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Breakthrough behavior of sulphur mustard vapor on whetlerite carbon

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Abstract

Sulphur mustard vapor breakthrough behavior on whetlerite carbon has been studied by using modified Wheeler equation. The values of pseudo-first-order rate constant (k_v) and kinetic saturation capacity (W_e) were calculated and the effects of various parameters such as bed height, air flow rate, concentration and temperature on the above parameters have also been studied. Rate constant is found to be increasing with air flow rate, while W_e is found to be invariable. Both k_v and W_e decrease with the increase of temperature, however, no significant effect on W_e and k_v is observed due to concentration change. The values of kinetic saturation capacity are used to predict the service lives/breakthrough times of carbon beds (when used in filtration systems).

Keywords: Whetlerite carbon; Wheeler equation; Adsorption; Adsorption properties

1. Introduction

Whetlerite carbon is one of the widely used adsorbents in nuclear, biological and chemical (NBC) filtration systems for retaining toxic chemicals from contaminated air streams [1,2]. Whetlerite carbon is nothing but activated carbon impregnated with salts of Cu(II), Cr(VI) and Ag(I) [3,4] and it provides sufficient protection against non-persistent chemical warfare agents such as hydrogen cyanide (HCN), phosgene and cyanogen chloride [5].

On the other hand, the performance of such carbon bed in NBC filtration system depends upon the adsorption capacity/kinetic saturation capacity of used adsorbent and the rate of adsorption or reactive removal of the contaminants. Adsorption capacity/kinetic saturation capacity depends on parameters such as temperature, concentration, bed geometry, flow rate of gas mixture, particle size and reactivity on the adsorbents surface [6]. Of these, flow rate of gas mixture was observed to be one of important parameters which affect the rate of adsorption prominently. In this regard, Jonas and Svirbely [7] and Wood and Moyer [8] have reported that at lower flow rates the rate of adsorption was low while the rate of adsorption increased with increasing air flow rates. Those observations were attributed to diffusion of vapor molecules and the same was found to be the rate limiting process. In order to understand this and the effect of above-mentioned parameters, Jonas and Svirbely [7] have utilized the modified Wheeler equation [9]. The Wheeler equation was derived from a continuity equation of mass balance between gas entering an adsorbent bed and the sum of gas adsorbed plus that penetrating through the bed and assumes that the rate controlling process is a first order and irreversible. The modified Wheeler equation is given below

$$t_b = (W_e/C_0 Q)[W - \rho_b Q/k_v \ln(C_0/C_x)]$$

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, which depends upon the weight, particle size and shape of the adsorbent can be determined experimentally. C_0/C_x is preselected depending upon the requirement. The value of C_0/C_x indicates the order of kinetics. According to Jonas et al., if $0 < C_0/C_x < 0.04$, the adsorption process follows the pseudo-first-order with respect to gas molecules, and if $0.04 < C_0/C_x < 0.65$, process follows second order and if $0.65 < C_0/C_x < 0.95$, the adsorption process follows the pseudo-first-order with respect to active sites [10–12].

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On the other hand, although the whetlerite carbon can provide sufficient protection against non-persistent agents, its efficiency against persistent agents such as sulphur mustard (HD) is not reported so far. Hence, we have attempted to understand the sulphur mustard vapor breakthrough behavior on whetlerite carbon by using modified Wheeler equation. For this purpose, we have tried to determine the adsorption parameters such as kinetic saturation capacity (W_e) and kinetic rate constant (k_v) of HD on whetlerite carbon by using modified Wheeler equation and also to find out the effect of various parameters such as bed length, flow rate, concentration and temperature on W_e and k_v. In addition, we also have tried to predict the service lives/breakthrough times of carbon bed (when used in filtration systems).

2. Experimental

2.1. Materials

Whetlerite carbon (1030 m^2/g, micro-pore volume 0.62 ml/g and W_0 is 0.7 ml/g) of particle size 12 × 30 BSS was procured from Active carbon India Ltd., Hyderabad. This carbon was degassed at 120 °C for 4 h and stored in air tight bottles.

2.2. Chemicals

Sulphur mustard (>99% GC) (HD) was obtained from Process Technology Development division of our establishment. Carbon tetrachloride (CCl_4) (99.5% purity), XAD-2 were obtained from Lancaster, England and the use of XAD-2 resin was described in Section 2.4.

2.3. Sulphur mustard gas mixture generation

The vapor breakthrough experiments were carried out with a gas generation assembly fabricated by Nucon Engineering (India). Fig. 1 shows the outline diagram of gas generation assembly. HD vapors were generated by using a slightly modified dynamic diffusion system (for low concentration) and purge method (for high concentration) [13]. Moisture free air was used for purging and dilution. Precautions were taken to avoid condensation by putting the heat tape around the gas lining. Concentration of gas mixture was measured by standard reported method, using XAD-2 resin [14]. The resin was thoroughly cleaned prior to its use, by repeated refluxing with water, methanol and CCl_4 sequentially in a Soxhlet assembly.

2.4. Vapor breakthrough experiments of HD

Vapor breakthrough experiments of HD were carried out in a column of 1.0 cm diameter using different bed heights of carbon, flow rates and concentrations of HD–air mixture, and temperature. The carbon was carefully filled to form bed while tapping the column in order to obtain reproducible packing density. The temperature of the carbon was maintained with circulating water around the column. The breakthrough of HD through the carbon bed was monitored for exit concentration (0.47 mg/m^3) with an

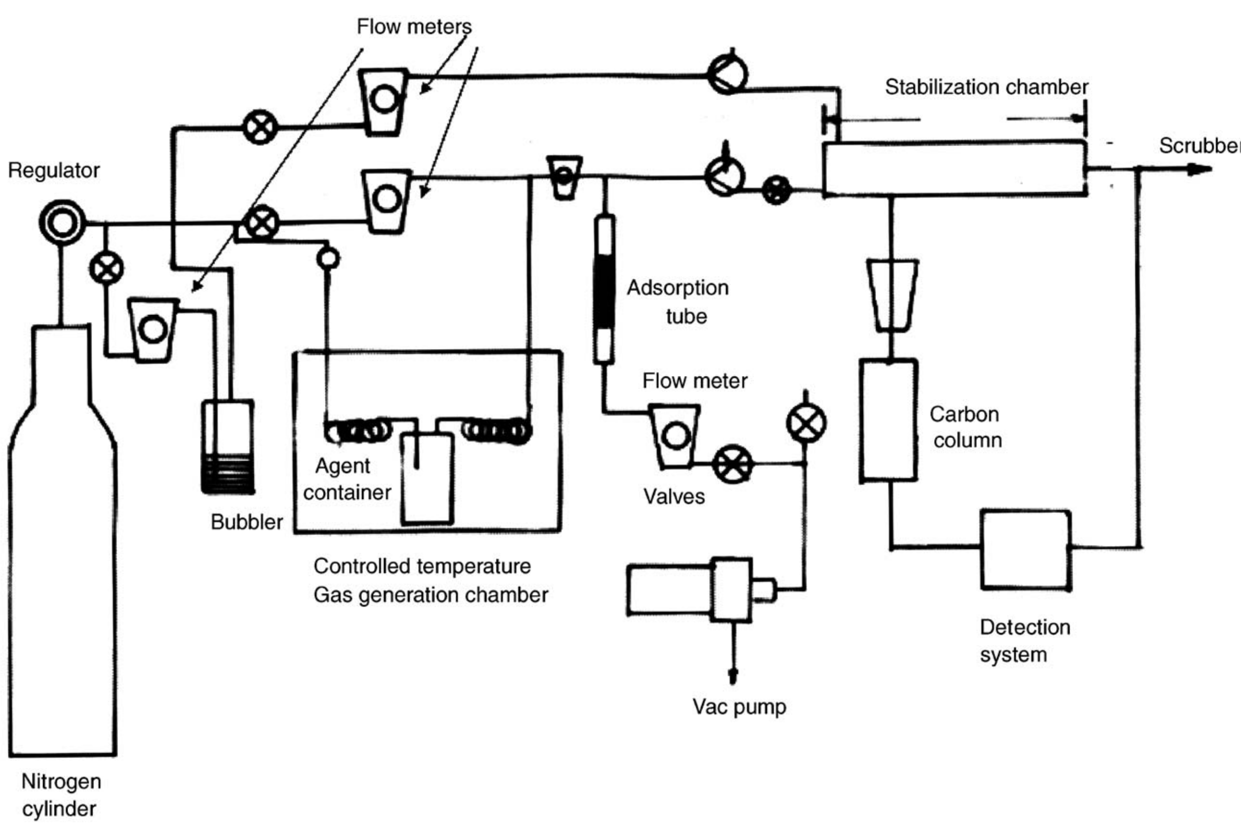

Fig. 1. Gas generation test rig for vapor breakthrough experiments on carbons.

instrument named AP2C containing flame photometric detector (GIAT industries, France).

2.5. Precautions to avoid exposure

Sulphur mustard (HD) is a well-known chemical warfare agent. It effects men and materials and has been documented as mutagenic, carcinogenic and cytotoxic [15]. Skin, eyes and respiratory track are the principle target organs and DNA is the most important molecular target of HD toxicity. 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. For every 5 min working environment was checked by chemical agent monitor (AP2C).

3. Results and discussion

Experimental values of HD vapor breakthrough time (t_b) at 0.47 mg/m^3 of exit concentration as a function of bed height were measured for whetlerite carbon at 0.600 mg/l and 1.0 lpm flow rate and they are illustrated in Fig. 2. In this case, breakthrough time increases from 2 to 38 min when bed height is increased from 0.75 to 1.15 cm and the same is shown in Fig. 2. It depicts that, at lower bed heights HD breaks through the carbon bed in seconds thus exhibiting insignificant breakthrough time values. It also indicates that, the carbon bed is integrated with operative part and a dead layer (h), which does not take part in adsorption. The value of dead layer is obtained from the above Fig. 2., and is determined to be 0.8 cm and the degree of utilization of the sorbent carbon is estimated to be 0.45 for 1.15 cm of the bed. This observation clearly indicates that, an optimum bed height is needed for getting meaningful breakthrough time values. Initially, the breakthrough time increases non-linearly with the bed height and then after an optimum height it shows a linear increase with the carbon bed height as depicted in the above plots and the same is consistent with the previous reported results by Shilov et al. [16] and Kubelka and coworker [17].

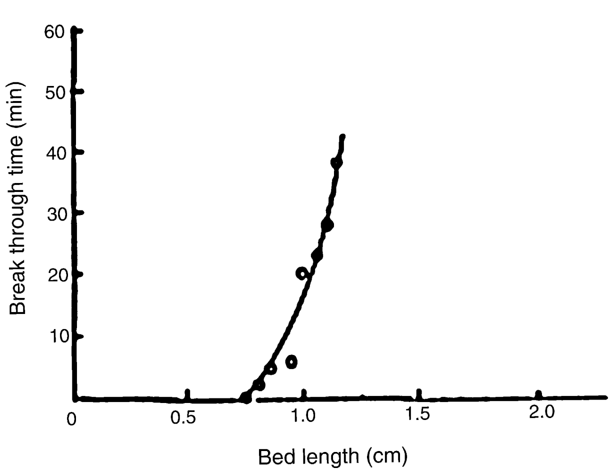

Fig. 2. Effect of bed length/bed height of whetlerite carbon on HD breakthrough time at 0.6 mg/l concentration, 1.0 lpm flow rate and 25 °C.

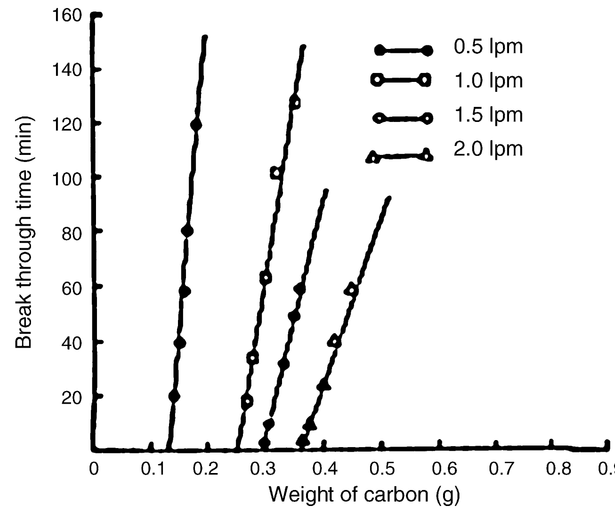

Fig. 3. Sulphur breakthrough time as a function of carbon weight (whetlerite carbon) at various flow rates, 0.25 mg/l concentration and 25 °C temperature.

In addition to this, we studied the effect of flow rate on kinetic saturation capacity (W_e) and rate constant (k_v) in the case of whetlerite carbon. For this purpose, we obtained experimental values of breakthrough time at various carbon weights by using various flow rates ranging from 0.5 to 2.0 lpm at 0.250 mg/l and 25 °C as shown in Fig. 3. The figure illustrates the linear curves indicating the pseudo-first-order reaction [12]. 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., $-\rho_b Q/k_v \ln(C_0/C_x)$ and the obtained results are furnished in Table 1. They illustrate that, the value of k_v increases steadily from 12311 to 20211 min^{-1} when the flow rate (Q) increases from 0.5 to 2.0 lpm in the case of whetlerite carbon whilst the value of kinetic saturation capacity (W_e) is found to be invariable. This observation indicates that rate limiting process is the diffusion of vapor 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 to 2.0 lpm. Though it does not change significantly, it clearly indicates that, at all the flow rates ranging from 0.5 to 2.0 lpm, the whetlerite carbon bed can hold/retain 0.3 g of HD from the contaminated vapor. From this data, it can be calculated that the carbon bed provides protection for 1200 min against 0.25 mg/l of HD at 1.0 lpm flow rate and 25 °C temperature. Thus, the above kinetics saturation capacity value is used to predict the service life of carbon bed against HD.

Table 1
Sulphur mustard kinetic saturation capacity and rate constant at various flow rates on whetlerite carbon at 0.25 mg/l and 25 °C

Flow rate (lpm)	Whetlerite	
	W_e (g/g)	k_v (min^{-1})
0.5	0.3	12311
1.0	0.3	14754
1.5	0.3	18756
2.0	0.3	20211

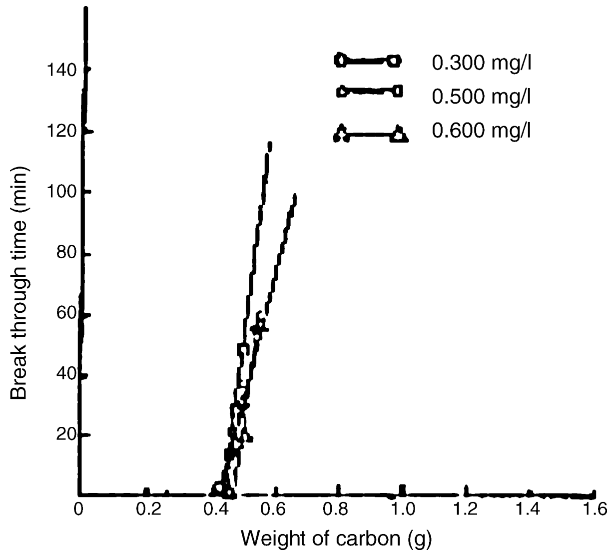

Fig. 4. Sulphur breakthrough time as a function of carbon weight (whetlerite carbons) at various concentrations, 1.0 lpm flow rate and 25 °C temperature.

Furthermore, the effect of concentration (Fig. 4) on k_v and W_e at 1.0 lpm flow rate and at 25 °C was also studied. The value of W_e is found to be 0.3 g/g at 0.3 mg/l and 0.6 mg/l concentrations of sulphur mustard vapor whilst the value of k_v is found to be changed from 8406 to 9380 min^{-1} (Table 2). These observations reveal that concentration in this range has no significant effect on the values of W_e and k_v.

These observations indicate that, the concentration variation within 0.3–0.6 mg/l has not affected either kinetic saturation capacity value or kinetic rate constant value significantly. Hence, it is 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. The kinetic saturation capacity value is found to be 0.3 g/g for whetlerite carbon at 1.0 lpm flow rate and at concentrations ranging from 0.3 to 0.6 mg/l. From these data, it is observed that the carbon bed (for all carbons) provides protection for 1000 min against 0.3 mg/l of HD, for 600 min against 0.5 mg/l of HD and for 500 min against 0.6 mg/l of HD at 1.0 lpm flow rate and 25 °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.

Finally, the effect of temperature (Fig. 5) on the values of W_e as well as k_v was also studied from 25 to 55 °C. The flow rate was maintained at 1.0 lpm and HD concentration at 0.5 mg/l and the obtained values of W_e and k_v are furnished in Table 3. They are found decreasing significantly with the increase of temperature which can be ascribed to the poorer adsorption of HD molecules at higher temperatures. From the obtained values of kinetic saturation capacity, the service lives/breakthrough times of carbon bed are predicted by calculations. From them, it is found that, breakthrough time/service life decreases from 600 to 200 min for whetlerite carbon when temperature is increased from 35 to 55 °C at 0.5 mg/l concentration and 1.0 lpm flow rate.

Table 2
Sulphur mustard kinetic saturation capacity and rate constant at various concentrations on whetlerite carbon at 1.0 lpm air flow rate and 25 °C

Concentration (mg/l)	Whetlerite	
	W_e (g/g)	k_v (min^{-1})
0.3	0.3	8406
0.5	0.3	7894
0.6	0.3	9380

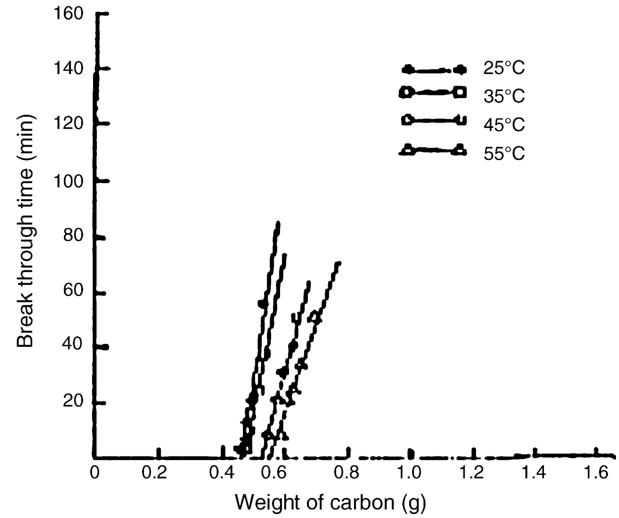

Fig. 5. Sulphur breakthrough time as a function of carbon weight (whetlerite carbon) at various temperatures, 0.5 mg/l concentration and 1.0 lpm flow rate.

Table 3
Sulphur mustard kinetic saturation capacity and rate constant at various temperatures on whetlerite carbon at 0.5 mg/l, 1.0 lpm and 25 °C

Temperature (°C)	Whetlerite	
	W_e (g/g)	k_v (min^{-1})
25	0.3	8231
35	0.3	8067
45	0.2	7304
55	0.1	6913

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

4. Conclusion

Breakthrough behavior of sulphur mustard vapor on whetlerite carbon has been studied by using modified wheeler equation. Effect of various parameters such as bed height, 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 height. 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 HD molecules on the surface of carbon. The concentration variation in between 0.3 and 0.6 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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