results are described in the later sections.

2. EXPERIMENT

2.1 Materials

Whetlerite carbon (1030 m^2/g), micro-pore volume 0.62 ml/g and W_0 are 0.7 ml/g) of particle size 12 × 30 BSS was procured from M/s Active carbon India Ltd., Hyderabad. This carbon was degassed at 120 °C for 4 h and stored in air tight bottles was used for experiments. GC-MS analysis was performed in E1 (70eV) in full scan mode with an Agilent 7890A GC equipped with a model 5973C mass selective detector (Model no 7890A5975C GC/MS from M/s Agilent Technologies). AP2C from Proengin, France based on flame photometry principle, fluoride ion selective electrode and MiniRae 3000 detector based on photo ionisation (PID) was used to monitor the environment and break through time (BTT).

2.2 Chemicals

Diisopropyl fluorophosphate (DFP) was synthesised in the special laboratory built mainly for the synthesis of highly toxic compounds. Full body protection including breathing protection were worn when handling the DFP, which includes both synthesis and performance evaluation of active carbon. The purity of DFP was checked by GC and FT-NMR (100 MHz). Carbon tetrachloride (CCl_4) (99.5% purity), XAD-2 were obtained from Lancaster, England and the use of XAD-2 resin was described in the later sections.

2.3 Vapour Generation

Vapour generation and assembly: DFP was filled in a 10 ml gas tight syringe and flow rate was adjusted to obtain the required concentration as shown in Fig 1. This syringe was connected to a glass air blast nebulizer and the inlet pressure was maintained at 1 kg.cm^{-2} to generate aerosol. A helical glass tube was attached with the nebulizer to a 5 lit glass chamber kept at 20 lpm air suction. Air from the glass chamber was sucked at a rate of 20 lpm. From the mixing chamber, the required flow rate of the aerosol was sucked and the carbon bed was evaluated. Experimental setup was established in fume hood of high exhaust capacity with scrubber attached. The exhaust air was passed through big carbon filters before sending the exhaust gas to scrubber. Individual protection was taken by wearing NBC suit, gloves, etc.

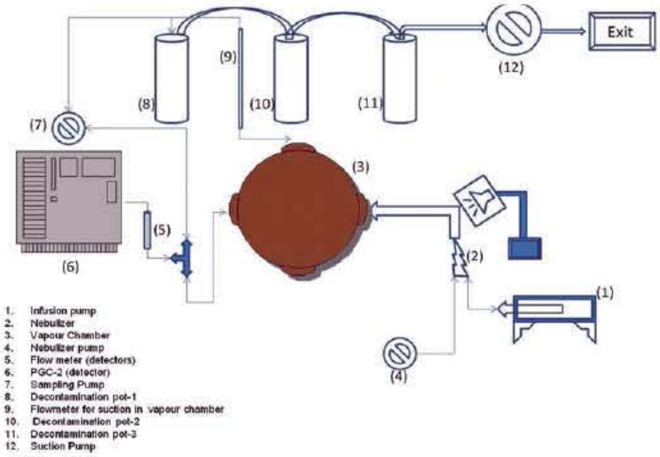

Figure 1. Scheme for gas generation apparatus and evaluation of carbon.

2.4 Vapour Breakthrough Experiments of DFP

Vapour breakthrough experiments of DFP were carried out in a column of 1.0 cm diameter using different bed heights of carbon, flow rates and concentrations of DFP–air mixture and temperature. The carbon was tapped continuously to form tight bed order to obtain reproducible packing density. The temperature of the carbon was maintained with thermostat. The breakthrough time of DFP through the carbon bed was monitored from exit concentration (0.4 mg/m^3) with an AP2C detector and Minirae3000 PID detector. The generated aerosol was adsorbed in XAD-2 resin, then desorbed with acetonitrile and concentrated with purged nitrogen and injected in GC-MS to arrive at the generated concentration.

2.5 Precaution to Avoid Exposure

DFP is a known toxic organo phosphorous compound. It effects men and materials and documented as carcinogenic and inhibitor of cholinesterase inside the body. Experimental set up was established in fume hood having high capacity vacuum with scrubber attached. The exhaust air was removed of any toxicity by passing through sodium hydroxide solution before passing the outlet to scrubber. Individual protection was taken by wearing NBC suits, gloves, etc. The environment was monitored by AP2C and PID detector.

3. RESULTS AND DISCUSSION

The effect of flow rate on kinetic saturation capacity (W_e) and rate constant (k_v) in the case of whetlerite carbon was studied by obtaining experimental values of BTT at various carbon weights by using various flow rates ranging from 0.5 l/m to 2.0 l/m at 0.250 mg/l and 25 °C constant temperature and graph was plotted as shown in Fig. 2.

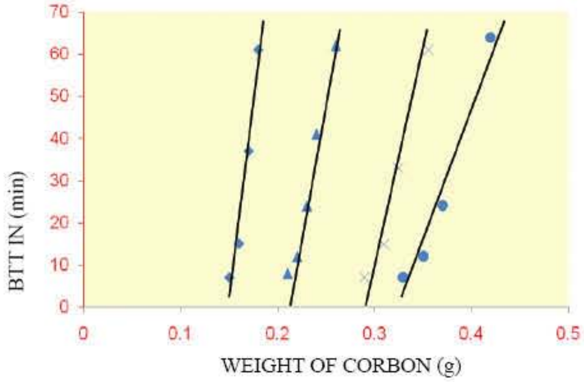

Figure 2. DFP breakthrough time as a function of whetlerite carbon weight. At various flow rates, concentration 0.25 mg/mL and at 25 °C ◊- 0.5 lpm, ▲ - 1 lpm, X- 1.5 lpm and •- 2 lpm of DFP

At various flow rates, concentration 0.25 mg/mL and at 25 °C, 0.5 lpm, 1 lpm, 1.5 lpm and 2 lpm of DFP constant temperature and graph was plotted as shown in Fig. 2. Figure 2 illustrates the linear curve which indicates the kinetic of reaction was governed by the pseudo-first-order rate constant[24]. Further, the values of k_v and W_e for the carbons mentioned are computed by making use of modified Wheeler equation. W_e is calculated from the slope of the above linear curve, i.e. (W_e/C_0Q) and k_v from the intercept, i.e., $-\rho_b QX \ln(C_o/C_x)/k_v$ and the obtained results are illustrated in Table 1. The results indicate that, the value of k_v increases steadily from 12740 min^{-1} to 23200 min^{-1} when the flow rate (Q) increases from 0.5 lpm to 2.0 lpm in the case of whetlerite carbon while the invariable value of kinetic saturation capacity (W_e) was observed. This observation indicates that the rate limiting process is due to the diffusion of vapour phase molecules on the surface of carbon granules. Moreover, the value of kinetic saturation capacity is found to be 0.3 g/g at various flow rates from 0.5 lpm to 2.0 lpm. Since there is no significant change in the value of kinetic saturation capacity, it clearly indicates that, the whetlerite carbon bed can hold/retain 0.3 g of DFP from the contaminated vapour at change of varying flow rates. It can be calculated from these data that the carbon bed provides protection for 1200 min against 0.25 mg/l of DFP at 1.0 lpm flow rate at 25 °C temperature. Thus, obtained value kinetics saturation capacity can be used to predict the service life of carbon bed against DFP[23].

Table 1. DFP kinetic saturation capacity and rate constant at various flow rates on whetlerite carbon at 25 mg/mL and at 25 °C

Flow rate (lpm)	W_e (g/g)	k_v (min^{-1})
0.5	0.3	12740
1.0	0.3	17400
1.5	0.3	19800
2.0	0.3	23200

Furthermore, the effect of concentration (Fig. 3) on k_v and W_e at 1.0 lpm flow rate at 25^{0}C was also studied. The value of W_e is found to be 0.3 g/g at 0.3 mg/l to 0.5 mg/l concentrations of DFP vapour, the value of k_v is found invariable from 9236 to 9806 min^{-1} as shown in Table 2.

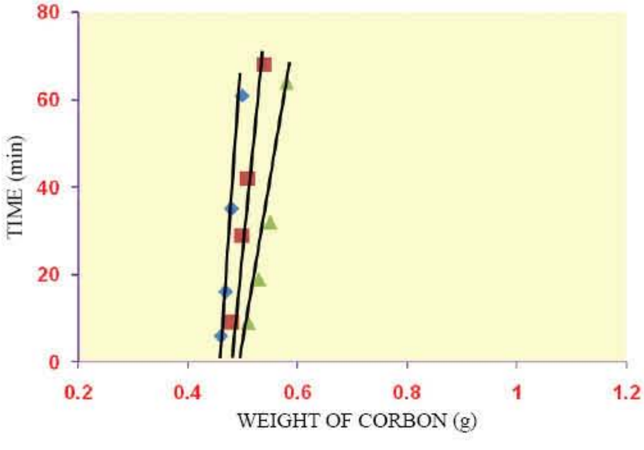

Figure 3. DFP breakthrough time as a function of carbon weight (whetlerite carbons) at various concentrations, 1.0 lpm flow rate and 25 °C temperature ◊- 300 mg/m^3, ■-400mg/m^3, ▲-500mg/m^3 of DFP.

Table 2. DFP kinetic saturation capacity and rate constant at different concentrations of DFP on whetlerite carbon at 1 lpm and at 25 °C

Concentration (mg/mL)	W_e (g/g)	k_v (min^{-1})
0.3	0.3	9236
0.4	0.3	8205
0.5	0.3	7806

These observations reveal that concentration in this range has no significant effect on the values of W_e and k_v. These observations also indicate that, the concentration when it is varied within 0.3 mg/l – 0.5 mg/l has not affected either kinetic saturation capacity value or kinetic rate constant value significantly. Hence, it is quite possible to predict the breakthrough time/service life of the bed of whetlerite carbon at the above concentrations by using the kinetics saturation capacity values. It is observed from these data that the carbon bed (for all carbons) provides protection for 1000 min against 0.3 mg/l of DFP, for 750 min against 0.4 mg/l of DFP and for 600 min against 0.5 mg/l of DFP at 1.0 lpm flow rate and 25^{0}C temperature. Thus the above kinetic saturation capacity value obtained from the plots is used to predict the service life of carbon beds against various concentrations.

Effect of temperature on the values of W_e as well as k_v was also studied from 25 °C to 45 °C as shown in Fig. 4. The flow rate was maintained at 1.0 lpm and DFP concentration at

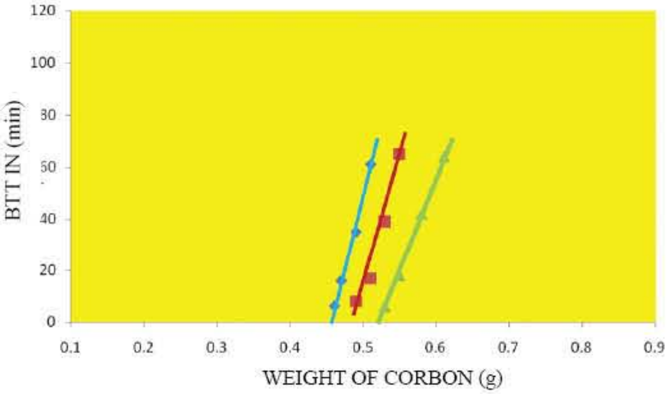

Figure 4. DFP breakthrough time as a function of carbon weight (whetlerite carbons) at various temperature, 1.0 lpm flow rate and 25 °C temperature ◊ - 25 °C, ■ - 35 °C, ▲- 45 °C.

Table 3. DFP kinetic saturation capacity and rate constant at different temperature of DFP on whetlerite carbon at 1 lpm and at 0.300 mg/m^3 from 25 °C to 45 °C of the carbon kept in the adsorption column

Concentration (mg/mL)	W_e (g/g)	k_v (min^{-1})
0.3	0.3	9428
0.4	0.29	8105
0.5	0.2	7394

0.5 mg/l kinetic saturation capacity has decreased significantly from 0.3 to 0.22, when the temperature was increased and the obtained values of W_e and k_v are mentioned in Table 3.

It indicates that with the increase of temperature DFP molecules are poorly adsorbed at higher temperatures. However, the rate constant decreases with increasing temperature. From the obtained values of kinetic saturation capacity, the service lives/breakthrough times of carbon bed are predicted by calculations. It is found from the data that, breakthrough time/service life decreases from 600 min to 440 min for whetlerite carbon when temperature is increased from 25 °C to 45 °C at concentration of 0.5 mg/l and 1.0 lpm flow rate.

The results obtained from the above studies, it is an evident that the above whetlerite carbon is capable of holding DFP vapors and suitable for providing sufficient respiratory protection against DFP. Hence, it is also expected that this carbon can provide sufficient protection against DFP and can be used in NBC filtration systems.

4. CONCLUSION

Breakthrough behaviour of DFP vapour on whetlerite carbon has been studied by using modified wheeler equation. Effect of various parameters such as bed weight, flow rate, concentration and temperature were interpreted in terms of kinetic saturation capacity and rate constant. Breakthrough time is observed to be increasing with the increase in bed weight of carbon. Rate constant value increases as flow rate increases, while kinetic saturation capacity value is invariable. This indicates that the rate limiting process is controlled by diffusion of DFP molecules on the surface of carbon. The concentration variation in between 0.3 mg/l and 0.5 mg/l has no significant effect on kinetic saturation capacity or rate constant. Temperature affected the W_e and k_v values adversely due to poorer adsorption at higher temperatures.

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