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Preliminary Study on Adsorption and Degradation of Methyl Bromide by Activated Carbon

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Abstract: Preventing emissions of methyl bromide is important for the recovery of the ozone layer. Methyl bromide is routinely emitted from fumigation facilities which could be prevented with equipment to capture the emissions. We examined the ability of activated carbon from coconut fibre to absorb methyl bromide. We showed that about 94 to 98% of the methyl bromide held in a tank was absorbed by activated carbon and not vented. About 95% of the methyl bromide was decomposed from the carbon using water at 80℃ for 16h. We showed regenerated carbon could be re-used for recovering more methyl bromide and it seemed to be little affected by a previous absorptive use. The properties of water and carbon together at 80℃ may be more effective at decomposing methyl bromide, rather than dry heat which requires temperatures as high as 900℃.

Introduction

Methyl bromide is widely used as fumigant for the treatment of quarantine pests worldwide. But methyl bromide is highly reactive to ozone and is classified as a potent stratospheric ozone depleter. About 37% of the global production of methyl bromide is now used for quarantine and pre – shipment treatments (Batchelor and Miller 2008). A range of alternatives to methyl bromide have been implemented for soil uses which has reduced the overall amount of methyl bromide.

However, although alternatives exist for many uses (TEAP 2006), they have generally not been implemented because methyl bromide for quarantine uses is not limited by the Montreal Protocol and therefore there has been little incentive to adopt alternatives (TEAP 2007).

methyl bromide used for quarantine treatments is used in a closed space or fumigation facility, and then released to the atmosphere after the treatment where it damages the ozone layer. If methyl bromide can be captured, absorbed and degraded, the amount emitted to the atmosphere from quarantine treatments could be reduced significantly. The use of recapture techniques could be used in the short term until methyl bromide-free alternatives become available as a more permanent solution.

Gan *et al.* (2000) studied 5 types of activated carbon that adsorbed methyl bromide and methyl iodide, and reported that granules of activated carbon made of coconut can absorb both chemicals. Leesch and Gerhard (1998) indicated that activated carbon can recover 95% of the methyl bromide which is vented from a closed fumigation chamber.

With this in mind, we examined the ability of activated carbon to absorb methyl bromide, the ability of hot water to remove methyl bromide from the activated carbon, and the prospects for re – using the activated carbon once the methyl bromide has been removed.

Materials and Methods

Materials

We used granular activated carbon 40 mesh produced from coconut shell. The samples of methyl bromide were obtained from the Lianyungang (Jiangsu) Seawater Chemical No. 1 Plant. We measured methyl bromide concentrations relative to a methyl bromide Standard of 200μg/ml which was obtained from SUPLECO USA. We used a portable photo-ionization gas chromatograph ("portable GC") to measure the methyl bromide concentrations (PHOTOVAC – 10S50, HAMILTON Co. Ltd. UK). We used an oxygen bag YD – 50 Type obtained from the Shanghai Huifeng Medical Instrument Co. Ltd to mix the pure fumigant to obtain the desired concentration.

Experiment Equipment

Figure 1 describes the fumigation chamber which has a capacity of $1m^3$.

Determine of Methyl Bromide Adsorbing rate by Activated Carbon

The oxygen bag was used to generate dif-

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ferent concentrations of methyl bromide (24, 48, 56g/m^3) at 25℃ and 30℃ in the fumigation chamber (Fig. 1). The concentration of methyl bromide in the chamber was recorded by the portable GC. A known concentration of methyl bromide was vented out of the chamber at a rate 500mL/m through the column which is loaded with 1 kilogram of activated carbon. The concentration of methyl bromide at the end of column was measured on the portable GC at1, 5, 10, 15, 20m intervals.

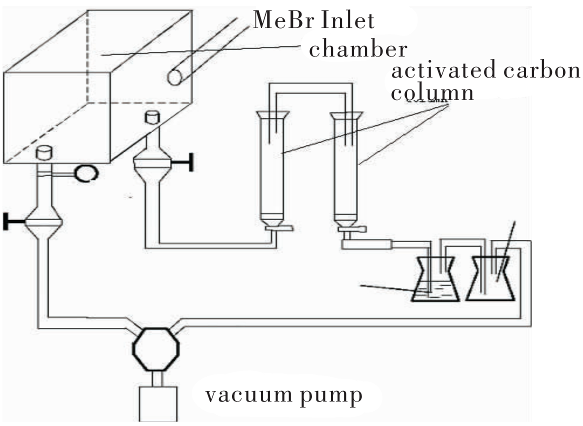

Fig. 1 Schematic of activated carbon test equipment

We repeated the test 4 times at each of the two temperatures to measure the difference between the initial methyl bromide concentration in the chamber and the average methyl bromide concentration being vented at the end of column. This enabled a calculation of the methyl bromide adsorption rates by the activated carbon at different temperatures. We repeated the test three times to get an average absorption rate.

Determination of Methyl Bromide Degradation

The activated carbon which adsorbed the methyl bromide vented from the fumigation chamber was taken out of the column and macerated. The macerated activated carbon was divided into 4 equal-sized parts. One part was weighed to 20g in 50mL conical flask. Fifty millilitres of methanol were added to the flask and after 10 minutes of stirring, the liquid was filtered by vacuum in Bush filter. The filtrate was collected in volumetric flask and is added to 50mL methanol.

The methyl bromide concentration was determined by gas chromatography equipped with an FED detector. Each of the remaining three parts was weighed to produce four 20g samples which were added to separate 50mL conical flasks containing 20mL of water. The flasks were placed at 60℃, 70℃ and 80℃ in a constant temperature bath.

At intervals of 8 h, 16 h, 24 h and 36h, a sample of the macerated activated carbon was removed from the bath and filtered. Fifty millilitres of methanol were added to the flask and after 10 minutes of stirring, the liquid was filtered by vacuum in Bush filter. The filtrate was collected in a volumetric flask and added to 50mL methanol.

The methyl bromide concentration was determined by gas chromatography. In addition, the filtrates from the 24 h and 36h macerated activated carbon were concentrated to 3mL by low-pressure, after which 5 mL of methanol was added and the concentration of methyl bromide was determined by gas chromatography. All treatments were repeated three times.

The gas chromatographic conditions for determination of the methyl bromide concentrations were: ANGILENT 6890 gas chromatograph with electron capture detection (ECD); Column: HP-50, 30m × 0.32mm × 0.25μm; Inlet temperature: 220℃; Column temperature: 70℃; Detector temperature: 320℃; Sample volume: 1μL. The quantity of methyl bromide was calculated by reference to the external standard methyl bromide concentration.

Regeneration of Activated Carbon

The activated carbon was regenerated by adding water at 80℃ followed by heating in an oven for 2h at 300℃. The regenerated activated carbon was then re-loaded into the absorption column and the trials are ready to begin again.

Results and Analysis

Absorption of Methyl Bromide by Activated Carbon

Most of the methyl bromide passed through the activated carbon column is adsorbed onto activated carbon (Table 1).

Table 1. Average concentration change of methyl bromide at venting after being absorbed by activated carbon (N = 3).

Temperature℃	methyl bromide applied rate (g/m^3)					
	24	48	56	24	48	56
	methyl bromide in tank (ppm)			methyl bromide at venting (ppm)		
25	6117.7	12331	13083	155.5	548.6	719
30	6249.7	12523	13530	168.9	621.5	733

The absorption rate of methyl bromide by activated carbon is shown in Table 2.

Table 2. Average percentage absorption rate of methyl bromide by activated carbon at 25 and 30℃ (N = 3).

Temperature℃	methyl bromide applied rate (g/m^3)		
	24	48	56
	methyl bromide in tank (ppm)		
25	97.64 ± 0.07	95.50 ± 0.11	94.49 ± 0.13
30	97.49 ± 0.12	95.04 ± 0.09	94.62 ± 0.14

Activated carbon has a strong affinity for methyl bromide. Methyl bromide recovery rate by activated carbon is about 95%. Temperature makes little difference to recovery rate.

Decomposition of Methyl Bromide from Carbon Using Hot Water

Figures 2, 3 & 4 show the methyl bromide decomposition at 40, 60 and 80℃, respectively.

After 36h, 83.88% – 92.28% of the methyl bromide was decomposed at 40℃; 96.45% – 98.60% at 60℃; and 99.84% – 99.98% at 80℃. At 80℃, methyl bromide was decomposed to 0.08 – 1.5g/kg in hot water after 36 hour. About 64% of the methyl bromide was decomposed at 80℃ after 8h, and about 95% after 16h. We conclude that methyl bromide is decomposed rapidly at 80℃ in hot water.

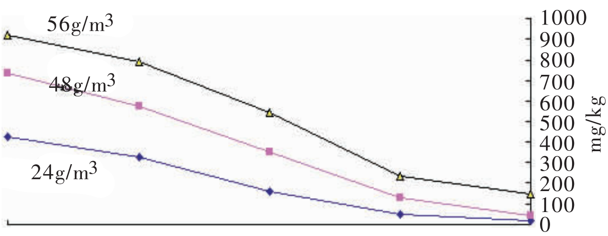

Fig. 2 Decomposition of methyl bromide in water at 40℃

Methyl Bromide Absorption by Regenerated Activated Carbon

Absorption of methyl bromide by regenerated activated carbon is not markedly different to the absorption of methyl bromide on activated carbon for the first time. Regenerated activated carbon could therefore be re-used to absorb methyl bromide vented from fumigation facilities.

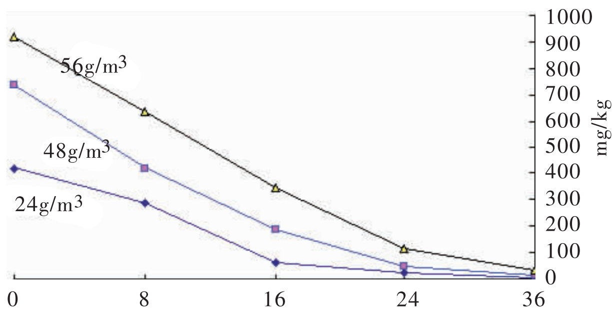

Fig. 3 Decomposition of methyl bromide in water at 60℃

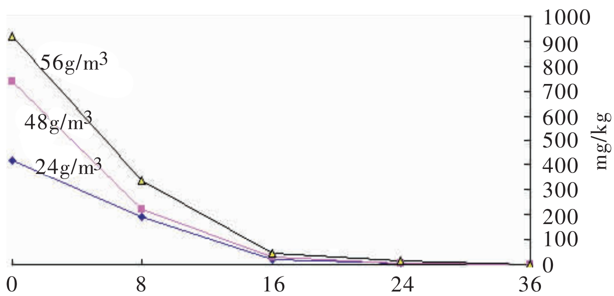

Fig. 4 Decomposition of methyl bromide in water at 80℃

Table 3. Percentage rate of methyl bromide being absorption by regenerated activated carbon at 25 and 30℃ (N = 3)

Temperature (℃)	methyl bromide applied rate (g/m^3)		
	24	48	56
	methyl bromide in tank (ppm)		
25	95.64 ± 0.17	94.50 ± 0.21	93.49 ± 0.23
30	93.37 ± 0.14	92.14 ± 0.19	91.62 ± 0.18

Discussion

The results of experiments indicate that methyl bromide emitted after a fumigation treatment could be adsorbed by activated carbon which is made of coconut. Activated carbon has a strong affinity for methyl bromide. The results are similar to those reported by Gan *et al.*

(2001) and Leesch & Gerhard (1998). Although the absorption was similar at 25℃ and 30℃ in our work, the rate of methyl bromide absorption is higher because absorption is inversely proportional to the temperature (based on the principle of Langmuir). Leesch and Gerhard (1998) considered zeolite to absorb methyl bromide similarly to activated carbon.

Methyl bromide may be decomposed from the activated carbon by hot water. The higher the temperature, the more rapidly methyl bromide is decomposed. At 80℃, methyl bromide took the least time to decompose. Gan *et al.* (2001) and Kitagawa (1998) thought that water and activated carbon provide a catalyzing active centre. After methyl bromide is adsorbed onto the surface of activated carbon, the CH_3-Br covalent bond could be ruptured by the molecular effect of water and, moreover, the rate of covalent bond rupture increased with increasing temperature. Without water, methyl bromide could be regenerated from activated carbon at an incineration temperature of 900℃.

Acknowledgements

We thank Dr Tom Batchelor (Touchdown Consulting Brussels) for editorial comments on the manuscript.

References

[1] Batchelor, TA & MK Miller. The role of the Montreal Protocol in reducing quarantine and pre – shipment uses of methyl bromide. *Proc. Int. Conf. on Controlled Atmosphere and Fumigation in Stored Products, Chengdu, China.* (2008): In press.

[2] Gan, J, NE Megonnel & SR Yates. Adsorption and catalytic decomposition of methyl bromide and methyl iodide on activated carbon. Atmos. Environ. (2001), 35: 941 – 947

[3] Kitagawa, H. Recovery Emission of Methyl Bromide by Adsorption (1998) http//: www. airiesor. jpwisee. pdfE98A0225pdf. pdf

[4] Leeesch, JG & FK Gerhard. Trapping Methyl Bromide on Activated Carbon (1998) http//: www. epa. gov/ozone/mbrairc1998077 leeschpdf