

Breakthrough behavior of diethyl sulphide vapor on active carbon systems

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Abstract

Breakthrough behavior of diethyl sulphide vapors on carbon systems such as active carbon, NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C has been studied by using modified Wheeler equation and the same was used to calculate the pseudo-first-order rate constant (k_v) and kinetic saturation of capacity (W_e) values. Effects of various parameters such as bed height, air flow rate, concentration and temperature on the above parameters have also been studied. Rate constant was found to be increasing with air flow rate, while W_e was found to be invariable. Both k_v and W_e decreased with the increase in temperature, however, no significant effect on W_e and k_v was observed due to concentration change. The values of kinetic saturation capacity were used to predict the service lives/breakthrough times of carbon beds (when used in filtration systems).

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1. Introduction

Vapor breakthrough behavior of carbon beds challenged with the air containing toxic chemicals is of great interest in connection with respiratory protection against hazardous chemicals [1–2]. Moreover, this carbon is also used as a catalyst carrier. One such carbon based catalyst is ASC (A: Cu(II), S: Ag(I), C: (Cr(VI)) whetlerite, i.e., activated carbon impregnated with salts of Cu(II), Cr(VI) and Ag(I) [3–4]. Whetlerite carbon has been widely used in nuclear, biological and chemical (NBC) filtration systems for the removal of non-persistent chemical warfare agents such as hydrogen cyanide (HCN), phosgene and cyanogens chloride [5]. Whereas, the efficiency/fate of such impregnated carbons against persistent agents such as sulphur mustard (HD) has not been reported so far. In this regard, Damico [6] studied chemical degradation of HD and its analogues on carbon supports. Similar kind of carbons those have reactivity towards sulphur mustard have been prepared by Prasad and Singh [7–8]. This type of reactive carbon can be utilized in NBC filtration systems for the reactive removal of persistent chemical warfare agents.

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 [9]. Adsorption capacity/kinetic saturation capacity depends on parameters such as temperature, concentration, and bed geometry, flow rate of gas mixture, particle size and reactivity on the adsorbents surface. Of these, flow rate of gas mixture is observed to be one of the important parameters and it affects the rate of adsorption. In this regard, Jonas and Svrbely [10] and Wood and Moyer [11] have reported that, at lower flow rates, the rate of adsorption was low while the rate of adsorption was found to be increasing with the increasing air flow rates. Those observations were attributed to the 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, Wheeler [12] have utilized the modified Wheeler equation. 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 assumed that the rate controlling process was of first order and irreversible [13]. The modified Wheeler equation is given below:

$$t_b = \left(\frac{W_e}{C_0 Q} \right) \left[W - \frac{\rho_b Q}{k_v \ln(C_0/C_x)} \right]$$

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 den-

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sity 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_x/C_0 is preselected depending upon the requirement. The value of C_x/C_0 indicates the order of kinetics. According to Jonas and Rehrmann, if $0 < C_x/C_0 < 0.04$, the adsorption process follows the pseudo-first-order with respect to gas molecules, and if $0.04 < C_x/C_0 < 0.65$, process follows second order and if $0.65 < C_x/C_0 < 0.95$, the adsorption process follows the pseudo-first-order with respect to active sites [14–15].

On the other hand, persistent chemical warfare (CW) agents such as HD, are highly toxic and difficult to handle. Hence, it is preferable to use the analogues of HD, which are less toxic for studying their breakthrough behavior on carbon beds. Diethyl sulphide (DES) is one of such chemicals which has similar structure like that of HD and also has bad smell and eye irritating nature. Hence, breakthrough behavior of diethyl sulphide vapor on carbons is worth studying. 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 DES on carbons 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 beds of active carbon, NaOH/CrO₃/C,

NaOH/CrO₃/EDA/C and RuCl₃/C (when used in filtration systems).

2. Experimental

2.1. Materials

Active carbon of surface area 1250 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. NaOH, RuCl₃·3H₂O, CrO₃ and ethylene diamine (EDA) were obtained from E Merck, India Pvt. Ltd. Diethyl sulphide (99%) was purchased from Fluka, USA and was used without further purification. Carbon tetrachloride (CCl₄) (99.5% purity), XAD-2 were obtained from Lancaster, England and the use of XAD-2 resin was described in Section 2.3.

2.2. Characterization

Carbons were characterized for their surface area by N₂ BET using Sorptomatic 1990 of Carlo Erba, Italy and results were published elsewhere [7].

2.3. Diethyl sulphide gas mixture generation

The vapor breakthrough experiments were carried out with a gas generation assembly fabricated by Nucon Engineering

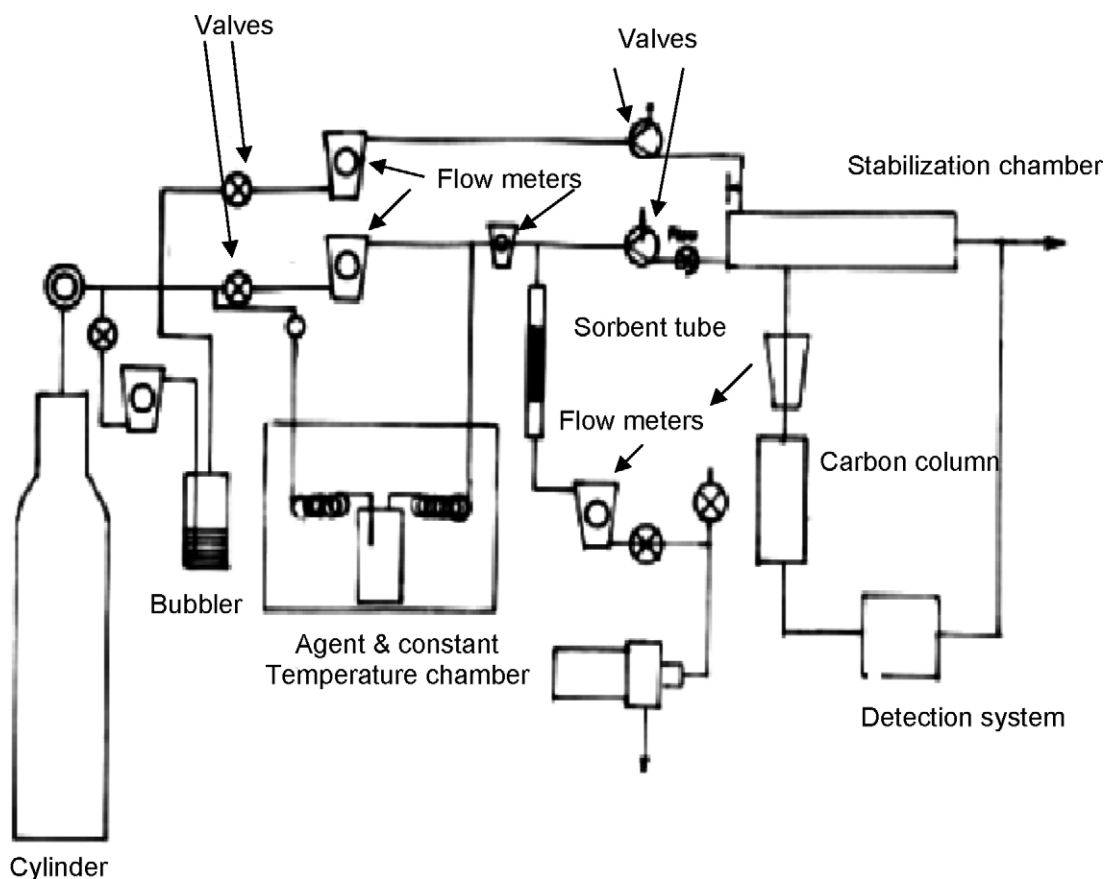


Fig. 1. Gas generation test rig for vapor breakthrough experiments on carbons.

(India). Fig. 1 shows the outline diagram of gas generation assembly. DES vapors were generated by using a slightly modified dynamic diffusion system (for low concentration) and purge method (for high concentration) [16]. 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 [17]. 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 DES

Vapor breakthrough experiments of DES were carried out in a column of 1.0 cm diameter using different bed heights of carbons, flow rates and concentrations of DES–air mixture, and temperature. The temperature of the carbon was maintained with circulating water around the column. The breakthrough of DES through the carbon bed was monitored for exit concentration (0.47 mg/m^3) with an instrument named AP2C containing flame photometric detector (GIAT Industries, France).

2.5. Precautions to avoid exposure

DES is an analogue of HD and it has a very pungent bad smell. It irritates the eye when exposed to it. Experimental set up 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 vapor breakthrough time (t_b) as a function of bed height for diethyl sulphide were measured for active carbon, $\text{NaOH/CrO}_3/\text{C}$, $\text{NaOH/CrO}_3/\text{EDA/C}$ and RuCl_3/C systems. Fig. 2 shows the plots of breakthrough time versus bed height for active carbon, $\text{NaOH/CrO}_3/\text{C}$, $\text{NaOH/CrO}_3/\text{EDA/C}$ and RuCl_3/C systems at 1.857 mg/l DES concentration ($C_x/C_0 = 0.00025$) and 1.0 lpm flow rate. In the case of active carbon, breakthrough time increases from 4 to 24 min. Whereas, in $\text{NaOH/CrO}_3/\text{C}$ system, breakthrough time increases from 4 to 21 min when bed height increases from 1.75 to 1.95 cm. And for $\text{NaOH/CrO}_3/\text{EDA/C}$ system breakthrough

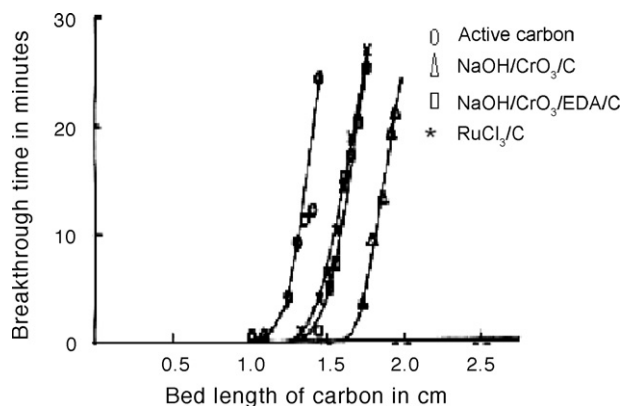


Fig. 2. Effect of bed length/bed height of carbons on diethyl sulphide breakthrough time at 1.857 mg/l concentration, 1.0 lpm flow rate and 25 °C.

time increases from 1 to 25 min when bed height is increased from 1.45 to 1.75 cm. RuCl_3/C also behaves in a similar manner. In addition to this, at lower bed heights DES breaks through the carbon beds in seconds thus exhibiting insignificant breakthrough time values. 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. [18] and Kubelka and co-worker [19]. By using the linear portions of the curves it is possible to predict the breakthrough time of carbon bed or service life of the respirator cartridge containing the same.

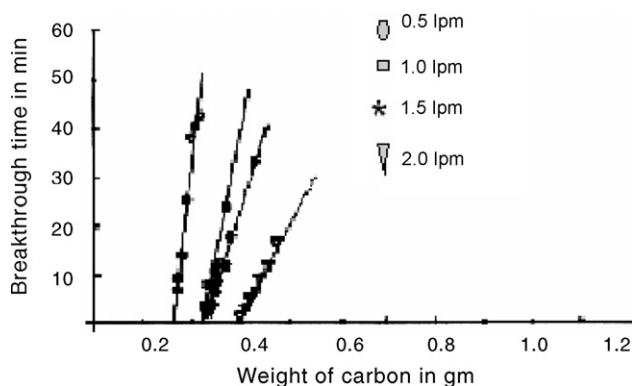


Fig. 3. Diethyl sulphide breakthrough time as a function of carbon weight (active carbon) at various flow rates, 1.857 mg/l concentration and 25 °C temperature.

Table 1
Inert saturation capacity and rate constant values for diethyl sulphide at various flow rates on carbons at 1.857 mg/l and 25 °C

Flow rate (lpm)	Active carbon		$\text{NaOH/CrO}_3/\text{C}$		$\text{NaOH/CrO}_3/\text{EDAC}$		RuCl_3/C	
	W_e (g/g)	k_v (min^{-1})	W_e (g/g)	k_v (min^{-1})	W_e (g/g)	k_v (min^{-1})	W_e (g/g)	k_v (min^{-1})
0.5	0.4	6172	0.4	4061	0.4	5186	0.4	8833
1.0	0.4	8918	0.4	6599	0.4	9294	0.4	9816
1.5	0.4	12811	0.4	9050	0.4	10372	0.4	13250
2.0	0.4	13622	0.4	11415	0.4	11855	0.4	17098

In order to study the effect of flow rate on kinetic saturation capacity (W_e) and rate constant (k_v), t_b values were obtained from the breakthrough experiments for different carbon weights using different flow rates ranging from 0.5 to 2.0 lpm at 1.857 mg/l (DES concentration) and 25 °C. Fig. 3 shows the plot of breakthrough time versus carbon weight at various flow rates for activated carbon. Including this plot, in all the cases of NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C, plots of breakthrough time versus carbon weight at various flow rates have given a straight line indicating the adsorption process to be the pseudo-first-order reaction. The values of kinetic saturation capacity (W_e) were calculated from slope, i.e., (W_e/C_0Q) and rate constant by intercept i.e., $[\rho_b Q/k_v \ln(C_0/C_x)]$ and the obtained results are furnished in Table 1. In the case of active carbon, when the flow rate is increased from 0.5 to 2.0 lpm rate constant increases non-linearly from 6172 to 13622 min⁻¹, whereas, kinetic saturation capacity (W_e) is found to be invariable. NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C also behave in similar a manner. Rate constants increase from 4061 to 11415 min⁻¹, 5186 to 11855 min⁻¹ and 8833 to 17098 min⁻¹, respectively. The values of kinetic saturation capacity do not change significantly. This observation indicates that rate limiting process is the diffusion of vapor molecules on the surface of carbon granules. Most likely, the external diffusion (bulk), internal (inter particle) diffusion and surface diffusion can collectively be manifested as the rate limiting process. Moreover, the value of kinetic saturation capacity is found to be 0.4 g/g for all the carbons 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 carbon bed can hold/retain 0.4 g of DES from the contaminated vapor. From this data, it can be calculated that the carbon bed provides protection for 215 min against 1.857 mg/l of DES 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 DES.

On the other hand, a few measurements with vapor concentration of 0.980, 1.857 and 4.0 mg/l were also made. Rate constant and kinetic saturation capacity for diethyl sulphide were computed by making use of the modified Wheeler equation. Kinetic saturation capacity (W_e) of diethyl sulphide on active carbon system (Fig. 4) for concentration 0.980–4.0 mg/l were obtained as 0.4–0.4 g/g and rate constant values varied from 9105 to 9604 min⁻¹. NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C also behave in a similar manner and the results are shown in Table 2. However, small variations in k_v values may be due to small changes in flow rates. These observations indicate that, the

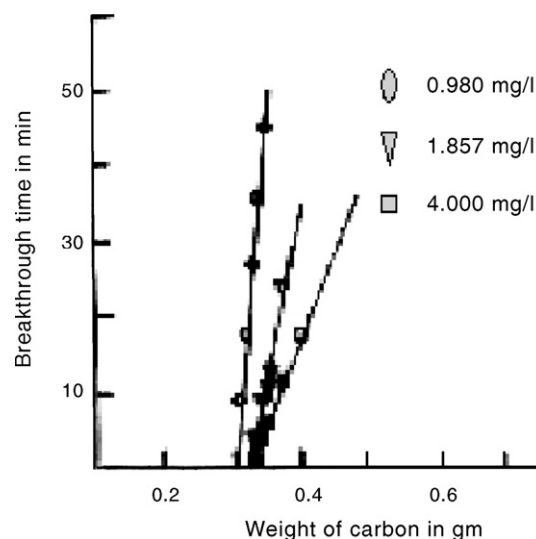


Fig. 4. Diethyl sulphide breakthrough time as a function of carbon weight (active carbons) at various concentrations, 1.0 lpm flow rate and 25 °C temperature.

concentration variation within 0.98–4.0 mg/l has neither effected kinetic saturation capacity value nor kinetic rate constant value significantly. Hence, it is possible to predict the breakthrough time/service life of the beds of above carbons at the above concentrations by using the kinetics saturation capacity values. The kinetic saturation capacity value is found to be 0.4 g/g for all the carbons at 1.0 lpm flow rate and at concentrations ranging from 0.98 to 4.0 mg/l. From these data, it is observed that the carbon bed (for all carbons) provides protection for 408 min against 0.98 mg/l of DES, for 215 min against 1.857 mg/l of DES and for 100 min against 4 mg/l of DES 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.

Moreover, the effect of temperature on W_e and k_v was also studied by varying temperature from 35 to 55 °C and the flow rate was 1.0 lpm and the DES concentration maintained was 1.857 mg/l. Breakthrough time as a function of carbon weight was plotted for active carbon, NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C systems for various temperatures and the same for active carbon is shown in Fig. 5. The kinetic saturation capacity values and rate constant values for diethyl sulphide for the above carbons at various temperatures are provided in Table 3. Rate constant and kinetic saturation capacity values markedly decrease due to poorer adsorption at higher temperatures. From the obtained values of kinetic satu-

Table 2

Kinetic saturation capacity and rate constant values for diethyl sulphide at various concentrations on carbons at 1.0 lpm and 25 °C

Concentration (mg/l)	Active carbon		NaOH/CrO ₃ /C		NaOH/CrO ₃ /EDAC		RuCl ₃ /C	
	W_e (g/g)	k_v (min ⁻¹)	W_e (g/g)	k_v (min ⁻¹)	W_e (g/g)	k_v (min ⁻¹)	W_e (g/g)	k_v (min ⁻¹)
0.980	0.4	9105	0.4	6603	0.4	9262	0.4	9843
1.857	0.4	8918	0.4	6599	0.4	9294	0.4	9814
4.0	0.4	9604	0.4	6593	0.4	9455	0.4	9847

Table 3
Kinetic saturation capacity and rate constant values for diethyl sulphide at various temperatures on carbons at 1.0 lpm flow rate and 1.857 mg/l concentration

Temperature (°C)	Active carbon		NaOH/CrO ₃ /C		NaOH/CrO ₃ /EDAC		RuCl ₃ /C	
	W _e (g/g)	k _v (min ⁻¹)	W _e (g/g)	k _v (min ⁻¹)	W _e (g/g)	k _v (min ⁻¹)	W _e (g/g)	k _v (min ⁻¹)
35	0.30	8623	0.27	5608	0.19	7290	0.40	6739
45	0.20	7408	0.17	5590	0.18	6562	0.27	6245
55	0.17	7046	0.1	5241	0.12	5965	0.17	5962

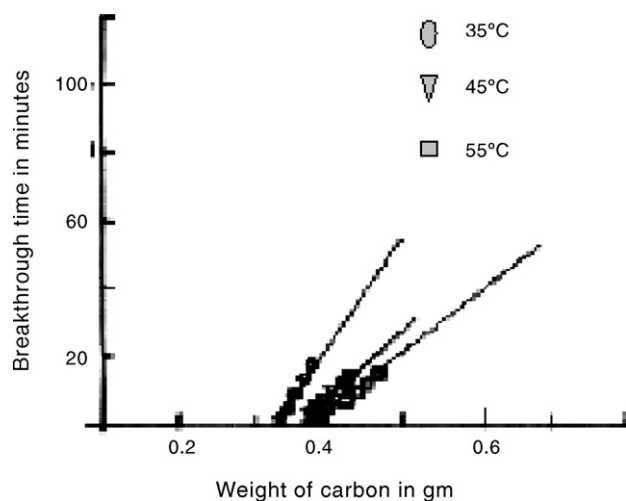


Fig. 5. Diethyl sulphide breakthrough time as a function of carbon weight (active carbon) at various temperatures, 1.857 mg/l concentration and 1.0 lpm flow rate.

ration 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 161 to 91 min for active carbon when temperature is increased from 35 to 55 °C, it decreases from 145 to 53 min for NaOH/CrO₃/C system when temperature is increased from 35 to 55 °C, it decreases from 102 to 64 min for NaOH/CrO₃/EDA/C system when temperature is increased from 35 to 55 °C and it decreases from 215 to 91 min for RuCl₃/C system when temperature is increased from 35 to 55 °C. These observations reveal that, in addition to the kinetic saturation capacity values, the breakthrough time/service life values also are ruined at higher temperatures due to poorer adsorption of DES.

From the above studies and the results obtained, it is understood that the above carbons are capable of holding DES vapors and suitable for providing sufficient respiratory protection against the same. Hence, it is also expected that the same carbons can provide sufficient protection against HD and can be used in NBC filtration systems. However, the breakthrough experiments with the real agent, HD can provide us with enough information which will be useful for confirming the fact that the above carbons can be used without any problem in NBC filtration systems for protection against deadliest agents such as HD.

4. Conclusion

Breakthrough Behavior of diethyl sulphide vapors on active carbon, NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C was

studied. 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 when the flow rate is increased and the value of kinetic saturation capacity is found to be invariable. This indicates that the rate limiting process is controlled by diffusion of DES molecules on the surface of carbon. The concentration variation in between 0.3 to 0.6 mg/l has no significant effect on kinetic saturation capacity or rate constant. Temperature affects the W_e and k_v values adversely due to poorer adsorption at higher temperatures.

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