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. Experiments demonstrated that 300 μM methyl bromide degraded with a rate constant of 6.5×10^{-3} min^{-1} in the presence of 3 mM thiosulfate, but at 1.0×10^{-3} min^{-1} in the presence of both 3 mM thiosulfate and 0.8 g/mL activated carbon. Under the latter scenario, >95% of the methyl bromide was adsorbed to the activated carbon surface. The destruction of methyl bromide in this scenario demonstrates that a pathway exists for the destruction of methyl bromide on the carbon surface. 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.

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.

Initial experimental results with 300 μM methyl bromide adsorbed to sheet graphite, a surrogate for activated carbon with electrical conductivity, indicated that methyl bromide degraded at a rate constant of 0.7×10^{-3} min^{-1} at an ionic strength of 10 mM, but that the rate constant increased to 2.3×10^{-3} min^{-1} at an ionic strength of 100 mM (15% of seawater levels). The latter rate constant is 35% of the 6.5×10^{-3} min^{-1} value observed in the presence of 3 mM thiosulfate in aqueous solution, a metric of the best available current technology. These results indicate that electrochemical reduction is a feasible alternative technology to current technology. While the kinetics are comparable, electrochemical reduction may significantly reduce operational costs by avoiding heating of activated carbon for volatilization of methyl bromide, and eliminating the need to supply thiosulfate. Future experiments are focused on optimizing this system, with the goal of achieving kinetics that equal or exceed those of the current thiosulfate-based system. Items to optimize include the applied voltage, and the characteristics of the carbon required to promote the electrochemical reduction.