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METHYL BROMIDE EMISSION CONTROL FROM COMMODITY FUMIGATION

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ABSTRACT

A proprietary process to control methyl bromide (MB) emissions to the atmosphere following commodity fumigation is being developed. The process consists of adsorbing the MB in the vent-stream from a fumigation process on activated carbon (carbon), reactivation of the carbon for further use as an adsorbent, thermal destruction of the desorbed MB and the recycling of its bromide content for reuse in the manufacture of new MB and/or other brominated compounds. Research was undertaken to observe the effects of several factors — temperature, relative humidity (r.h.), MB vent-stream concentration and carbon type — on the amount of MB that could be adsorbed (loaded) on the activated carbon. Tests revealed that for a given type of carbon temperature has the greatest effect on the loading, although r.h. also affects its loading. Loading decreases as temperature and r.h. increase. At a given temperature and r.h., the loading varies significantly for different carbon types. These differences are consistent with the type of pore structure of the carbon, which depends on the raw materials and activation procedures used during its manufacture. Temperature in the carbon column rose in response to the adsorption of MB. The adsorption zone could be followed (by monitoring the temperatures) through the column from the inlet at the start of an adsorption run to column exhaustion or breakthrough at the end of the run. Breakthrough was reached when the MB concentration in the column exhaust stream reached 500 ppm (2 mg/L). Because of the heating of the column, vent-stream r.h. was less critical than first anticipated. The temperature increase due to the heat of adsorption lowered the r.h. on the adsorption zone, decreasing the negative effect on adsorption capacity normally associated with high humidities.

INTRODUCTION

When methyl bromide (MB) was found to be an ozone depletor, the agricultural community increased pressure to modify its application technology so that it might still be used without being emitted to the atmosphere. It has been estimated that non-use of this agricultural

chemical in the state of California alone would result in a loss of 300 million dollars in imports and exports. A great deal of pressure has been brought either to convince other countries to adopt the provisions of the US Clean Air Act (CAA) (which calls for the banning of MB in the year 2001) or to amend it to permit certain uses of MB. If the CAA is amended, it will probably include the proviso that emissions be controlled to acceptable levels. The USDA-ARS has therefore been looking into ways to trap, recycle, incinerate or chemically destroy MB after fumigation and before being emitted into the atmosphere. Several review articles have extolled the virtues of using activated carbon and other materials as sorbent materials to remove volatile organic compounds (VOC's) and other compounds from air and water streams (Parmele *et al.*, 1979; Goldhaar and Graham, 1991; Graham, 1992; Knaebel, 1995). In 1995 the Horticultural Crops Research Laboratory, a part of the USDA Agricultural Research Service, entered into a cooperative research and development agreement with GFK Consulting, Ltd. of San Clemente, CA, to research the potential use of activated carbon to capture MB (following fumigation) and transport it to a central treatment facility where it would be desorbed and disposed of in an environmentally sound manner. We here present the results of the first phase of that research: the adsorption of MB on activated carbon under different conditions.

MATERIALS AND METHODS

The adsorption experiments were carried out in C-200, the bench-scale carbon adsorption column (BSAC), shown in Fig. 1. The C-200 BSAC was modeled after the ventilation conditions used at a 72,000 ft³ (2,040 m³) tarpaulin fumigation chamber at the San Diego port facilities. Following fumigation, fresh air was admitted around the periphery of the chamber and the contents evacuated at a rate of 10,000 ft³/min (280 m³/min). After a 30-min ventilation, the MB concentration in the chamber was reduced to less than 5% of its original value. The BSAC was designed to treat approximately 1/3,500 of this flow, or 83.4 L/min (2.9 ft³/min), long enough (30 min) for the chamber concentration to drop to 5% of its original value. The C-200 column had a diameter of 7.6 cm (3 inches) and a height of 99 cm (39 inches). It held approximately 2,300 g of clean carbon. The absolute humidity of the inlet air stream was adjusted in T-110 by vigorously bubbling air through temperature-controlled water. T-120 served to disengage and eliminate any entrained water droplets from the air stream. Following the humidity adjustment, MB gas (99.9%) from a commercial pressure cylinder was introduced to achieve an initial concentration of 16,000 ppm (v/v) (64 mg/L in air). The concentration was gradually reduced to 0 ppm over a period of 30 min to simulate what actually happens during the aeration of a fumigation chamber. A total of 38.5 g MB was added during this period. The average concentration for the period was approximately 3,800 ppm (15 mg/L). When calculating the concentration profile, we assumed perfect back mixing during the ventilation period. The instantaneous MB flow rate was controlled as per both the indications of a rotameter calibrated for MB and the weight of MB lost from the cylinder on a Mettler top-loading balance mode P10N, denoted K-110 in Fig. 1.

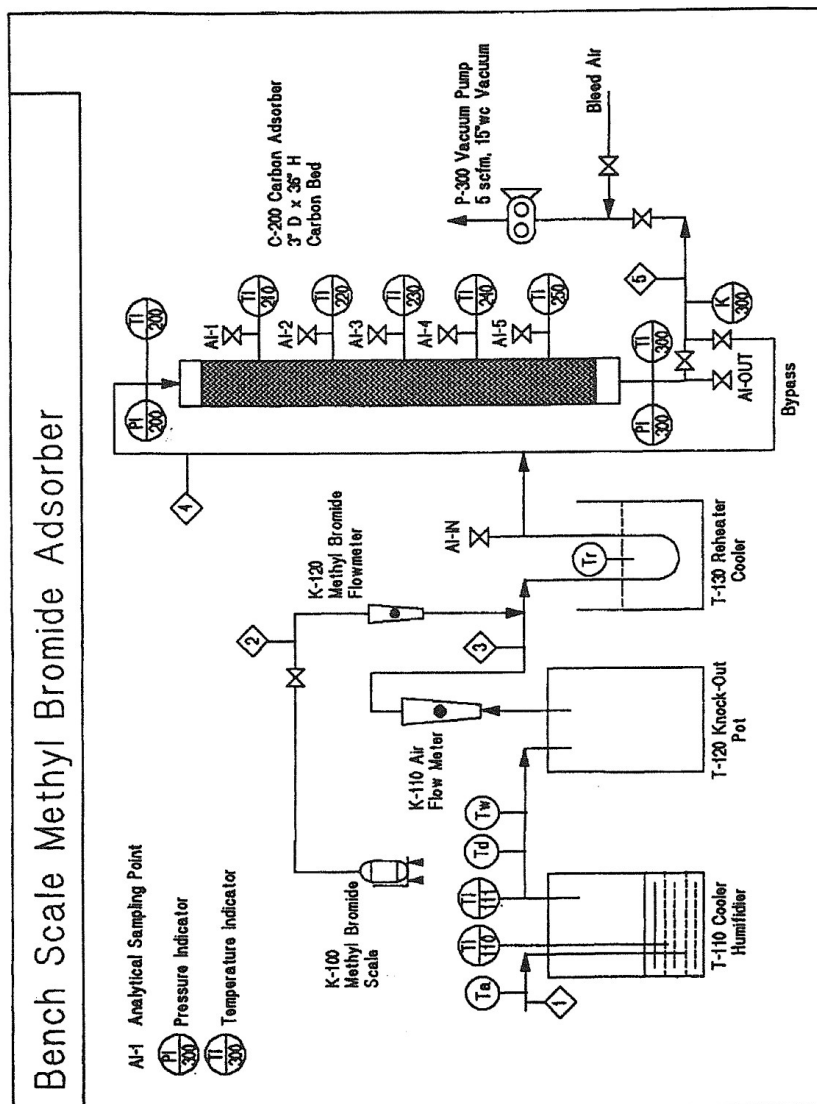


Fig. 1. The design of the bench-scale adsorber used to determine the loading of MB on various activated carbons under various conditions. TI- markings denote places where temperatures were taken; AI- markings denote places where gas grab samples were removed and analyzed by GLC; PI- markings denote places where pressure readings were taken to provide flow data.

Following the introduction of the MB into the air stream, the mixture was further heated or cooled in T-130 to achieve the desired column inlet temperature and relative humidity (r.h.). The target inlet temperatures ($8, 15$ or $25 \pm 3^\circ\text{C}$) were used with r.h.'s of 50 or $95 \pm 5\%$. Temperatures were automatically recorded at positions marked "TI-110, 111, ..., TI-250, TI-300" in Fig. 1. A PC software program from Iotech Inc. (Temp-Book/66 Data Acquisition System) linked to type "T" thermocouples was used to record all temperatures except those at T_a , T_d , T_w and T_r (Fig. 1), which were taken manually with thermometers. Temperatures in T-110 and T-130 were manually adjusted throughout each run to maintain the desired temperature and r.h. in the air stream, as monitored by T_d and T_w (dry bulb and wet bulb, respectively). Pressures in the system were measured using simple U-tube manometers filled with water. A typical inlet pressure was -330 mm (-15 inches) of water. A typical pressure drop across the column was 190 mm (7.5 inches) of water. Stream flow through the column was verified by a venturi tube — placed between the column and the pump — attached to a Dwyer incline manometer. Gas grab samples were collected at points named "AI-IN, AI-1, ..., AI-5 and AI-OUT". The pipe carrying the MB was passed through the water bath (T-130) to achieve the proper temperature and r.h. to be tested on the column of carbon.

Since the adsorption of the MB on activated carbon is an exothermic reaction, we used the temperatures at the various thermocouple locations in the column to determine the progress of the adsorption front. The average temperature at a given location increased as long as the adsorption occurred upstream, i.e. the adsorption front was upstream of the location of the thermocouple. Once the adsorption front passed the location of the thermocouple, the temperature started to decrease towards the column inlet temperature (see Fig. 2). The adsorption front at any given location approximately coincided with the peak average temperature at that location. Static pressures at the column inlet and outlet were monitored to determine the pressure drop for both the various types of carbon and the various operating conditions. The procedure also verified the overall integrity of the system since such major leaks as open sample connections were easily detected by the abnormal pressure readings they generated. The air flow was measured with a rotameter (K-110) preceding the adsorption column and, again, following the column using the venturi tube (K-300) coupled to an incline manometer. Grab samples of gas were analyzed on a Hewlett Packard Gas Chromatograph model 5860 equipped with a flame ionization detector and a heated gas injection loop. These grab gas samples showed the progress of the adsorption front through the column as well as verifying the MB "break-through" at the bottom of the column. Breakthrough was defined as the moment when MB concentration at the outlet reached 2 mg/L (500 ppm).

The main tool for measuring breakthrough at the outlet of the column was an on-line MTI portable gas chromatograph model P100 equipped with a thermal conductivity detector. This chromatograph monitored the outlet stream every 3 min for the presence of MB. The MTI operated in conjunction with an IBM Thinkpad laptop computer with a 486 Intel chip.

A Gast model R5325A-2 rotary vane pump, capable of pulling the required velocity of air/fumigant mixture through the column bed, drove the whole system by generating a

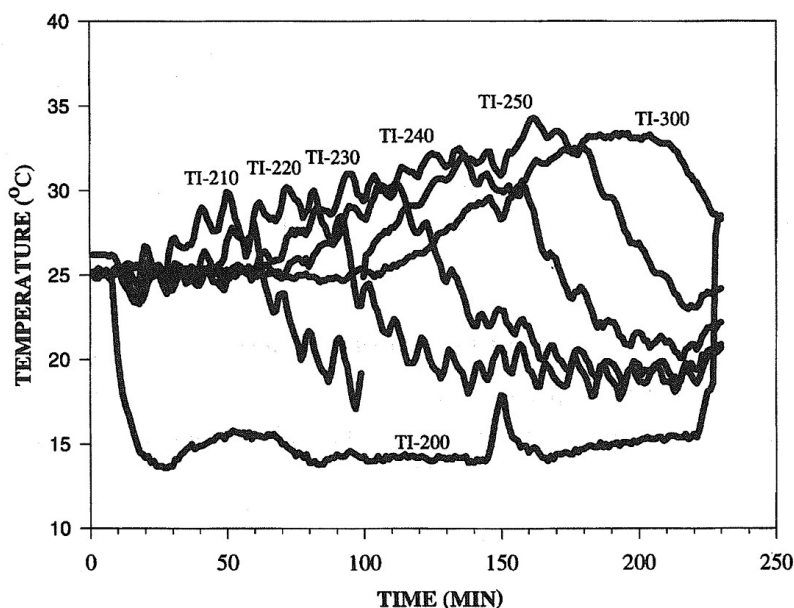


Fig. 2. Temperatures in the column during a typical loading experiment. TI- designations refer to positions shown in Fig. 1.

vacuum at the end of the column. The pump exhausted directly into a laboratory hood. The entire system, from the preconditioning portion (T-110) to the pump (P-300), ran under vacuum during the testing periods. Working under vacuum was important for the safe operation of the experiments since any leaks only permitted room air to flow into the system, preventing MB from escaping into the room.

In most cases, the column was operated with repetitive 30-min ventilation periods ("runs") until breakthrough was observed at the outlet of the column. During each run, the column was normally charged with 38.5 g MB in 2,500 L (87 ft³) air. The runs continued until the column outlet concentration reached 500 ppm MB (2 mg/L). The carbon was weighed at the beginning and end of each trial. The weight gain was due to the adsorbed MB plus water (either adsorbed or desorbed during the trial). Most of the trials were carried out during the winter months. We noticed that the moisture content (m.c.) of the clean carbon increased between its initial arrival in the summer of 1995 and its use in the winter of 1995/1996. Fresno usually experiences weeks of cold with high r.h. during the winter, and this winter was no exception. The clean carbon, since it was stored in 55-gal fiberboard drums which are quite permeable to moisture in the air, merely adsorbed water from its surroundings. The amount of water in either clean or loaded carbon was determined by the standard xylene method (ASTM method D-2867-83, reapproved 1988). Following each run, the carbon containing the MB was divided into two equal portions. A polished 2-mm carbon-steel bar (3 × 10 cm) was placed into each portion. Each portion —

with its steel bar — was then placed in a 1-L (quart) Mason jar. The first portion was placed in a room held at $26 \pm 2^\circ\text{C}$, and the second in cold storage at $-10 \pm 2^\circ\text{C}$, in order to determine if any corrosion would occur due to the production of hydrobromic acid when MB is hydrolyzed.

Several trials were made at a higher average MB concentration to determine the possible effects of concentration on the sorption. The same amount of MB was introduced in each run during a trial; however, this was done at 10-min intervals instead of 30-min intervals as in the previous trials.

RESULTS AND DISCUSSION

The adsorption of MB by activated carbon for a given trial could easily be followed by observing the temperatures along the axis of the carbon column. Figure 2 shows the temperature profile for one of the typical higher concentration, 10-min-run trials. The gas inlet (TI-200) temperature for this run was held at 15°C . At 15 min into the trial, MB was introduced into the effluent air stream. The temperature did not rise immediately because the thermocouple was located a few cm below the upper surface of the carbon. The temperature at TI-210 was already rising before the temperature at TI-200 peaked after 50 min. The successive thermocouples peaked at approximately 20-min intervals until the bottom position was the warmest, indicating imminent breakthrough of the MB. The temperature variations at each position during the trial followed the 10-min addition intervals used in this example. Temperatures were highest at the beginning of each run when the concentration was high and dropped off as the concentration decreased over the 10-min intervals. The same peaking and fluctuation of the temperatures at each position occurred in the lower concentration trials, when the MB additions were made at 30-min intervals. Figure 3 shows the appearance of interstitial MB from the locations used for the thermocouples. The MB in the interstitial space appeared after the temperature peaked at each location. As the carbon at each position became loaded, the MB in the interstitial spaces at that position increased until it reached the average concentration of each run (in this example, approximately 8,400 ppm). Because we did not have enough channels to record all the positions simultaneously, we unplugged the top thermocouple when the temperature had fallen and plugged in the bottom one to record the later rise in temperature there.

Adsorption capacities under various conditions are shown as % load (g MB/100 g carbon) in Table 1. Adsorption capacity was influenced by all of the variables tested: carbon type, MB concentration, temperature and r.h. Norit carbon, derived from peat, consistently had the lowest MB adsorption capacity; Westates carbon, derived from coconut shells, the highest. The different capacities are probably due to both the different raw materials in each carbon and the differences in the activation process used to produce each of the final products; source and activation process together determined pore size and structure.

Activated carbon is used for the sorption of many products in different applications:

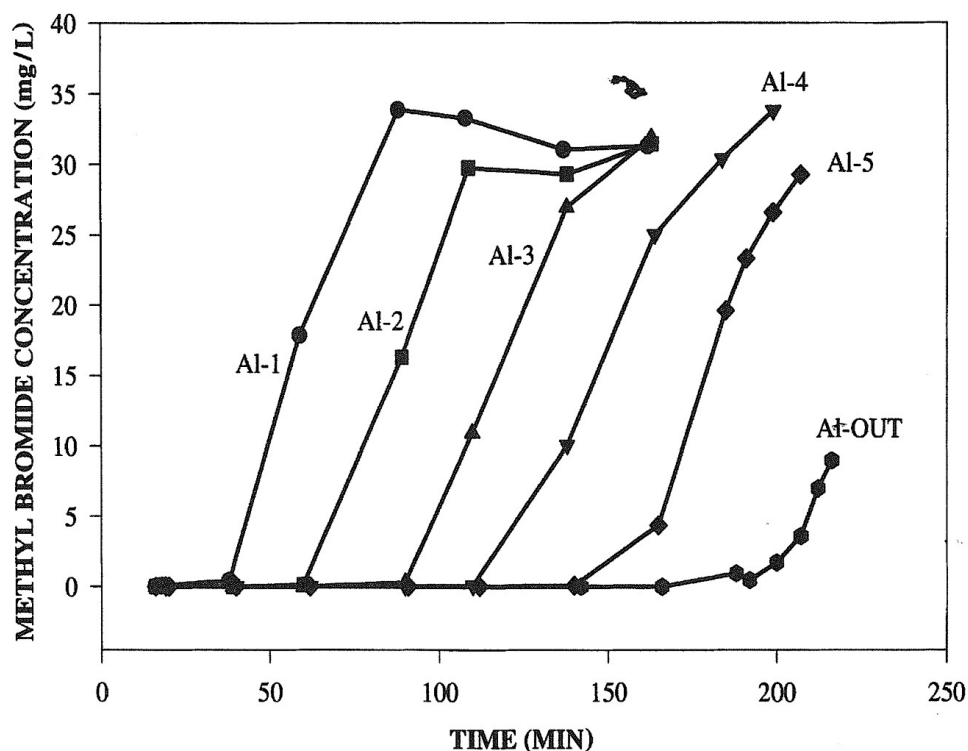


Fig. 3. Concentrations in the column during a typical adsorption experiment. Al- designations refer to those in Fig. 1. The breakthrough curve is shown as Al-OUT.

removal of high molecular weight color bodies from products, cleanup of chlorinated solvents from contaminated ground water and adsorption of low molecular pollutants from water and air streams (Goldhaar and Graham, 1991). The pore structure makes a given carbon more or less suitable for a given application. A significant amount of the pore volume of peat- and bituminous coal-based carbons is in macropores (>500 Å in diameter) and mesopores (20–500 Å in diameter). On the other hand, a majority of the pore volume of coconut-shell carbons is in micropores (<20 Å in diameter). Large molecules, such as color bodies, are preferentially adsorbed in macro- and mesopores, whereas smaller molecules, such as MB, are most effectively adsorbed in micropores. This explains the high capacity of the Westates carbon which has the highest amount of micropores of the three tested (Graham, 1992).

As expected, the adsorption capacity of the carbon was higher in every case when the concentration average was higher (i.e. 34 mg/L in a 30-min run compared with 34 mg/L in a 10-min run). It was also apparent that the adsorber inlet temperature and r.h. play an important role in determining the adsorption capacity of each carbon. Comparing the experiments at any r.h., shows that as temperature decreased from 35 to 8°C, capacity for each carbon

TABLE 1
The loading of MB on three different types of activated carbon
under various humidity and temperature conditions

Type of carbon	Average ppm	Inlet temperature (°C)	% r.h.	% load	% pre-treat water	% post-treat water
Calgon	3800	15	50	12.5	—	2.4
Calgon	3800	15	100	10.6	1.6	2.0
Calgon	3800	15	50	13.4	—	0.9
Calgon	3800	25	50	10.5	—	0.8
Calgon	3800	25	75	7.3	—	3.5
Calgon	3800	25	100	7.5	—	3.1
Westates	3800	8	75	18.3	—	1.8
Westates	3800	15	50	15.8	5.4	2.6
Westates	3800	15	100	13.6	—	4.0
Westates	3800	25	50	10.5	6.0	3.9
Westates	3800	25	100	8.8	0.7	5.6
Norit	3800	15	50	12.5	—	1.4
Norit	3800	15	100	6.4	2.4	3.6
Norit	3800	35	50	5.5	—	3.2
Calgon	8500	8	75	18.3	—	0.6
Westates	8500	15	50	22.6	—	1.0
Norit	8500	8	75	12.6	—	3.2
Norit	8500	35	50	8.2	—	1.8

Moisture on the carbon both before and after the adsorption are given for some of the loading experiments.

increased. Likewise, as the r.h. increased for a given inlet temperature, adsorption capacity decreased. As the r.h. approaches 100%, water starts to condense in the pores, occupying space that would normally be available for organic molecule adsorption, thus reducing capacity for organic molecules. Table 1 shows the results of the moisture test for the carbons both before (% pre-treat water) and after (% post-treat water) for several of the trials. At 50% r.h., the carbons lost water in each of the two trials tested for this. Conversely, at 100% r.h., the carbons gained water in each of the three trials so tested.

It is well known that the adsorption capacity of activated carbon decreases sharply as the r.h. approaches 100%. We found much less decrease in capacity at 100% r.h. than expected. This is because the r.h. of air in contact with the carbon is lowered as soon as the adsorption starts due to the heat liberated by the adsorption reaction. At the inlet concentrations used for these trials, sufficient heat was liberated to dehumidify the gas below the critical 100% r.h. figure.

CONCLUSIONS

These experiments were undertaken to find a suitable way for trapping MB from the effluent stream resulting from aeration of a fumigation chamber. We investigated the

effects of temperature, r.h. and average effluent MB concentration on the loading of MB onto activated carbons. The experiments were done over a wide range of temperatures and r.h.'s because commodity undergoing fumigation can be either dry or wet and be stored under either ambient or refrigerated conditions. Durable commodities, such as grain and nuts, do little to increase the r.h. over the period of a fumigation; perishable commodities, such as peaches and plums, may increase the r.h. of the fumigant/air mixture during the fumigation period. Refrigerated commodities, such as imported grapes, if fumigated when the surrounding air is warm and humid, will create a fumigant/air mixture of 100% r.h. in the chamber. The cold commodity acts like a condenser.

From the research we have conducted, it appears that, although higher temperatures and humidities reduce adsorption capacity, at least those carbons derived from coconut shells and coal adsorb sufficient quantities of MB to provide a practical method for minimizing atmospheric emissions from commodity fumigations. For such large chambers as those used in San Diego and Long Beach, a transportable adsorber measuring $6.1 \times 2.4 \times 2.4$ m ($20 \times 8 \times 8$ ft) loaded with 8,600 kg (19,000 lb) of carbon would be capable of adsorbing the MB from several fumigations. Assuming a conservative 10% loading capacity for the carbon (10 g MB/100 g carbon), and a $2,039 \text{ m}^3$ ($72,000 \text{ ft}^3$) fumigation chamber that uses 130.8 kg of MB to achieve a dosage of 64 g/m^3 (64 oz/1,000 ft^3), each adsorber would be sufficient for at least seven fumigations. This assumes that 95% of the MB charged into the chamber is adsorbed by the carbon. In reality, some MB is sorbed by the commodity during fumigation and only the amount desorbed by the commodity during aeration would be recovered by the carbon. Once the MB has been loaded on the carbon, the carbon can be transported to a reclamation site where it can be desorbed with an appropriate hot gas (air, nitrogen or steam). This process will desorb both MB and volatiles collected from the commodity. The clean carbon would then be ready for reuse at another fumigation site. The MB desorbed during the reactivation process could be oxidized to hydrobromic acid and thus recovered in a convenient form for reuse in manufacturing various brominated chemicals, including MB.

Further experiments will be conducted to verify that the carbon can be recycled by the process herein described and to determine the effect recycling has on carbon's capacity for adsorbing MB. We are planning a series of tests, where volatiles from commodities will be sorbed on the carbon together with MB, to determine the effect of the volatiles on the capacity of the carbon. The sorption/desorption of volatiles and/or MB over many cycles will give a good indication of the practicality of re-using the carbon.

This process provides a procedure which does not interfere with the established fumigation schedules used for quarantine purposes. Because there is no attempt to recycle the MB directly on fumigations following the one from which it was adsorbed, there is no need for concern about the effect of adsorbed commodity volatiles on subsequent fumigations. There is also no need for concern about the disposal of secondary hazardous wastes because 100% of the trapped MB and adsorbed commodity volatiles are thermally destroyed during the bromine recovery process.

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REFERENCES

- Anon. (1988) *ASTM Committee D-28 Standards on Activated Carbon*. American Society for Testing and Materials, Philadelphia, USA. 59 pp. (Available from Westates Carbon Corp., 2130 Leo Ave., Los Angeles, CA 90040, USA).
- Goldhaar, A. and Graham, J.R. (1991) The capture and recycling of benzene and other VOC's from refinery waste water and vapor streams. In: *Proc. 1st Annual Int. Exhibition and Conf. Covering Environmental and Safety Concerns in the Energy Industries*, Houston, TX, USA. 11 pp.
- Graham, J.R. (1992) *Carbon Application for Groundwater Clean-up* (65th Annual Meeting of the Arizona Water and Air Pollution Control Association, Mesa, AZ, 6–8 May 1992). 5 pp.
- Knaebel, K.S. (1995) For your next separation consider adsorption. *Chem. Eng.* **73**, 92–102.
- Paramele, C.S., Oconnell, W.L. and Basdekis, H.S. (1979) Vapor phase adsorption cuts pollution, recovers solvents. *Chem. Eng.* **57**, 59–70.