

# DEVELOPMENT OF A 1-D ADSORPTION KINETIC MODEL TO DESCRIBE MEBr RECOVERY FROM A HIGH-HUMIDITY FUMIGATION EFFLUENT STREAM

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## Introduction

Methyl bromide (MeBr) is an effective pesticide used in commodity fumigation, but is also an O<sub>3</sub>-depleter and scheduled to be phased out of U.S. production by 2001. In an adsorption kinetic study, an activated carbon adsorption column system is designed to maximize MeBr separation-recovery from a high-humidity post-fumigation effluent stream, and hence minimize atmospheric MeBr emissions, thus hopefully providing environmentally sound justifications for the continued use of this valuable fumigant.

MeBr-H<sub>2</sub>O vapor separation efficiency is measured by a partition coefficient ( $a_{12}$ ), which reflects the adsorbent's ability to adsorb MeBr (relative to H<sub>2</sub>O) out of the fluid stream.  $a_{12} = (W_1/W_2)/(C_1/C_2)$ , and is an indicator of adsorbent selectivity and performance. Activated carbon is chosen because of its high  $a_{12}$  value relative to other adsorbents.

Results from a previous MeBr-H<sub>2</sub>O vapor equilibrium adsorption-desorption study are coupled with the current study to examine mechanisms giving rise to observed kinetics of breakthrough profiles and propagation of mass transfer zones (MTZ) and thermal peaks. In addition to equilibrium mechanisms in the previous study (e.g. MeBr-H<sub>2</sub>O vapor competitive adsorption, hysteresis, hydrolysis), kinetic mechanisms are evaluated, including: interphase mass-heat transfer, advection, diffusion, heats of adsorption-desorption, and wall heat transfer.

Understanding the mechanisms behind equilibrium and kinetic adsorption-desorption behavior is pertinent to model development, validation, and subsequent design of an adsorption column that maximizes MeBr separation-recovery.

## Experimental

A 1-D dynamic adsorption model is developed to describe adsorption-desorption kinetics and mechanisms involved in the separation (adsorption) and regeneration-recovery (desorption) of MeBr from a high-humidity fumigation effluent stream. The model is subjected to validation and sensitivity-optimization

analyses, and serves as a template for the experimental design of a column to maximize MeBr separation-recovery, with minimal requirements of time and adsorbent amount.

Deviation of adsorbate concentration ( $C_i$ , g/m<sup>3</sup>) from equilibrium ( $C_i^*$ , g/m<sup>3</sup>) serves as the driving force for adsorption-desorption rate  $dW_i/dt$ . Equilibrium isotherm results from a previous study, describing adsorbent capacity ( $W_i$ , g/g adsorbent) and heat of adsorption ( $dH_i$ , J/g adsorbent) vs.  $C_i^*$ , are incorporated into the kinetic model to describe axial-temporal ( $z-t$ ) variabilities of the state variables (SVs):  $C_i$ ,  $C_i^*$ ,  $W_i$  ( $i$  = adsorbate species: 1=MeBr, 2=H<sub>2</sub>O), fluid ( $T_g$ ) and adsorbent ( $T_s$ ) temperatures.

The equilibrium  $W_i-C_i^*$  and  $dH_i-C_i$  experimental data are obtained via flow microcalorimetry over the ranges: 0 - 100 g/m<sup>3</sup> MeBr, 0 - 200 °C, 0 - 100 % RH. Transient kinetic data, consisting of real-time measurements of pressure drop,  $C_i$ ,  $T$ , and RH at various axial locations, are obtained from a pilot plant activated adsorption column in a research study conducted at the ARS Horticultural Crops Research Laboratory (Fresno, CA).

Identification of mechanisms involves evaluation of terms in differential mass and thermal balance equations that give rise to changes in the SVs. These terms are governed by the model's parameters, including: interphase mass ( $K_c$ ) and heat ( $U$ ) transfer, hydrolysis rate ( $k_f$ , adsorbent phase only), advection ( $u_0$ ), axial mass ( $A_z$ ) and thermal ( $K_z$ ) diffusion, heats of adsorption ( $dH$ ) and hydrolysis ( $dH_{hydroly}$ ), and radial wall heat transfer ( $h_w$ ). The system of equations is solved via finite differences, with application of appropriate initial and boundary conditions (ICs, BCs) for adsorption-desorption modes.

## Results and Discussion

Effects of the model's adjustable ( $K_c$ ,  $U$ ,  $h_w$ ,  $A_z$ ,  $K_z$ ,  $k_f$ ) and structural-operating parameters (column diameter  $D_{ads}$  and length  $L_{ads}$ , adsorbent particle size  $D_p$ , porosity  $\epsilon$ , volumetric flow rate  $\dot{V}$ , ambient temperature  $T_{amb}$ , heating rate HR)

on adsorption-desorption kinetics are evaluated. Some parameters are obtained via published generalized correlations where available (Hill, 1977; McCabe and Smith, 1985). Otherwise,  $(z, t)$ -independent optimal parameters are regressed to maximize correlation with observations.

Parameter effects on adsorption-desorption breakthrough times ( $t_{ads}$ ,  $t_{des}$ ) are examined.  $t_{ads}$ , defined as the time required for column outlet MeBr concentration to reach 500 ppm, is inversely related to the mass transfer zone (MTZ) migration rate through the column.  $t_{des}$  is defined as the time required for MeBr recovery ( $R_{MeBr}$ ) from the adsorbent surface to reach a setpoint value (e.g. 50 %, 90 %, 99 %). Sensitivity-optimization analyses are conducted to obtain an optimal set of parameters that minimizes ( $t_{ads} + t_{des}$ ) while maintaining high degrees of MeBr separation-recovery, so that more post-fumigation batches can be processed in a shorter time.

Model run results generate typical  $t_{ads}$  and  $t_{des}$  values of 30 min and 15 min, respectively. Allowing an additional 15 minutes for adsorbent regeneration and return to ambient temperature after the desorption mode, a practical batch run cycle can be completed in 1 hour, within which time approximately 2 kg MeBr can be separated (adsorbed) from a high-humidity fluid stream that is initially 15,000 ppm MeBr, using:  $L_{ads} = 1$  m,  $D_{ads} = 16$  in.,  $D_p = 0.37$  cm,  $e = 0.468$ ,  $v = 80$  m<sup>3</sup>/min, and  $T_{amb} = 298$  K.

Effects of desorption mode type (hot-air, steam), on  $t_{des}$  and  $R_{MeBr}$  are examined. The effect of increased heating rate HR (°C/min) during hot-air desorption is to decrease  $t_{des}$  for a specified  $R_{MeBr}$  (or equivalently, to increase  $R_{MeBr}$  for a specified  $t_{des}$ ). During steam desorption, increased competitive adsorption between MeBr and enhanced H<sub>2</sub>O vapor acts to decrease  $t_{des}$  and/or increase  $R_{MeBr}$ , as H<sub>2</sub>O vapor molecules replace MeBr on the adsorbent surface.

### Conclusions

The observed formation and migration of mass transfer zones (MTZs) and thermal peaks (produced by the heat of adsorption) through the column, and variabilities of the SVs, are well-described by the kinetic model. The model predicts typical batch cycle times of approximately 1 hour.

Evaluation of individual mass and thermal terms enables potentially complex physical mechanisms to be identified. Coupling between mass and thermal balance

equations exists via the T-dependence of  $C_i^*$ , which decreases with T at constant  $W_i$  (results of previous equilibrium study), and an adsorption-desorption rate term  $dW_i/dt$  within the thermal  $dH$  term. Such couplings enable effects of thermal properties (e.g.  $U$ ,  $h_w$ ,  $K_z$ ,  $dH$ ,  $dH_{hydroly}$ ) on mass-related SVs ( $C_i$ ,  $C_i^*$ ,  $W_i$ ), and of mass properties ( $K_c$ ,  $k_f$ ,  $A_z$ ) on thermal SVs ( $T_g$ ,  $T_s$ ), to be discerned.

It is hoped that the results of this study sheds light on physical mechanisms governing competitive adsorption-desorption kinetics between MeBr and H<sub>2</sub>O vapor, gives rise to future optimization design studies to maximize post-fumigation MeBr separation-recovery (and hence minimize emissions of this O<sub>3</sub>-depleting fumigant), and justifies the continued use of MeBr as a fumigant pesticide.

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