

Kinetics of Adsorption of Sulfur Mustard Vapors on Carbons Under Static Conditions

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Activated carbon of surface area 1250 m²/g was impregnated with 4% sodium hydroxide plus 3% Cr(VI) as CrO₃ with and without 5% ethylenediamine (EDA) and 5% ruthenium chloride by using their aqueous solutions. These carbons along with active carbon were studied for the adsorption of sulfur mustard (HD) under static conditions at 30 ± 1°C. Kinetics of adsorption have been studied by using the linear driving force model (LDF) and Fickian diffusion model. The kinetic parameters, such as equilibration constant/rate constant (k_a), equilibration capacity, diffusional exponent (n), and adsorbate-adsorbent interaction constant (K), have also been determined. The diffusional exponent being less than 0.5 indicates Fickian diffusion of HD molecules in the studied carbons. Chemical interaction also seems to be the second mechanism (although minor) and is involved in the HD uptake rate (the first being the Fickian diffusion). The adsorbate-adsorbent interaction constant did not vary significantly, indicating that probably HD chemically interacts to a small extent with the metal salts present on the surface of active carbon as impregnants. © 2005 American Institute of Chemical Engineers *AIChE J.* 52: 678–682, 2006

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Introduction

Microporous activated carbons have been widely used in filtration systems to remove chemical warfare (CW) agents of organic nature from contaminated air streams. Non-persistent CW agents (low boiling and low molecular weight), such as hydrogen cyanide, cyanogen chloride, phosgene, etc., have been removed successfully by whetlerite impregnated carbons from contaminated air streams. They react with the impregnants, such as copper, chromium, and silver, on the surface of active carbons.^{1–5} Therefore, much interest has been paid on impregnated carbons and their ability to remove non-persistent CW agents from contaminated air. However, not much work has been carried out on the adsorption and reaction of persistent (low volatile and high molecular weight) CW agents, such as sulfur mustard (2, 2'-dichlorodiethyl sulphide) and its simu-

lants.⁶ This CW agent is termed as “H” in its impure form, and the distilled/pure form of the same is known as HD. Regarding this, Karwacki et al.⁷ reported recently the adsorption, thermal desorption, and decomposition of HD on active carbon. Following this, Prasad et al.^{8,9} studied the reactions of sulfur mustard on impregnated carbons. Later, they¹⁰ studied the kinetics of adsorption and reaction of diethyl sulfide (a stimulant of HD) on carbons.

Most likely, the adsorption kinetics involves the diffusion in micropores with pore widths considerably smaller than the mean free path of the gas molecules at atmospheric pressure. Therefore, if one bears in mind the pore size distribution in carbons, the modeling of the kinetic process is difficult.¹¹ However, several researchers have used various models, such as Fickian,¹² linear driving force (LDF),¹³ a combined barrier resistance/Fickian diffusion model, and Langmuir type second order kinetics,¹⁴ to describe the adsorption kinetics in porous materials and carbon molecular sieves. Inspired by these, we have attempted to study the adsorption of HD on carbons, such as active carbon, NaOH/CrO₃/C, NaOH/CrO₃/EDA/C, and

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Table 1. Kinetic Parameters of Adsorption of Sulfur Mustard on Carbons

Type of Carbon	Equilibration Constant (k_a) (min^{-1})	Equilibration Capacity (mg)	Equilibration Time (min)	Diffusion Coefficient (cm^2/sec)	Diffusional Exponent (n)	Adsorbate-Adsorbent Interaction Constant (K)
Active carbon	0.50×10^{-5}	385	34560	4.20×10^{-9}	0.03	0.72
NaOH/CrO ₃ /C	2.80×10^{-5}	342	40320	2.40×10^{-8}	0.02	0.78
NaOH/CrO ₃ /EDA/C	1.73×10^{-5}	324	50400	1.48×10^{-8}	0.02	0.74
RuCl ₃ /C	1.66×10^{-5}	340	47520	1.42×10^{-8}	0.03	0.71

RuCl₃/C, under static conditions in order to understand the mode of diffusion of HD on carbons.

Experimental Procedures

Materials

Activated carbon of particle size 12×30 BSS, and of coconut shell origin, was obtained from Active Carbon India Ltd., Hyderabad. Sulfur mustard of purity more than 99% was obtained from Process Technology Development Division of our establishment. NaOH, RuCl₃·3H₂O, CrO₃, and EDA were obtained from E. Merck, India.

Impregnated carbons

Activated carbon was impregnated with aqueous solutions of NaOH (4%), Cr(VI) oxide (3% Cr(VI)), EDA (5%), and RuCl₃·3H₂O (Table 1). The incipient wetness technique was used for impregnation. These impregnation experiments on active carbon were carried out at room temperature by slowly mixing the above solutions and active carbon (carbons were not washed after impregnation). The obtained metal impregnated carbons were dried at 110°C for 6h and stored in airtight bottles. Metal impregnant contents were determined after extracting the carbons in the acidic and basic media by using the recently reported titrimetric methods.⁸⁻¹⁰

Surface area analysis

Impregnated and unimpregnated carbons were characterized for surface area (N₂ BET) using a Gemini 2765 surface area analyzer (Micrometrics, USA). The results are described in Table 2.

Adsorption

To carry out the adsorption of HD under static conditions, 1.0 g of carbon, either impregnated or unimpregnated, was taken in a glass assembly of 20 mm diameter and 5 cm length

with a perforated porcelain disk. The porcelain disk adsorbed HD insignificantly (0.1-0.2 mg) when a blank run was carried out without any adsorbent. The glass assembly containing a carbon bed (0.5-0.6 cm length) was placed in a desiccator containing 3.0 ml of HD in its bottom. The desiccator containing the adsorbent and adsorbate was kept at $(30 \pm 1^\circ\text{C})$ room temperature, and the vapor pressure of HD in the desiccator was not measured; presumably it was 0.09 mm Hg at $(30 \pm 1^\circ\text{C})$, and the remaining 759.91 mm Hg was due to atmospheric air.¹⁵ The gravimetric analyzer could not be used for this study due to the corrosive nature of the adsorbate. The kinetics of adsorption of HD on the carbons were studied by monitoring the weight gain every 10 min. The conventional manual weighing method was used to record the weight gain. The carbons were degassed at 120°C for 6h and then cooled over a desiccant (fused calcium chloride) before adsorption studies.

Several adsorption parameters, such as equilibration time, equilibration capacity, equilibration constant/rate constant diffusional exponent, and adsorbate-adsorbent interaction constant, were determined and are summarized in Table 2.

Results and Discussion

Adsorption of sulfur mustard (HD) was studied on active carbon, NaOH/CrO₃/C, NaOH/CrO₃/EDA/C, and RuCl₃/C systems. To illustrate the kinetics of adsorption, weight change was plotted vs. time, and the data are represented in Figure 1. Figure 1 describes the kinetics of adsorption of HD on active carbon, NaOH/CrO₃/C, NaOH/CrO₃/EDA/C, and RuCl₃/C systems. These adsorption curves were used to find out the values of equilibration capacity and equilibration time, which are described in Table 1. Figure 1 illustrates the similar shapes of HD adsorption uptake curves on active and impregnated carbons. Significant changes in shapes of HD uptake curves are observed in the case of impregnated carbons, indicating the different adsorption rate. These observations can be attributed to the fact that the impregnants influence both the rate and capacity by changing pore chemistry and geometry. Most likely, the adsorption process involves diffusion in micropores with pore widths considerably smaller than the mean free path of the gas molecules at atmospheric pressure. It is likely that processes such as molecular diffusion, Knudsen diffusion, surface diffusion, diffusion in micropores, and chemical interaction, could all make significant contributions to HD adsorption on the above mentioned carbons. Moreover, by keeping the pore size distribution of carbons in mind, modeling kinetics of HD adsorption is difficult.¹¹

In spite of this, we used two models for studying the adsorption kinetics. One is the LDF model and the other is the

Table 2. Surface Characteristics of Carbon Systems

S. No	Amount of Impregnant Loaded on Carbon (wt %)	Impregnated Carbon/Active Carbon	Surface Area (m^2/g) (N ₂ BET)	Micropore Volume (ml/g)
1	—	Active carbon	1250	0.68
2	NaOH (4%) CrO ₃ (Cr(VI) 3%)	NaOH/CrO ₃ /C	912	0.53
3	NaOH (4%) CrO ₃ (Cr(VI) 3%)	NaOH/CrO ₃ /EDA/C	855	0.5
4	EDA (5%) RuCl ₃ · 3H ₂ O	RuCl ₃ /C	950	0.52

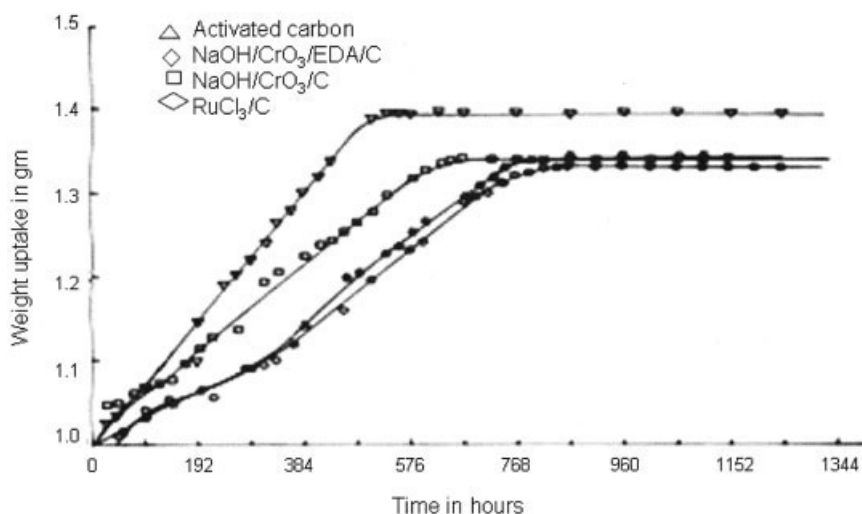


Figure 1. Kinetics of uptake of sulfur mustard on carbons.

Fickian diffusion model.¹² In order to study the adsorption kinetics by the LDF¹³ model, the following equation is used:

$$m_t = m + m_e(1 - e^{-k_d t}) \quad (1)$$

Here, m_t is weight of adsorbent with adsorbate at time t , m is initial weight of the adsorbent, m_e is equilibration capacity, and k_d is rate constant. The values of rate constant were calculated from the plots of $\ln(1 - m_t/m_e)$ against time t (Figure 2) and are given in Table 1. The curves deviate from linearity for all the carbons at a time greater than 300 hrs. Hence, the values of kinetic rate constant are computed using the slopes of the straight line (linear) portions. This deviation from linearity at longer intervals of time can be attributed to the wide pore size distribution of carbons. The values of rate constant are found to be of the order of 10^{-5} min^{-1} . In addition to this, the data depicted in Table 1 show that the rate constant values in the present case increase from $0.5 \times 10^{-5} \text{ min}^{-1}$ to $2.8 \times 10^{-5} \text{ min}^{-1}$, $1.7 \times 10^{-5} \text{ min}^{-1}$, and $1.6 \times 10^{-5} \text{ min}^{-1}$ for the active carbon, NaOH/CrO₃/C, NaOH/CrO₃/EDA/C, and RuCl₃/C systems, respectively.

Equilibration time values are also obtained from Figure 1; they increase from 34,560 min to 40,320, 50,400, and 47,520

min from active carbon to the NaOH/CrO₃/C, NaOH/CrO₃/EDA/C, and RuCl₃/C systems, respectively. This observation can be attributed to the impregnants, which work as barriers and effect the movement of the adsorbate molecules due to which the molecules take a longer time to occupy the available surface. Moreover, the impregnants react with the physically adsorbed HD molecules and lead to the formation of reaction products,⁸⁻¹⁰ which poison the surface of the impregnated carbon. These observations indicate that the impregnants influence the adsorption process by two ways, first by effecting the movement of adsorbate molecules¹⁶ and second, by chemical interaction. Owing to these, the shapes of the adsorption kinetic curves change for impregnated carbon relative to active carbon due to the difference in adsorption rate. However, the equilibration capacity/adsorption capacity decreases by increasing surface coverage or decreasing available surface¹⁷; thereby the rate constant should decrease from the original to impregnated carbon. But in contrast, the equilibration constant values and rate of adsorption values increase from active carbon to impregnated carbons. These observations can be ascribed to the extensive chemical interaction between impregnant materials and adsorbate, that is, HD. Although the chemical interaction is taking place, the adsorption kinetics are expected to be greatly influenced by the rate of diffusion and nature of diffusion of HD molecules. Further, if we assume the surface concentration of adsorbate (HD) to be constant and that diffusion is controlled by the concentration gradient through the granule, then the kinetics of the diffusion can be expressed by the Fickian diffusion model, and the same¹⁸⁻²⁰ is used to investigate the adsorption kinetics of HD.

For this purpose, we have plotted (Figure 3) $\log M_t/M_e$ against $\log t$ for active carbon to the NaOH/CrO₃/C, NaOH/CrO₃/EDA/C, and RuCl₃/C systems. The plots deviate from linearity for all the carbons at longer intervals of time. However, the diffusional exponent (n) values have been computed by using the slopes of straight lines (linear) portions at initial intervals of time. This deviation from linearity at longer intervals of time can be ascribed to the wide pore size distribution of carbons. The values of diffusional exponent are 0.03, 0.02, 0.02, and 0.03 for active carbon to the NaOH/CrO₃/C, NaOH/

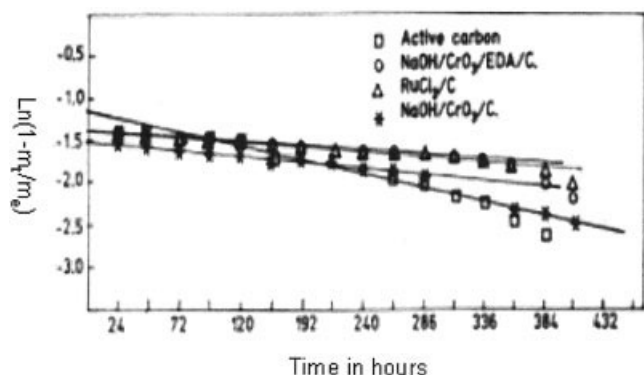


Figure 2. Kinetics of adsorption of sulfur mustard on carbons.

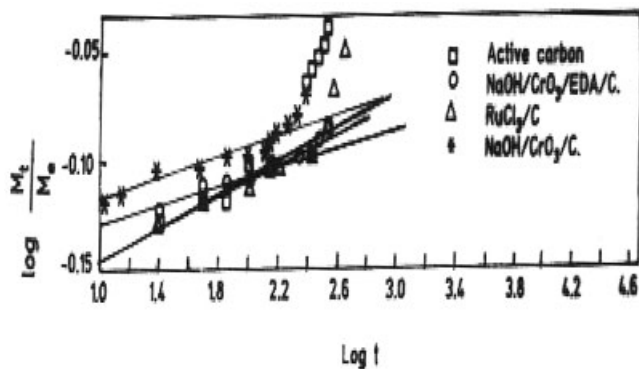


Figure 3. Kinetics of diffusion of sulfur mustard on carbons.

CrO₃/EDA/C, and RuCl₃/C systems. Being less than 0.5 indicates a Fickian mode of diffusion of HD on carbons; these values are included in Table 1. Subsequently, the values of the adsorbate-adsorbent interaction constant (K) were determined from the intercepts of straight lines on the Y-axis and found to be 0.72, 0.78, 0.74, and 0.71 respectively. The K values seem not to vary significantly; however, the extent of chemical reaction of HD with impregnated carbons is found to be significant (65-90%) in 96 hours.⁹ Though the extent of chemical interaction is large, even then there is no significant change in K values for impregnated carbons, indicating the invalidity of K values to predict the chemical interaction of the adsorbate with the impregnants present on the surface of the carbons.

In addition to this, the values of adsorption capacity were obtained from Figure 1 for active carbon to the NaOH/CrO₃/C, NaOH/CrO₃/EDA/C, and RuCl₃/C systems and are included in Table 1. As the surface area decreases for the carbons (Table 2), the value of equilibration capacity also decreases, indicating it to be dependent on surface area, porosity, and presumably the surface functional groups.²¹ The interaction between the adsorbate and functional groups of carbon may also result in varying adsorption capacities^{4,22}; this may be worth investigating further. Equilibration capacity decreases after impregnation of the active carbon due to decrease in surface area, indicating the changes in HD adsorption and desorption behaviors on active and impregnated carbons. That this is directly related to the porous structure of carbons is clear from the pore size distribution curves (Figure 4). Pore maxima in active carbon, NaOH/

CrO₃/C, NaOH/CrO₃/EDA/C, and RuCl₃/C systems are around 4.13 Å, 5.18 Å, 4.8 Å, and 5.2 Å, respectively (Figure 4), which indicates that these carbons are microporous in nature. They also indicate minute changes in microporosity of the impregnated carbons relative to the activated carbon, and this observation can be attributed to the effect of impregnants on the porous structure of carbon. Pore size distribution being wide in the studied carbons could not adversely affect the applicability of the LDF model at initial intervals of time; however, at longer intervals of time, the curves obtained by making use of the LDF model deviate from linearity, questioning its applicability. Nevertheless, the initial linear portions can be used to evaluate the adsorption parameters, which makes the LDF model persuasive. Moreover, pore size distribution also indicates that HD diffusion follows the Fickian mechanism as the maxima of pores in different carbons are around less than 10 nm.¹⁹ In addition to this, chemical interaction may be a second mechanism (although minor) that is involved in the HD uptake rate and influences the values of the equilibration constant and rate of adsorption.

Conclusion

Adsorption studies of HD on the carbon surface with and without metal impregnants under static conditions have resulted in the determination of various adsorption and diffusion parameters. HD adsorption kinetics follow Fickian diffusion along with chemical interaction (probably the second mechanism for HD uptake, the first being the simple Fickian diffusion). Equilibration constant/rate constant, equilibration time, diffusion coefficient, and diffusional exponent values are found to increase in the case of impregnated carbons when compared to unimpregnated carbon. The vapor pressure of HD (0.09 mm Hg at 30±1°C) is very low and due to this equilibration takes a longer time of duration. Analysis of the adsorbate-adsorbent interaction constant (K) for impregnated and unimpregnated carbons was also done. It indicates that, even though there is significant chemical interaction between impregnants and HD, the K values (adsorbate-adsorbent interaction constant) do not change significantly, indicating the invalidity of the K value for predicting the chemical interaction.

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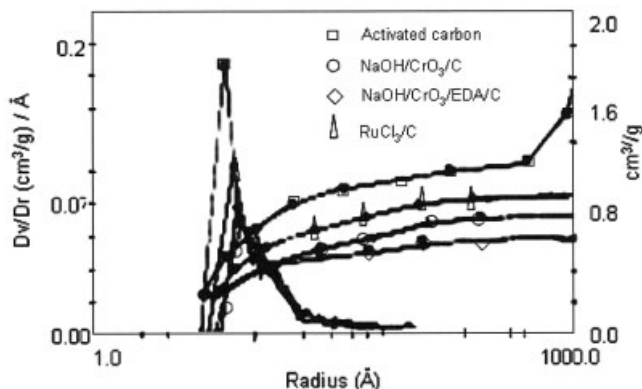


Figure 4. Pore size distribution of carbons.

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