

# Methyl Bromide Recovery on Activated Carbon with Repeated Adsorption and Electrothermal Regeneration

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Methyl bromide is commonly used as a postharvest fumigant. Because it has been identified as an ozone-depleting substance, production of methyl bromide has been targeted for phaseout. Methyl bromide readily adsorbs onto activated carbon. In situ carbon regeneration is being investigated as a means of decreasing the expense of methyl bromide recovery. Heating by passing an electrical current through an adsorbent bed is an efficient means of regenerating carbon and can be performed in the same vessel in which adsorption occurs. Carbon adsorbs roughly 10% of its weight in methyl bromide and can be repeatedly regenerated using electrothermal desorption. Methyl bromide desorbed in this manner is easily condensed at moderate temperatures. Carbon was submitted to 12 adsorption/regeneration cycles and then compared with virgin samples in terms of adsorption equilibria and adsorption rate. The regenerated carbon experienced no loss of mass and exhibited nearly the same capacity as the fresh samples.

## Introduction

The insecticidal properties of methyl bromide were first reported by LeGoupil.<sup>1</sup> Methyl bromide is widely used as a fumigant because of its beneficial properties. It is able to penetrate sorptive materials, but because of its low boiling point, low water solubility, and ability to disperse in air, it leaves little residue. Methyl bromide can be used against both insects and bacteria. Few insects have developed resistance to it.<sup>2</sup>

In 1996, world methyl bromide consumption was 68 424 metric tons, roughly one-third of which occurred in United States.<sup>3</sup> Most of the methyl bromide produced is used for pretreating soil in preparation for planting. A lesser, but still significant, amount is used for warehouse-type fumigations.

Citing the results of atmospheric model simulations, which suggest that methyl bromide might be a significant ozone depleter,<sup>4</sup> the Montreal Protocol<sup>5</sup> targeted methyl bromide for phaseout by both developing and developed countries. According to the international agreement, 1995 production was to be decreased to 1991 levels. There would be subsequent step decreases in production in the years 1999, 2001, 2003, and 2005. Phaseout would be completed in the year 2005, with the exemption of production for certain uses deemed essential, such as preshipment and quarantine fumigations. In 1998, an amendment to the Congressional Appropriations Bill brought the Clean Air Act<sup>6</sup> into alignment with the Montreal Protocol.

Around the world, organizations such as the United States Department of Agriculture (USDA) are investigating alternatives to methyl bromide. Unfortunately, no chemical has been found that works as well as methyl bromide at controlling such a wide spectrum of pests at such low dosage levels. This leads to the question: Can the depletion of ozone by methyl bromide be prevented by means other than banning its production? The answer is yes. Uses of methyl bromide where

the chemical is contained in a closed area, such as chamber fumigations, readily lend themselves to engineering solutions.

One solution is adsorption onto activated carbon. Methyl bromide readily adsorbs onto peat-, shell-, and coal-based carbons.<sup>7</sup> Adsorption of about 1 kg of methyl bromide per 10 kg of carbon can be achieved at methyl bromide concentrations in air encountered during commodity fumigations. Capital expenses for such processes are relatively small and include the costs of the original load of carbon, fans, and ductwork leading from the fumigation chamber to the container housing the carbon. This container could alternatively be located inside the chamber itself, thus requiring no ventilation ductwork. Periodically, the carbon would be transported to an industrial reactivation facility. In conventional practice, the carbon would be heated in a furnace to roughly 900 °C, causing the methyl bromide to desorb.<sup>8</sup> The methyl bromide would then be incinerated, and the exhaust would be sent to a scrubber. The liquid effluent from the scrubber would be disposed of at a disposal facility. It should be noted that, for a specific application, condensation is less costly than incineration with scrubbing. However, industrial reactivation facilities must generally deal with a wide variety of adsorbed chemicals. For such facilities, condensation is not a practical alternative. In addition, incineration also requires costly special permits.

The cost for reactivation including transportation is on the order of \$1.32/kg of carbon. An incineration process might burn off 10% of the carbon, which would need to be replaced at a cost of \$2.20/kg of carbon. Say, for example, that 1 kg of methyl bromide is collected on 10 kg of carbon; reactivating that carbon would cost \$1.32/kg × 10 kg = \$13.20. On the order of 1 kg of carbon would be destroyed during the reactivation and would need to be replaced at the cost of \$2.20. Thus, the operating expense for this process is about \$15.40 per kg of methyl bromide initially adsorbed. The range of methyl bromide usage is roughly between 50 kg/month for a small user and upward of 500 kg/month for a large user.

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A relatively new method of carbon regeneration is the conduction of an electric current directly through the carbon bed to heat the carbon through electrical resistance (Joule) heating. This method is termed "electrothermal regeneration." Over the past 25 years, more than 15 patents have been issued for inventions concerning electrothermal regeneration of various adsorbents (see, for example, refs 9–12). The company Activated Carbon Projects L.L.C. was formed to commercialize patents developed by DuPlessis and to customize processes utilizing activated carbon. These inventions lower equipment costs, improve efficiency, and simplify system requirements, thereby decreasing the expertise required to operate such systems.

Relatively few investigations into electrothermal carbon regeneration have been reported in the literature. Marfin and Shumyatskii<sup>13</sup> investigated heating characteristics of carbon beds during direct electrical heating in the absence of an adsorbate. In addition to demonstrating the efficacy of Joule heating, they found that the resistivity of the bed decreased when the bed was compacted. Stankiewicz and Schreiner<sup>14</sup> conducted a similar investigation employing two carbon beds (368 and 1007 g) containing adsorbed water. Prior to and during electric heating, the adsorbent bed was placed under a vacuum. They presented a plot of the percent of water desorbed versus time during the regeneration but did not discuss how this quantity was determined. Experiments were carried out until the adsorbed water was completely removed. They found improved desorption with direct electrical heating as compared with indirect electrical heating or heating using a flowing gas phase.

Petkovska et al.<sup>15</sup> investigated the electrothermal desorption of 111-trichloroethane ( $T_{111}$ ) from 6 g of carbon fibers. They flowed nitrogen through the bed during desorption and then measured the concentrations of  $T_{111}$  in the effluent. Presumably, these concentration profiles in time were integrated to show removal of roughly 60–90% of the initial  $T_{111}$ . It was noted that, during their experiments, the electrical resistivity of the bed decreased with increasing temperature. Petkovska et al. and others have attributed this phenomenon to semiconductivity. It seems possible that the greater contact pressure that occurs as the bed expands with increased temperature might also play a role in decreasing resistivity.

Petkovska and Mitrovic<sup>16</sup> presented a heterogeneous, one-dimensional model of the adsorption column reported by Petkovska et al.<sup>15</sup> Petkovska and Mitrovic<sup>17,18</sup> presented microscopic-level desorption models of the desorption process.

Baudu et al.<sup>19</sup> conducted desorption experiments of dichloromethane, 111-trichloroethane, toluene, and tetrachloroethylene from granular activated carbon and activated carbon fibers. They used a technique similar to that of Petkovska et al.,<sup>15</sup> using air as a purge gas during regeneration and measuring concentrations in the effluent, but did not note a resulting efficiency for adsorbate removal. They did report that, during Joule heating of carbon, a greater fraction of the total adsorbed mass was released at higher concentrations when the power introduced to the carbon bed was greater and when the air flow rate was lower. They also reported that the bed resistivity decreased with increased adsorbed moisture.

Brasquet and Le Cloirec<sup>20</sup> investigated the adsorption

of a variety of chemicals onto granular activated carbon and activated carbon cloth. Their subsequent use of both Joule heating and induction heating to desorb these chemicals was noted but was not discussed in detail.

Thermoelectric heating is sufficiently simple that it could be utilized for on-site carbon regeneration by a nonchemically oriented company. The desorbed methyl bromide could then be recovered by condensation.

Although in situ regeneration of carbon would require a greater capital investment by the fumigator, for larger users, the decrease in operating costs could lead to a greater investment return.

This leads to a question about the relative efficacy of in situ regeneration using electrothermal heating as compared to conventional reactivation at an industrial facility. Although full activity can be restored by reactivation at an industrial facility, more than 10% loss in carbon mass could be expected.

Therefore, an objective of the present research was to compare the activity of carbon that had undergone multiple (12) adsorption/regenerations cycles to the activity of virgin carbon (which is assumed to have the same physicochemical characteristics as reactivated carbon). The multiply regenerated carbon and virgin carbon were analyzed with respect to adsorption equilibria and effective adsorption rate for the range of temperatures and methyl bromide concentrations experienced during venting of agricultural chamber-type fumigations.

The objective of the present research is to determine the feasibility of on-site adsorption and regeneration. This includes determining that a single load of carbon can undergo repeated cycles of methyl bromide adsorption and regeneration without substantial loss of activity. This also includes determining the effects of methyl bromide electrothermal desorption on its subsequent condensation.

## Materials and Methods

**Adsorption/Regeneration.** The adsorbent chosen for investigation was activated coconut shell carbon (CC-601, Westates Carbon). Previous experimental results showed that coconut shell carbon displays excellent adsorptivity for methyl bromide as compared to other carbons and other adsorbents (Leesch et al.).<sup>7</sup>

Commodity fumigations using 16.5 ppt (parts per thousand, volumetric) methyl bromide (64 g/m<sup>3</sup> or 4 lb/1000 ft<sup>3</sup>) are typical. Following an industrial-scale fumigation, as the contaminated air is evacuated from the chamber and is replaced by fresh air, the chamber approximates a well-mixed vessel. Ideally, the methyl bromide concentration for a chamber during aeration is given by eq 1.

$$y = y_0 \exp\left(\frac{-tF}{V}\right) \quad (1)$$

where  $y$  is the concentration,  $F$  is the volumetric flow rate, and  $V$  is the chamber volume. As a first approximation, the mass of a chemical that will adsorb onto a given mass of adsorbent is proportional to the concentration of that chemical in the gas stream flowing through the bed. From eq 1, it is seen that the concentration of methyl bromide in the gas stream decreases with time. If a theoretical fumigation uses a total of 1 kg of methyl bromide for a 16-m<sup>3</sup> chamber (typical of actual concentrations used in practice),

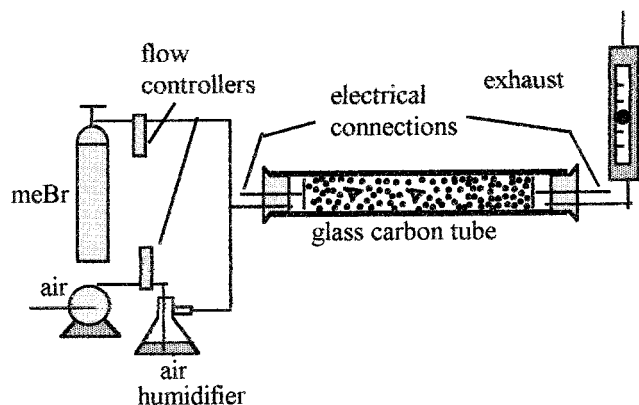


Figure 1. Schematic for methyl bromide adsorption.

although 10 kg of carbon might be sufficient to adsorb 0.98 kg of this methyl bromide, an infinitely long carbon bed would be required to adsorb 100% because the gas-phase concentration would decrease to zero. Therefore, to maximize methyl bromide uptake on the carbon bed, the flow is discontinued to the adsorber when the concentration in the ideal chamber reaches 0.2 ppt. For a flow rate of one-seventh of the chamber volume per minute, the time average concentration flowing to the adsorber would be 3.7 ppt. This concentration was used as a basis for evaluating the performance of the carbon bed.

The experimental setup for adsorbing methyl bromide onto carbon is shown in Figure 1. Two columns were employed during the experiments. The columns were fabricated from a tube (3.7 cm i.d.) of heavy-walled Pyrex (Corning, Inc., Corning, NY). The bed lengths of the columns were 23.4 and 86.7 cm. The shorter and longer tubes held 71 and 454 g of carbon, respectively. Silicone stoppers were placed in the ends of each tube.

A thermometer inserted between the tube and insulation measured temperatures to 150 °C during heating. Two 3.18-mm ( $1/8$ -in.) copper–constantan thermocouples (T-type) were inserted from one end to measure temperatures at the axial center and midway between the center and the end of the column following heating. The axial center was chosen for the first thermocouple because it is the hottest location in an ideal bed assuming convective heat transfer at the ends. The second position was chosen to obtain an estimate of the temperature profile in the bed. We considered that measurements nearer the electrodes would be suspect. Temperatures from the thermocouples were extrapolated to the time at which power was discontinued to determine the maximum temperature of the bed. The electrical leads were stainless steel washers held with nuts on machine screws that were passed through the respective silicone stoppers.

The air and methyl bromide flow rates were maintained by Sierra 840 series mass flow controllers (Sierra Instruments, Inc., Monterey, CA). Air flow was 3.5 standard L/min (slm) (5.4 cm/s). In industrial practice, superficial velocities on the order of 30 cm/s or higher would be used. Methyl bromide was delivered to provide roughly 3.7 ppt. Because water vapor can compete with methyl bromide for adsorption sites, the effect of humidity on methyl bromide adsorption was also investigated. The humidity was varied by bubbling the air stream through water (see Figure 1) or by flowing it through a desiccant chamber (molecular sieve 3A, Silica Gel Desiccant Products Co., Inglewood, CA). All temperatures

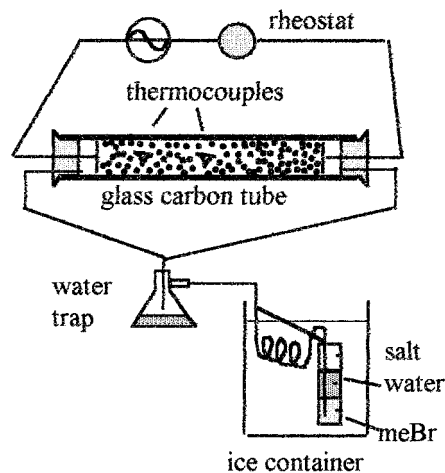


Figure 2. Schematic for carbon regeneration/methyl bromide desorption.

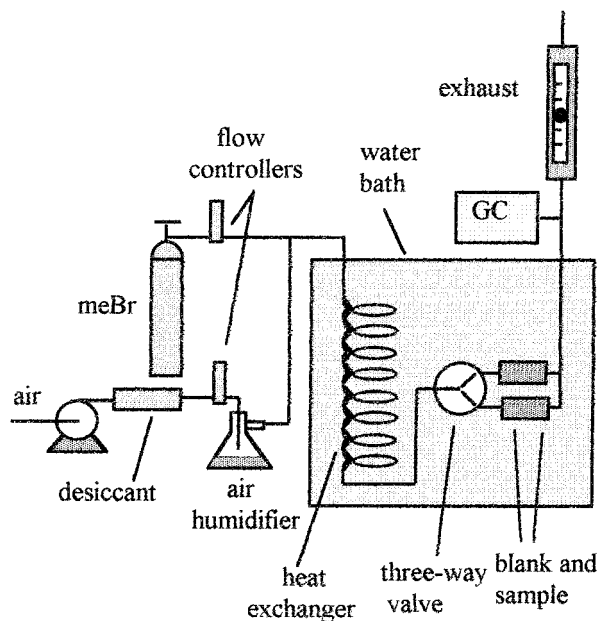
were at ambient conditions, approximately 23 °C. The combined streams were introduced at one end of a packed column. Several times during the course of an adsorption, the carbon tube was weighed. The effluent from the bed was analyzed using an MTI P-200 gas chromatograph (GC) (Agilent Technologies, Palo Alto, CA) and an Omega HX94 relative humidity probe (Omega Engineering, Inc., Stamford, CT). The chromatograph employed a PoraPlot U column (Varian U.S.A., Walnut Creek, CA) with a thermal conductivity detector. For the GC, the column temperature was 150 °C, the injection time was 10 s, and the inlet pressure was atmospheric. The flow rate was verified using a rotometer at the outlet.

The experimental setup for carbon regeneration is shown in Figure 2. Prior to regeneration, the tube was insulated with 2 cm of fiberglass- and foil-layered bubble wrap. A rheostat provided a 60 Hz ac voltage. The voltage was adjusted during the course of an experiment to prevent excessive current fluxes, which can lead to electrical arcing and hot spots in the bed.

A carrier gas was not used during the heating. This served to provide a more highly concentrated methyl bromide exhaust. It is well-documented that heating carbon in the presence of oxygen causes the oxidation of adsorption sites, which leads to increased water adsorptivity. The desorbate exited the carbon tube through both ends. The exhaust stream was passed through a liquid trap where condensed liquid was separated from the methyl bromide gas stream.

For the methyl bromide recovery experiments, the stream was then led to a 9.52-mm ( $3/8$ -in.) copper heat transfer coil (total length, 1 m) positioned in an ice bath. The volume fraction of methyl bromide required to condense at 0 °C and atmospheric pressure is 0.895. The heat transfer coil led to a graduated volumetric cylinder that was used to measure the volume of condensed methyl bromide. To prevent the condensed methyl bromide from contacting air (and therefore evaporating), the methyl bromide was introduced under a layer of water inside the volumetric cylinder. Following each regeneration, the bed and outlet tubing was purged with 0.5 slm of nitrogen for 2 min to remove any condensed liquid. For a given column, the original load of carbon was used for all experiments.

**Evaluation of Physicochemical Characteristics.** The experimental apparatus for obtaining the physico-



**Figure 3.** Schematic of adsorption apparatus for equilibria/rate measurements.

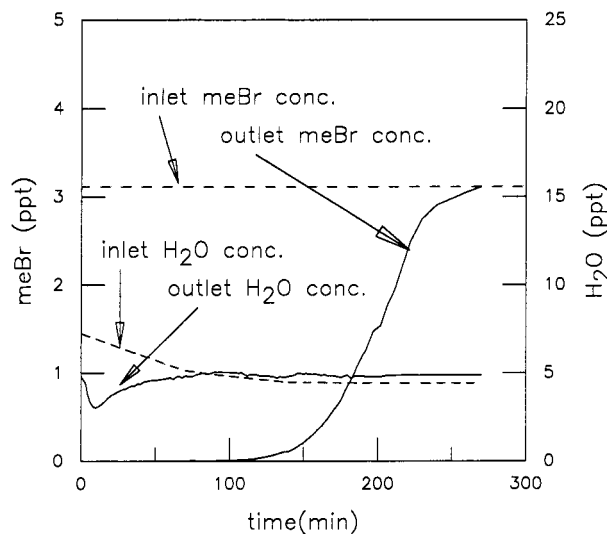
chemical parameters is shown in Figure 3. The air and methyl bromide flow rates were maintained using Sierra 840 series mass flow controllers (Sierra Instruments, Inc., Monterey, CA). For these experiments, the air flow was 2 standard L/min (slm). The methyl bromide concentration ranged between 2 and 20 ppt. Because ambient humidity would be present during a commercial application, some water vapor was introduced during the experiments. The water vapor concentration was controlled by flowing the air stream first through a desiccant (molecular sieve 3A, Silica Gel Desiccant Products Co., Inglewood, CA) and then over a layer of water in an Erlenmeyer flask (see Figure 3). The resulting water vapor concentration was approximately 10 ppt. For some experiments, the humidity was increased by bubbling the air stream through a layer of water to provide up to 30 ppt water vapor.

The adsorption apparatus was contained in a constant-temperature water bath. The air stream was brought to the desired temperature by flowing it through a 9.52-mm ( $3/8$ -in.) copper heat transfer coil (total length, 1 m) that led to a three-way valve. From the three-way valve, the air stream either flowed to the carbon bed or was diverted to a blank. Two stainless steel inline filters with 90- $\mu$ m sintered steel elements (SS-6F-90, Nupro Company, Willoughby, OH) were used to hold the carbon bed and as a blank. The blank was employed to minimize the pressure difference when switching from flow to bypass and from flow to carbon bed. The sides of the filter elements were sealed with an acrylic-based paint to permit flow only in the axial direction, thereby permitting the use of a standard one-dimensional fixed-bed numerical model for analysis of the experimental data.

At the lower methyl bromide concentrations of interest for adsorption rate data, the sealed sides of the filter elements did not measurably adsorb methyl bromide. However, adsorption isotherms were also desired for pure methyl bromide. When pure methyl bromide passed through the sealed filter element, the methyl bromide was dissolved by the paint, preventing accurate weight measurements. Therefore, adsorption isotherms

**Table 1. Summary of Experimental Conditions and Results for Adsorption Cycling**

H <sub>2</sub> O conc (ppt)	methyl bromide concentration (ppt)								
	3.0		3.6		4.2				
	MeBr (g)	H <sub>2</sub> O (g)	MeBr (g)	H <sub>2</sub> O (g)	MeBr (g)	H <sub>2</sub> O (g)	MeBr (g)	H <sub>2</sub> O (g)	
0	3	9.1	0.0	1	9.8	0.0	2	10.6	0.0
3	12	8.5	0.3	10	10.1	-0.3			
14	9	7.2	3.1	8	8.3	2.7	7	8.9	2.4
22	6	6.0	6.9	4	8.0	6.1	5	8.0	5.1



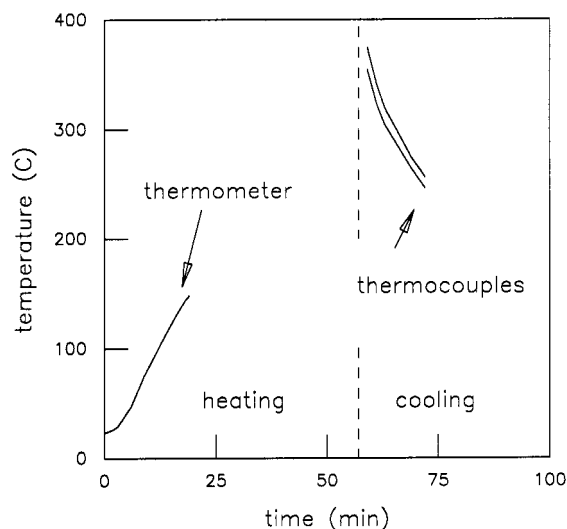
**Figure 4.** Methyl bromide and water vapor concentrations during adsorption, low humidity, expt 12.

for pure methyl bromide were obtained using unpainted filter elements.

For the experiments discussed here, 1.0-g samples were employed. The clean dry carbon mass was used in the analysis. The carbon was sieved between no. 20 and no. 32 mesh screens (0.84–0.50 mm). The effluent stream was analyzed for water vapor and methyl bromide using an MTI P-200 gas chromatograph (GC) (Agilent Technologies, Palo Alto, CA). The chromatograph employed a PoraPlot U column (Varian U.S.A., Walnut Creek, CA) with a thermal conductivity detector. The GC column temperature was 150 °C, the injection time was 10  $\mu$ s, and the inlet pressure was atmospheric. The flow rate was verified using a rotometer positioned at the outlet. The adsorbent samples were weighed following each adsorption experiment.

## Results and Discussion

**Multiple Adsorption/Desorption.** *Adsorption.* A series of 13 experiments were conducted to determine the effect of repeated cycles of adsorption and desorption on methyl bromide uptake. These experiments were carried out on the 23-cm bed. Results from this series of experiments are summarized in Table 1. The two primary control parameters were the water vapor and methyl bromide concentrations in the air. The water vapor concentration was varied between 0 and 22 ppt. The methyl bromide concentration was varied between 3 and 4.2 ppt. At time zero, flow of methyl bromide and water vapor in air was introduced to the carbon bed. Figure 4 provides an example of the inlet and outlet concentrations of methyl bromide and water vapor during an adsorption experiment. Integration of the



**Figure 5.** Bed temperature during regeneration, expt 3.

area between the inlet and outlet concentration lines corresponds to the mass of methyl bromide or water vapor adsorbed.

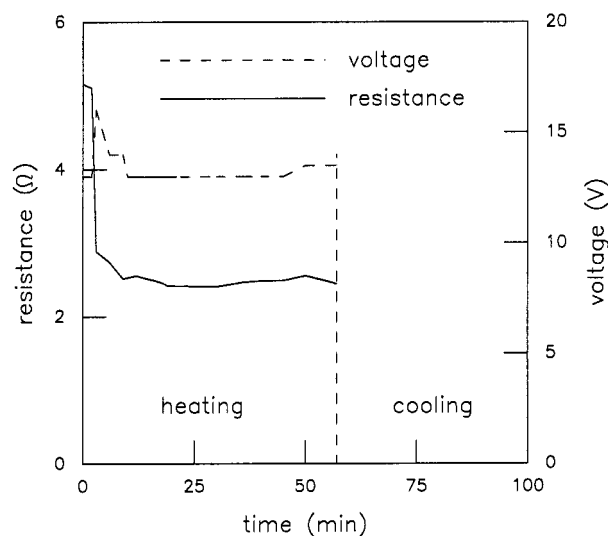
Because the carbon holds much more methyl bromide than is contained in the flowing air, methyl bromide forms a creeping front. This front traverses the carbon bed at a fraction of the superficial velocity of the flowing air (the velocity of the flowing gas stream through the tube if no carbon were in the tube), roughly 0.1 cm/min as compared to 5.4 cm/s. At early times, the outlet concentration of methyl bromide is close to zero, as very little methyl bromide flows out the bed until the front reaches the exit.

Water vapor adsorbs onto carbon in a manner different from methyl bromide. As seen in Figure 4, at lower humidities, water saturates the carbon relatively quickly. After saturation, the outlet concentration is the same as the inlet concentration. At higher humidities, the carbon bed continues to adsorb water throughout the experiment, causing some initially adsorbed methyl bromide to desorb. The negative effect of humidity on methyl bromide adsorption is shown in Table 1. However, even at high humidities, the carbon bed adsorbs a substantial amount of methyl bromide (~10% methyl bromide by weight).

**Desorption.** After a carbon bed has been saturated, it must be regenerated for reuse. Conventionally, if the carbon is transported to a facility for reactivation, the carbon is heated in a furnace at temperatures above 900 °C. Such high temperatures can damage the carbon and reduce its adsorptivity. It is possible that a load of carbon will need to be completely replaced after four or five regenerations. The ability to regenerate carbon at a lower temperature, if possible, for a given adsorbent, allows the carbon to retain its activity and is therefore of great importance.

To prevent thermal degradation of the silicone stoppers, the temperature to which they were subjected was limited. The electrodes were positioned roughly 2 cm away from the silicone stoppers. This permitted somewhat higher temperatures at that end of the carbon bed. The temperatures at the silicone stoppers were not allowed to exceed roughly 100 °C. Nearly uniform high bed temperatures were obtained.

Figure 5 shows typical temperatures at the axial center of the tube during heating and temperatures at



**Figure 6.** Bed resistance and applied voltage during regeneration, expt 3.

the axial center and midway between the center and the end following heating. As can be seen, during heating, the temperature increases linearly with time. When the temperature in the center reached 150 °C, the thermometer was removed from its central position and inserted adjacent to the left- or right-side silicone stopper. When this temperature reached roughly 100 °C, power was discontinued. It is seen that, for the first 5 min after the power had been switched off, the temperature declines rapidly. Following this more rapid decline, the temperature decreases more gradually. It is hypothesized that some current conducts through the thermocouples, heating them to temperatures somewhat higher than that of the surrounding bed. Thus, the thermocouples initially cool more quickly until they match the temperature of the surrounding bed. The gradual decline in temperature is indicative of the heat lost through the insulation. A larger-diameter unit would have a smaller surface area per unit volume and would therefore retain heat more efficiently.

It was found that excessive currents could cause electrical arcing and hot spots. Therefore (as seen in Figure 6), as the resistance through the bed decreased with temperature, the voltage was manually decreased to provide a relatively constant current. The bed resistance as a function of time seen in Figure 6 is typical of that observed for the other regeneration experiments. The resistance initially ranged between 5 and 9 Ω. If the initial bed resistance was higher than this, the stoppers were pressed harder against the bed to decrease the resistance. The bed resistance toward the end of the experiments ranged between 3 and 4 Ω and corresponded with the initial resistances.

Figure 7 shows the corresponding current and power (assuming no phase difference between the voltage and current) during regeneration. Because the regeneration process does not destroy the carbon, it is straightforward to determine the amount of mass remaining on the carbon following regeneration by weighing the carbon after each experiment. We call this mass "carryover." We hypothesize that the carryover consists principally of nonactivated carbonaceous deposits on the macropores. We believe this is the case because the cumulative weight gains appear to have little effect on subsequent adsorptions.

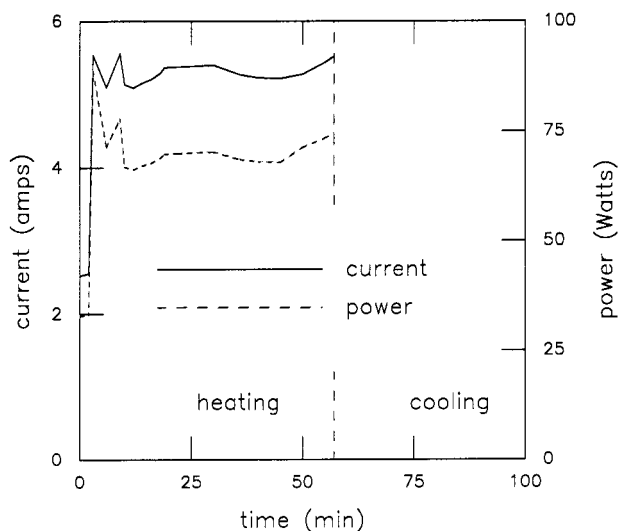


Figure 7. Applied current and power during regeneration, expt 3.

Table 2. Summary of Experimental Conditions and Results for Desorption Cycling

expt	max $T$ (°C)	mass not desorbed (g)	accumulated mass (g)	percent of carbon mass
1	—	0.4	0.4	0.6
2	395	0.4	0.8	1.1
3	375	0.2	1.0	1.4
4	415	0.0	1.0	1.4
5	—	0.4	1.4	2.0
6	345	0.4	1.8	2.5
7	365	0.3	2.1	3.0
8	335	0.5	2.6	3.7
9	375	0.1	2.7	3.8
10	365	0.3	3.0	4.2
11	410	0.2	3.2	4.5
12	—	—	—	—
13	400	0.8	4.0	5.6

Table 2 compares the maximum temperatures during the regenerations with the carryover for the successive experiments. For the first 11 regenerations, on average an additional 0.3 g of material remains on the carbon following each regeneration. Following adsorption 12, the bed was not immediately regenerated. First, 43 g of pure methyl bromide was introduced to the bed (experiment 13), and then the bed was regenerated. This was done to determine the effect of higher loading on carryover. Following experiment 13, an additional 0.8 g of material remained on the carbon. Over the course of the multiple adsorptions and regenerations, a total of 4.0 g of material accumulated on the carbon. This is 5.6% of the initial carbon mass.

Various correlations relating the amount of mass carried over following carbon regeneration to operating parameters such as maximum temperature, time of desorption, experiment sequence, mass of water adsorbed, and/or mass of methyl bromide adsorbed were analyzed. The best correlation indicated that the carryover corresponded proportionally to the total mass of methyl bromide and water adsorbed and to the experiment sequence and inversely to the temperature rise.

The exhaust from the carbon bed reached the liquid trap at roughly ambient temperatures. The liquid trap was found to be efficient at collecting water from the exhaust. Usually, the liquid trap contained only water. Sometimes there was also up to 20 wt % bromine, hydrobromic acid, and methanol and other unidentified

Table 3. Summary of Results for Methyl Bromide Condensation at 0 °C

expt	MeBr (ppt)	MeBr + H <sub>2</sub> O adsorbed (g)	H <sub>2</sub> O recovered (g)	MeBr recovered (g)
14	10	115.0	4	71 slush
15	10	131.1	5	48 liquid
16	10	136.2	6	63 liquid
17	5	41.8	5	13 liquid

substances. The corrosiveness of bromine and hydrobromic acid would need to be considered in the design of an industrial-scale unit.

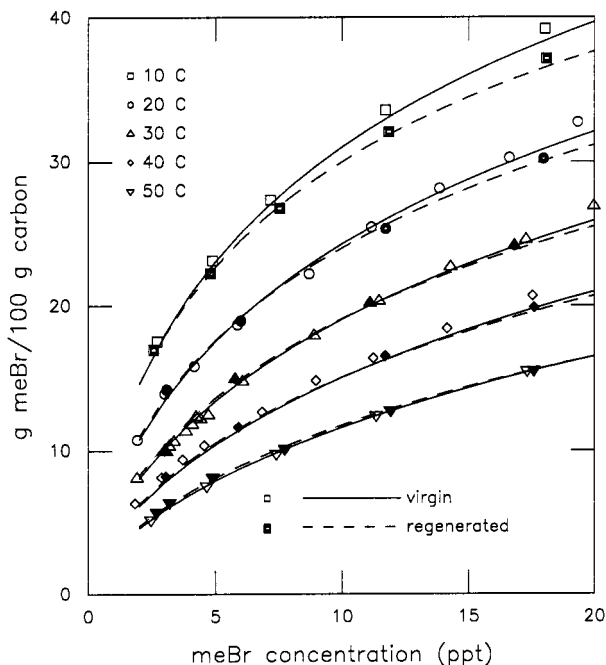
**Methyl Bromide Recovery.** Methyl bromide recovery by condensation of desorbing methyl bromide was investigated utilizing the 86-cm bed. To increase the amount of methyl bromide available for recovery, methyl bromide was adsorbed at 10 ppt. As shown in Figure 2, methyl bromide and other desorbates flowed through the liquid trap and then to a heat exchanger coil and a volumetric cylinder. The condensation temperature of methyl bromide decreases as its gas-phase concentration decreases. For example, 895 ppt condenses at 0 °C, but 500 ppt requires -12.7 °C to condense. During heating, as methyl bromide desorbs, its gas-phase concentration in the dead volume of the bed and tubing increases. Only when the methyl bromide concentration is sufficiently high can it condense inside the heat transfer coil.

It was desired to prevent the contact of this condensed methyl bromide with air that might occur at the outlet of the system, the volumetric cylinder. Liquid methyl bromide is denser than water. It was therefore thought that introducing the condensed methyl bromide below a layer of water in the volumetric cylinder would prevent contact with air. Instead of forming a layer under the water, the methyl bromide formed a slush-like hydrate with the water that overflowed the cylinder. Great Lakes Chemical Corporation suggested using saltwater brine instead.<sup>21</sup> When brine was used, methyl bromide successfully formed a distinct layer under the water.

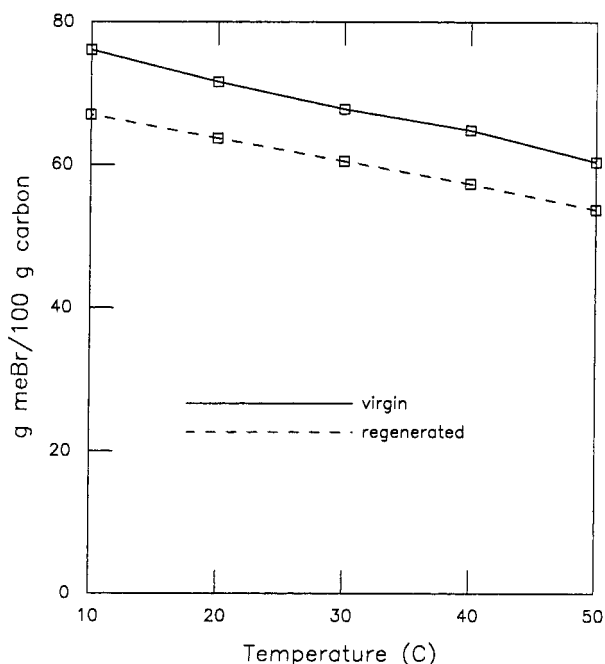
Table 3 shows the resulting methyl bromide recoveries. The ability to condense at the moderate temperature of 0 °C is remarkable. Condensation at this temperature shows that the gas-phase methyl bromide leading to the condenser had greater than 90% purity. Lower temperatures could easily be obtained using nitrogen cooling or refrigeration. Further, the stream leaving the condenser could be recycled to the original carbon bed or sent to a second carbon bed to prevent release to the atmosphere of any methyl bromide not condensed.

#### Evaluation of Physicochemical Characteristics.

**Equilibrium Constant.** Figure 8 is a plot of the adsorption isotherms obtained from virgin and regenerated carbon. The ordinate represents methyl bromide loading per 100 g of carbon; the abscissa represents methyl bromide concentration in air. It is seen that the regenerated carbon retains the same adsorptive capacity as virgin carbon at lower methyl bromide concentrations and higher temperatures. At higher methyl bromide loadings (high concentrations combined with low temperatures), the capacity decreases by about 3%. Recall that the regenerated carbon increased in mass by 5.6% after 12 regeneration cycles. It is clear that the accumulated material is not located in the smallest pores. If this were the case, then at higher temperatures and low methyl bromide concentrations, the adsorption isotherms for regenerated carbon would be lower in value than those for virgin carbon. For this reason, it



**Figure 8.** Experimental and model adsorption isotherms for virgin and regenerated carbon ( $P = 1$  atm,  $T = 10$ – $50$  °C).



**Figure 9.** Experimental total surface coverage for virgin and regenerated carbon ( $P = 1$  atm,  $T = 10$ – $50$  °C).

also appears that the accumulated material on the regenerated carbon is not adsorbed methyl bromide. The accumulated mass likely consists of inactive carbonaceous deposits. The high adsorptivity of the regenerated carbon is exceptional. Generally, an industrial reactivation facility treats all carbon the same—heating at 900 °C in a furnace where 10% or more carbon loss per regeneration could be expected.

Figure 9 shows adsorptivity as a function of temperature for 100% methyl bromide. For pure methyl bromide, the regenerated carbon retains 89% of the adsorptive capacity of virgin carbon.

The ideal Langmuir equilibrium constant is given by eq 2 for  $n = 1$ , where  $\theta$  is the fractional methyl bromide

coverage of the adsorption sites ( $Q/Q_s$ ),  $P$  is the pressure, and  $y$  is the methyl bromide concentration. The adsorption isotherms presented in Figures 8 and 9 were transformed by eq 2 to check conformity with the ideal Langmuir equilibrium constant.

$$b = \frac{\Theta}{(1 - \Theta)(Py)^n} \quad (2)$$

It was found that the adsorption isotherms did not conform to the ideal. An empirical equation for the equilibrium constant was desired. With that aim, a least-squares fit of eq 2 with respect to the power  $n$  was performed. The following procedure was followed: A value of  $n$  was assumed, and  $b$  was calculated for each set of data. Each value of  $b$  thus calculated was divided by the value of  $b$  calculated for  $y = \sim 12$  ppt (roughly midway between the low and high concentrations) at the corresponding temperature. This was done so that, for a given temperature and carbon type, all values of  $b$  had the same temperature weighting. The value  $n = 0.661$  provided a least-squares fit to the combined data.

Including an Arrhenius temperature dependence of the equilibrium constant yields eq 3

$$b = \frac{\Theta}{(1 - \Theta)(Py)^{0.661}} = K \exp\left(\frac{\Delta H}{RT} - \frac{\Delta H}{R(303 \text{ K})}\right) \quad (3)$$

A least-squares fit of eq 3 with respect to the heat of adsorption,  $\Delta H$ , yielded a value of  $-20\,200 \text{ J mol}^{-1}$ . It was found that the concentration and temperature dependence of the fractional coverage,  $\theta$ , for virgin and regenerated carbon are the same.

The average values of  $K$  were found to be  $0.085\,67 \text{ atm}^{-0.661} \text{ ppt}^{-0.661}$  for fresh carbon and  $0.101\,056 \text{ atm}^{-0.661} \text{ ppt}^{-0.661}$  for regenerated carbon. The equilibrium constant for regenerated carbon is 18% higher than that for virgin carbon. This results from dividing  $Q$  by a smaller maximum adsorptive capacity,  $Q_s$ , for regenerated carbon when obtaining  $\Theta$ .

Superimposed on the experimental isotherms in Figure 8 are the isotherms derived from the equilibrium constant expression given by eq 3. As can be seen, the agreement is quite reasonable.

Using the equilibrium constant expression, the effective rate of adsorption is given by

$$r = mk \left[ (1 - \Theta)(Py)^{0.661} - \frac{\Theta}{b} \right] \quad (4)$$

where  $m$  is the carbon mass and the effective rate constant,  $k$ , is evaluated by fitting a fixed-bed model of the adsorption bed to the experimental data for virgin and regenerated carbon.

**Adsorption Rate Constant.** A dynamic heterogeneous one-dimensional model of the adsorption of methyl bromide onto carbon was developed with the aim of fitting the effective adsorption rate constant to the experimental data. Implicit in the model development are the following assumptions: (1) The ideal gas law applies. (2) Isothermal conditions exist. (3) Adsorption dynamics are adequately described by a single-step kinetic model involving the reversible adsorption of methyl bromide. (4) The omission of external and intrapellet mass transfer limitations does not significantly alter the concentration profiles on the macroscale. (5) Adsorber axial concentration profiles in the gas phase are assumed to develop rapidly relative to the rate

**Table 4. Summary of Experimental Adsorption Parameters**

parameter	virgin carbon	regenerated carbon
preexponential factor, $K$	0.08671 atm <sup>-0.661</sup> ppt <sup>-0.661</sup>	0.101056 atm <sup>-0.661</sup> ppt <sup>-0.661</sup>
heat of adsorption, $\Delta H$	20 200 J mol <sup>-1</sup>	20 200 J mol <sup>-1</sup>
preexponential factor, $A$	$1.5 \times 10^{-7}$ mol s <sup>-1</sup> atm <sup>-0.661</sup> ppt <sup>-0.661</sup> g <sup>-1</sup>	$1.4 \times 10^{-7}$ mol s <sup>-1</sup> atm <sup>-0.661</sup> ppt <sup>-0.661</sup> g <sup>-1</sup>
activity	100%	100% of virgin carbon at moderate concentrations and temperatures

of adsorption. (6) Pressure gradients are negligible at the space velocities used. (7) Axial dispersion of mass is negligible. (8) No radial gradients exist.

A transient material balance for methyl bromide in the adsorber void yields

$$0 = -M \frac{\partial Y}{\partial Z} - r \quad (5)$$

where  $M$  is the mass flow rate and  $z$  is the axial coordinate. The model incorporates plug-flow boundary conditions

$$Y_0 = Y_{in} \quad (6)$$

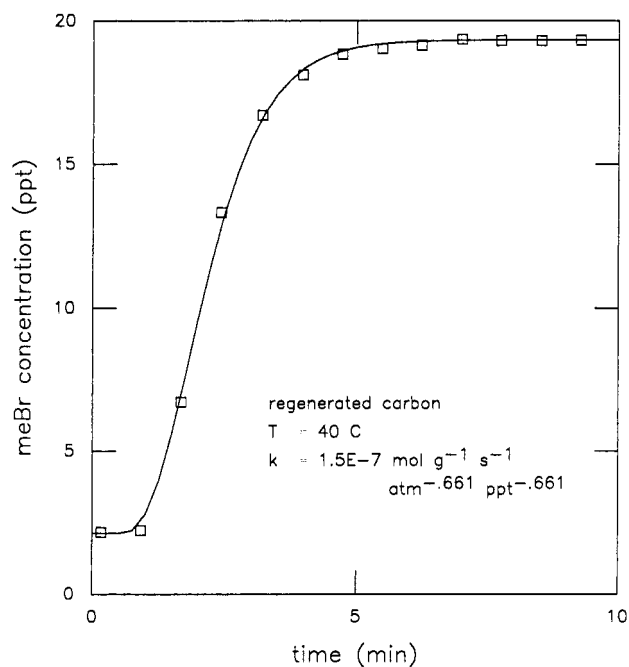
The material balance for the  $i - 1/2$  carbon node yields

$$m \frac{\partial Q}{\partial t} = r \quad (7)$$

**Method of Solution.** The partial differential equations representing the material balance for the reactor void and carbon particles were discretized using an implicit backward difference approximation for the gas flow and a reaction term centered at the  $i - 1/2$  node. The model incorporates 21 nodes along the adsorber axis, with each step representing 1/20th of the total carbon mass, and a time step of 0.1 s. All equations were solved iteratively until convergence was reached at each time step. The simulation imposed a minimum of five iterations. Convergence for a given time step was deemed achieved when the change in the gas-phase methyl bromide concentration was less than 0.001 ppt. The value of the effective rate constant,  $k$ , was obtained by visually comparing the model simulation results with the experimental elution profiles.

**Fitting the Mathematical Model.** Experimental elution profiles were obtained in the range of 10–50 °C. Figure 10 provides an example of experimental and simulated methyl bromide exit concentrations as functions of time. Nonzero exit concentrations at early times during the experiments were found to be caused by a small bypass flow around the filter element. A temperature dependence of the rate constant was not discernible. However, there was a concentration dependence. For virgin carbon with an inlet concentration of above 4 ppt methyl bromide, the rate constant was  $(1.5 \pm 0.1) \times 10^{-7}$  mol s<sup>-1</sup> atm<sup>-0.661</sup> ppt<sup>-0.661</sup> g<sup>-1</sup> [regenerated rate =  $(1.4 \pm 0.1) \times 10^{-7}$  mol s<sup>-1</sup> atm<sup>-0.661</sup> ppt<sup>-0.661</sup> g<sup>-1</sup>]. For inlet concentrations of roughly 3–4 ppt, the rate constant decreased to  $(1.3 \pm 0.1) \times 10^{-7}$  mol s<sup>-1</sup> atm<sup>-0.661</sup> ppt<sup>-0.661</sup> g<sup>-1</sup> for virgin and  $(1.2 \pm 0.1) \times 10^{-7}$  mol s<sup>-1</sup> atm<sup>-0.661</sup> ppt<sup>-0.661</sup> g<sup>-1</sup> for regenerated. Clearly, it is possible that the rate constants for virgin and regenerated carbon are the same.

At inlet concentrations lower than roughly 3 ppt methyl bromide, the model does not fit the elution profile well. The experimental elution profiles have a shallower slope and are more elongated than predicted by the model; however, the model does correctly predict the mass of methyl bromide adsorbed. It appears that



**Figure 10.** Comparison of experimental and simulated elution profiles for regenerated carbon ( $T = 40$  °C).

the methyl bromide adsorbed at early times adsorbs more slowly than that adsorbed later. However, it is possible that this behavior is instead an equilibrium-constant-related phenomenon. Table 4 summarizes the above results.

**Effect of Humidity.** As was previously noted, the reused carbon was submitted to 12 regeneration cycles in the absence of a purge stream. This led to the well-documented oxidation of adsorption sites and a subsequent increased affinity for water adsorption. An industrial process for regenerating spent carbon would necessarily incorporate a purge stream of nitrogen, steam, or other gas to prevent this occurrence.

At lower humidities, humidity appeared to have little, if any, effect on methyl bromide adsorption. This was true for both the virgin and regenerated samples. At relative humidities above roughly 50%, water vapor competes with methyl bromide for adsorption sites.

In addition, water vapor adsorbs more slowly than methyl bromide. Therefore, high relative humidities resulted in methyl bromide elution at earlier times, and following elution, water displaced some previously adsorbed methyl bromide. This was reflected by outlet methyl bromide concentrations that were higher and water vapor concentrations that were lower than the corresponding inlet concentrations for a period of 10–60 min, depending on the relative humidity. For practical applications, when high relative humidities are experienced, the relative humidity could be decreased by preheating the gas stream before introducing it into the carbon bed.

## Summary and Conclusions

Several conclusions can be drawn from our research. Using electrothermal desorption, the carbon employed underwent 12 cycles of adsorption and regeneration while maintaining a high methyl bromide adsorptivity. Although water vapor does decrease methyl bromide uptake, even at high humidities, methyl bromide uptake is substantial. This means that a carbon bed can be repeatedly reused in an industrial application. Finally, electrothermal regeneration provides high methyl bromide concentrations, which serve to decrease condenser heat transfer requirements. The ability to repeatedly reuse a carbon bed and the low condenser heat transfer requirements serve to qualitatively decrease the capital and operating expenses of the process. Therefore, the use of electrothermal regeneration for the on-site regeneration of carbon is economically feasible.

Carbon that had undergone 12 adsorption/regeneration cycles using electrothermal heating was compared with virgin carbon for adsorption of methyl bromide. It was found that the regenerated carbon retained 97–100% of its original adsorptivity in the temperature range and methyl bromide concentration range associated with chamber fumigations. A small 3% adsorptivity decrease occurred at the highest methyl bromide loadings (high methyl bromide concentrations combined with low temperatures).

The heat and rate of adsorption remained the same following the regeneration cycles. This implies that a carbon bed for adsorbing methyl bromide from agricultural applications could be repeatedly reused without appreciable loss of activity.

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## Nomenclature

$A$  = preexponential factor in reaction rate expression,  $\text{mol s}^{-1} \text{ atm}^{-0.661} \text{ ppt}^{-0.661} \text{ g}^{-1}$

$b$  = equilibrium constant,  $\text{atm}^{-n} \text{ ppt}^{-n}$

$F$  = volumetric flow rate,  $\text{m}^3 \text{ s}^{-1}$

$\Delta H$  = heat of adsorption,  $\text{J mol}^{-1}$

$K$  = preexponential factor in equilibrium constant expression,  $\text{atm}^{-0.661} \text{ ppt}^{-0.661}$

$k$  = effective adsorption rate constant,  $\text{mol s}^{-1} \text{ atm}^{-n} \text{ ppt}^{-n} \text{ g}^{-1}$

$M$  = molar flow rate of bulk gas stream,  $\text{mol s}^{-1}$

$m$  = carbon mass, g

$n$  = power law constant (eq 2)

$P$  = pressure, atm

$Q$  = adsorptivity,  $\text{mol g}^{-1}$

$Q_s$  = adsorptivity for total surface coverage,  $\text{mol g}^{-1}$

$r$  = rate of adsorption,  $\text{mol s}^{-1}$

$R$  = gas constant,  $8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$

$T$  = temperature, K

$t$  = time, s

$V$  = volume of fumigation chamber,  $\text{m}^3$

$y$  = volume fraction of methyl bromide, ppt

$y_{\text{in}}$  = volume fraction of methyl bromide at the inlet, ppt

$z$  = axial coordinate

## Greek Letters

$\theta$  = fraction adsorbate coverage

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