

THE EFFECT OF THE CATALYTIC ACTIVITY OF VARIOUS ACTIVATED CARBONS ON METHYL BROMIDE HYDROLYSIS RATE

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Introduction

Methyl bromide is widely used as a fumigant for soil, commodity and structure pest control. The use of methyl bromide was scheduled to be discontinued by the year 2001 because of its ozone depletion concern. However, recent amendments have extended its use to the year 2005. Currently, various techniques are being tested to reduce methyl bromide emissions during fumigation operations. Activated carbon has been proposed to trap methyl bromide from fumigation effluents, with the adsorbed methyl bromide either being destroyed thermally or recovered for reuse. Both approaches, however, require complex and expensive facilities, which discourage their use. Activated carbon is known to adsorb and also promote the hydrolysis of methyl bromide, forming methanol and $\text{HBr}^{1,2,3,4}$. Methyl bromide hydrolysis reaction rates have been determined with carbons of varying catalytic activity. Very rapid methyl bromide hydrolysis occurs at elevated temperatures (e.g., 80°C), and the rate of hydrolysis is related to the carbon's catalytic ability. Catalytic activated carbon offers a safer and less expensive alternative for destroying methyl bromide recovered from fumigation treatments. The technique would also be simple and safe enough for on-site application.

Experimental

Production of Bromide

20 ml of methyl bromide gas was injected into a capped vial containing 2 g of activated carbon. The mass of methyl bromide was weighed and individually recorded before and after the fumigant addition. The average weight difference was 71-73 mg. The treated vials were kept in the freezer overnight. The vials were uncapped while still cold, 1 ml of distilled water was added, and the vial was recapped with an

unpunctured septum. The wetted activated carbon samples were then incubated at different temperatures (20 , 50 and 80°C) in a constant temperature room (20°C), incubator (50°C) and water bath (80°C).

After 1, 3, 8, 24, 48 and 96 h into incubation, three replicates were removed from each treatment each time. Samples were stored in the freezer until extraction and analysis. For extraction, the samples were decapped, and the charcoal content was washed into a container with 50 ml water, followed by 40 seconds of stirring. The extract was then diluted by 20 times, and aliquot was transferred into an IC vial for analysis. IC conditions were AS-14 column; Buffer: 3.5 mM Na_2CO_3 and 1.0 mM NaHCO_3 ; 1.2 ml min^{-1} flow rate.

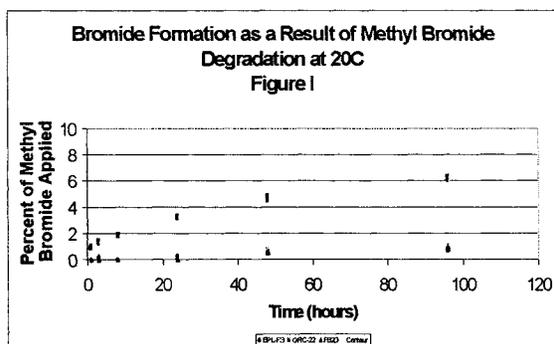
Dissipation of Methyl Bromide

The above procedure was followed up to the point of extraction. For extraction, the samples were decapped, and 4 ml acetone and 5 g dry sodium sulfate were immediately added, followed by immediate recapping. The sample vials were then stirred for 2 minutes, and a subsample of the clear extract was transferred into a GC vial. Two μL of the extract was injected into the GC for analysis. GC analysis was done using RTX-624 column and MEBR2. The temperature program was as follows: 50°C for 3.0 minutes, and then increased at $30^\circ\text{C}/\text{min}$ to 150°C . Methyl bromide was eluted at 1.88 minutes.

Results and Discussion

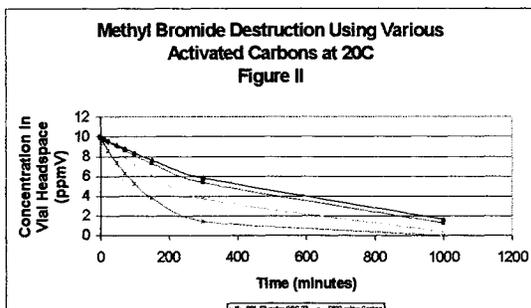
Four activated carbons were tested for methyl bromide destruction using two techniques. The initial testing analyzed the formation of bromide as a result of the hydrolysis reaction of the methyl bromide. Data show the bromide formation rate was higher for the coconut-based

activated carbon than for the bituminous coal based activated carbons (Figure I).



Data at 50°C and 80°C show similar trends, however the bromide formation increases at a faster rate with increasing temperature. The faster rate is consistent with the typical effect of temperature on reaction kinetics.

This data indicates that the coconut-based activated carbon destroyed methyl bromide at a faster rate than the bituminous coal-based activated carbons. However, subsequent tests were performed to determine the rate of methyl bromide destruction by analyzing the methyl bromide concentration. When the methyl bromide concentrations were analyzed, the data was reversed when compared to the formation of bromide from the initial tests (Figure II).



The data show the bituminous coal-based activated carbons destroyed methyl bromide at a faster rate than the coconut based activated carbon. Again, the higher temperature data show similar trends. However, the decomposition rates increased with increasing temperature.

Typical characterization tests such as apparent density, ash, butane activity, and iodine number show no correlation with the ability to decompose methyl bromide. The order of ability to destroy methyl bromide does, however, follow the peroxide number order for each carbon

tested. The peroxide number is a general indicator of catalytic activity⁵.

Conclusions

The destruction of methyl bromide is related to the catalytic activity of the activated carbon as determined by the peroxide number. Bromide formation is not a good indicator of methyl bromide destruction.

References

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