

DESTRUCTION OF METHYL BROMIDE ON ACTIVATED CARBON USING THIOSULFATE OR ELECTRICITY

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During post-harvest applications, methyl bromide fumigants currently are vented to the atmosphere from fumigation chambers. Elimination of these emissions is desirable due to concerns about their contribution to stratospheric ozone depletion. However, methyl bromide has proven particularly effective for insect control in post-harvest applications due to rapid kinetics. Fumigants exhibiting similarly rapid kinetics have not yet been demonstrated. One alternative is to capture the emitted fumes on activated carbon. However, disposal of the methyl bromide-saturated activated carbon would be costly, both because this saturated carbon would require disposal as a hazardous waste, and because such a disposal would require continuous replacement of activated carbon. An alternative would be to heat the carbon to volatilize the methyl bromide and reuse it as a fumigant. However, such recycling of methyl bromide raises concerns for agricultural product quality, because other constituents, including flavors, are likely to be similarly recycled, potentially contaminating commodities in subsequent fumigations.

For these reasons, it is desirable to destroy methyl bromide after each fumigation. The most feasible option currently available involves capturing methyl bromide on activated carbon after each fumigation, and then heating the activated carbon to volatilize the methyl bromide. The methyl bromide is then purged through a thiosulfate solution to destroy the methyl bromide. The purpose of this research is to evaluate whether this configuration could be improved to reduce the cost.

First, this research evaluated whether heating the carbon to volatilize the methyl bromide was necessary, as the heating cost is anticipated to account for a significant fraction of the operational costs of this process. One assumption behind the need for volatilization of the methyl bromide is that methyl bromide adsorbed to the activated carbon surface is not available for destruction by aqueous thiosulfate. We demonstrated that methyl bromide can be destroyed by thiosulfate while sorbed to the carbon surface. Destruction rates were comparable to the rates observed in aqueous solution. Products included bromide and methyl thiosulfate. These results suggest that methyl bromide could be destroyed at full-scale without heating the activated carbon and treating the resulting fumes in a separate thiosulfate bath. Rather, the methyl bromide-saturated activated carbon bed could be filled with a thiosulfate solution, permitting destruction of methyl bromide adsorbed to the activated carbon surface. The relatively harmless product of the destruction reaction, bromide, would remain in the solution, which could be drained as a relatively harmless wastewater. The activated carbon bed could be dried by venting with air prior to being placed back into service for the next run. However, at full-scale, the mass loading of methyl bromide on the carbon surface would necessitate thiosulfate concentrations near its solubility limit (low molar concentrations). While the carbon bed was reusable below the solubility limit, the initiation of crystal formation rapidly degraded the sorption capacity of the carbon during the next sorption cycle, suggesting a danger for treatment by thiosulfate.

Second, this research evaluated whether this process could be further simplified by eliminating the need for the supply of a thiosulfate solution. Hypothesizing that the thiosulfate-mediated destruction of surface-bound methyl bromide involved a reduction reaction, the potential for the electrolysis of surface-bound methyl bromide was evaluated. Under this scenario, the activated carbon would be transformed into an electrode, such that methyl bromide adsorbed to the carbon would be directly destroyed by electrons supplied from the electrical grid, without the need for supplying a thiosulfate chemical stream. Again, the activated carbon bed would be filled with water to facilitate completion of the electrical circuit. Saltwater, often available at post-harvest fumigation facilities (e.g., ports), could serve as a low-cost water supply for such uses because the high ionic strength would facilitate completion of the electric circuit.

We optimized the voltage requirements needed for the electrolysis. At methyl bromide loadings on activated carbon relevant to full-scale, we achieved ~80% destruction of methyl bromide over 30 h with Coulombic efficiencies approaching 100%. Bromide was verified as a product. Future experiments will evaluate the dependence of the reaction on carbon types and the design and testing of a pilot-scale facility.