

## THE USE OF AGRICULTURAL BY-PRODUCTS TO CAPTURE METHYL BROMIDE FOLLOWING POST-HARVEST FUMIGATION

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**Abstract.** Activated carbons were prepared from plum and peach stone as well as almond and walnut shell and comparatively evaluated as sorbents to minimize the atmospheric emission of methyl bromide following postharvest fumigations. A variety of methods were used to make the activated carbons and each is described. Sorbent evaluation was at the laboratory-scale, with the most effective methods tested at pilot-scale. The effect of scaling on several key experimental features is highlighted. In addition, several methods for the characterization of activated carbon were developed and are discussed as tools for predicting sorbent performance.

**Presentation Summary.** The purpose of this work is to test the viability of certain agricultural by-products as raw materials for the preparation of activated carbon (AC) that serves to trap methyl bromide (MB) vapors following post-harvest fumigations. The potential advantages of this approach are:

- More cost-effective method of MB capture
- Local source(s) of AC
- Value-added additional use for agricultural by-products

Activated carbon (AC) was prepared from almond shell, plum stones, peach stones, and walnut shells. AC is made in at least two stages: pyrolysis under nitrogen, in which the raw material is carbonized, and activation/oxidation where the porous structure and surface characteristics of the finished product are developed. Several procedures were utilized that differed by varying the temperature of the pyrolysis step, changing the gas(es) used in the activation step, and treating either the raw material (pre-treatment) or the freshly activated carbon (post-treatment) with acid, air and or water. To supply AC for “screening” sorbent performance relative to respective pyrolysis and activation/oxidation methodologies, preparations were conducted in tube furnace with a capacity of ~150g of raw material. A larger furnace with a capacity of ~8kg was used to subsequently prepare several of the most sorptive AC forms.

Screening of different ACs was performed on the laboratory-scale parallel adsorbent column tester (PACT) which allows simultaneous testing of up to 6 different adsorption columns holding ~4.5g of AC each. A pilot- or bench-scale adsorbent column (BSAC), which holds ~ 2kg of carbon, was used to evaluate the sorption of only the most effective AC forms. For both apparatuses, the activated carbon was dosed with MB over 30min to simulate the aeration of a chamber at 64mg/L MB. Dosing was repeated until breakthrough, when a MB concentration at or above 500ppm leaving the AC column is observed.

The physicochemical characteristics of the AC forms were also evaluated. The solvent displacement densities (where the volume of carbon is determined by the amount of methanol,

hexane, and water the AC displaces) and packing density (where the carbon volume is determined by how much AC can be packed into a given space) were used to approximate porosity. The number of hydrogen donating functional groups on the AC surface, as determined by titration, was used to estimate surface charge. Finally, the distribution of MB between the gas and sorbent phase was measured by batch-process adsorption isotherms by injecting a small amount of MB into a vial containing ~50mg of carbon, allowing residence time for equilibrium, and subsequent headspace sampling with gas-chromatographic quantification. Each of these tests did not require expensive, specialized equipment and represent a low-cost way of predicting carbon performance.

The “scalability” of MB sorption onto AC is a critical element of this research. We report the effect of scale on the procedural components of AC preparation, the change in AC quality, the flow rates and reaction times, and other practical challenges associated with scaling preparations from the gram to kilogram range. Additionally, the effect of scale in testing the sorption capacity of AC was examined, particularly with respect to how the diameter and loading of the adsorbent column changes the amount of water vapor (relative humidity) in the sample stream.