MODELING OF DIFFUSION-ADSORPTION KINETICS OF 1-METHYLCYCLOPROPENE (1-MCP) IN APPLE FRUIT AND NON-TARGET MATERIALS IN STORAGE ROOMS

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ABSTRACT

The purpose of this research was to model the kinetics of adsorption of 1-Methylcyclopropene (1-MCP) in apple fruit and 'non-target' solid materials found in apple storage rooms. A distinction is made between diffusion into the material and the adsorption. The process was therefore described by Fick's second law of diffusion of the gas through the pores of the material coupled with adsorption of the gas on the material's binding sites. A finite element formulation of the model, describing the diffusion and adsorption mechanisms separately, was first developed. The values of the relevant parameters were estimated based on head space measurements of the decrease of 1-MCP in dedicated jars with the different materials. The diffusion coefficient, adsorption coefficient and concentration of active site in the various solids were determined and were in the order of 10-9m2/s, 101 m3 mol-1s-1 and 10-4 mol m-3 respectively. The model was validated with separate experimental data.

1 . INTRODUCTION

1-methylcyclopropene (1-MCP) has been shown to suppress ethylene responses and extend the postharvest shelf life and quality of numerous fruits and vegetables. In particular, apple, tomato, and avocado fruits have shown remarkable results (Sisler and Blankenship, 1996; Sisler and Serek, 1997, Blankenship and Dole, 2003, Sisler and Serek, 2003, Watkins, 2006, Huber, 2008). In a current commercial formulation it is complexed with α–cyclodextrin to form a powder which provides a more stable, convenient and safe means for storing and transporting. 1-MCP gas is generated when water is mixed with the soluble powder (Daly et al., 2000; Prange and DeLong, 2003; Vallejo and Beaudry, 2006; Nanthachai et al., 2007).

Numerous studies on the use of 1-MCP are mainly on describing plant responses to applied dosages (Blankenship and Dole, 2003), and the loss of 1-MCP gas used in a treatment is attributed only to the plant material under investigation. In some cases 1-MCP depletion data obtained from jar test experiments were empirically fitted to decay-type curves from which comparison of the sorption capacities of various produce, the initial rate of 1-MCP sorption and time required for 1-MCP to decline by half were deduced (Vallejo and Beaudry, 2006; Nanthachai et al., 2007). Such results have no direct application for the purpose of modeling and simulating the transport of 1-MCP gas in fruit storage rooms. To our knowledge, no previous attempts have been made to quantify the physical diffusion and biochemical adsorption mechanisms governing the kinetics of 1-MCP gas in materials. The main objective of this research work is to develop a coupled multiphase diffusion-sorption model of 1-MCP in apple fruit and bin materials and determine the relevant diffusion and sorption parameters for different materials and apple fruit. Experimental and mathematical procedures required to enable the prediction were developed and used.

2 . MATERIALS AND METHODS

2.1 Apple fruit and non target solid materials investigated

Golden Delicious apples (*Malus domestica* Borkh., cv. Golden Delicious), were purchased in December 2008 from a local auction in Belgium. Before purchase all fruits used for the test were stored at 1% O_2, 1.5% CO_2 and 1°C. All fruits used for the test were free of visual defects. Fruits were kept at 1°C in normal air before and during the experiment. The volume and weight of the apples used in the test were 234 ml ±14 ml and 211g ± 12.7 g. The surface area of the apple fruits were 238 ± 10 cm^2.

Bin materials included in this investigation were high density polyethylene (HDPE) from plastic bins (EuroPoolSystem International B.V., Rijswijk, The Netherlands), oak and poplar wood (from used wooden bins). In addition to bin construction material, corrugated cardboard that is frequently used as a bin liner was investigated. In each case three rectangular sample pieces having external surface areas of 250 cm^2 were cut out of bins stored in normal air indoor. Sample pieces were taken from used bins which were visually in good condition.

2.2 Gas exposure

Apple fruits and 'non-target' solid materials were placed individually into 1.8 l air tight glass jars fitted with rubber septa and held at 1°C. 1-MCP gas was added to the treatment jar headspace from another 1.8 l glass jar containing the 1-MCP gas at a concentration of 2 µl l^{-1}, by using a rubber bulb (Figure 1). The gas source was prepared by mixing 2 ml distilled water to 0.0062g SmartFresh^{TM} powder in a wide mouth glass bottle of size 75 ml measuring 4 cm in diameter and 8 cm in height. A 10 ml gas sample was injected into a gas chromatograph (Inter science, Compact GC) fitted with a 15m long, 0.53mm i.d. stainless steel column packed with MXT-Wax, 0.5u and equipped with a flame ionization detector (FID).

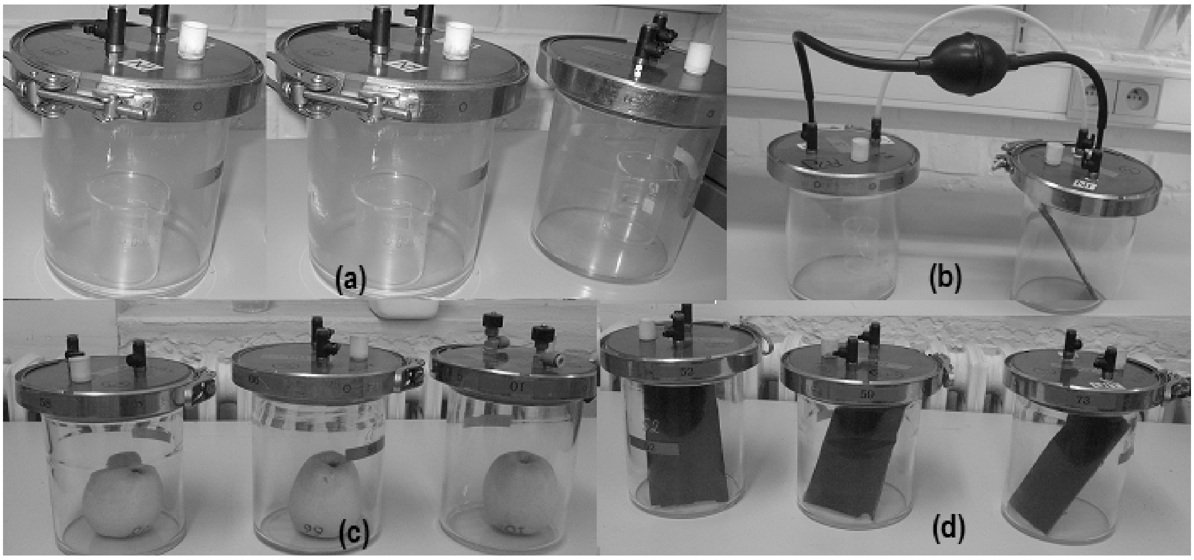


Figure 1 *Photo of the set up of the jar tests: (a) stock 1-MCP gas generation; (b) gas transfer to testing jar; (c) jar test on apple fruit; (d)jar test on HDPE plastic bin material. Target gas generation was in such a way that 1 µL L^{-1} was obtained in sample containing jar. The temperature of the experiments was* $1°C$

2.3 Model formulation

The model was based on Fick's second law of diffusion and was solved using the finite element method (FEM) on the geometry of the experimental set-up. The shape of the head space inside the jar and the solid testing samples were drawn to their exact shape and dimension (Figure 2). In the case of apple a sphere with equivalent volume was used as a representative geometry.

The fundamental equation to solve is the mass conservation balance for the 1-MCP gas inside the jar. The 1-MCP gas distributes itself in the headspace and in the material's mass. The transport in the headspace is described by a pure diffusion equation:

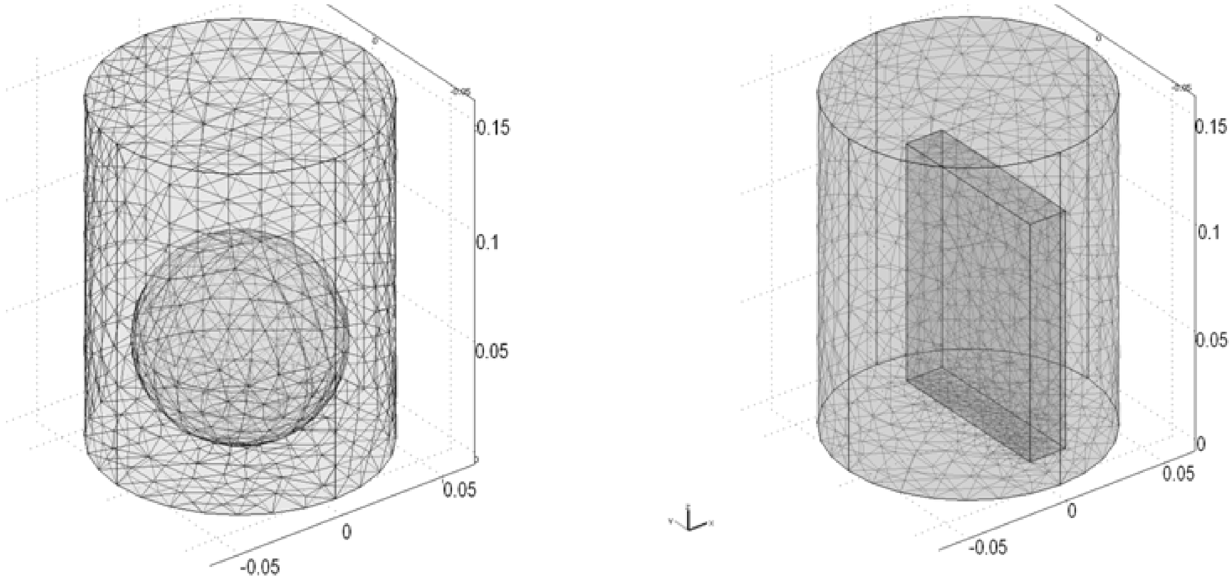
$$\frac{\partial c_a}{\partial t} = \nabla \bullet D_a \nabla c_a \tag{1}$$

where c_a (mol m^{-3}) is the concentration of 1-MCP gas in the gas phase, D_a (m^2 s^{-1}) is the diffusion coefficient of 1-MCP gas in air, t (s) is the time and ∇ (m^{-1}) the gradient operator. The diffusivity of 1-MCP gas in air, D_a, was predicted using the kinetic theory of gases (Christi, 1993). The use of this theory is justifiable for the fact that the gas mixture was dilute and the experiment was at atmospheric pressure.

In the solid 1-MCP exist in both the gas phase and adsorbed phase. The adsorption was assumed irreversible and is given by Eqn. (2).

$$c_a + s \xrightarrow{k_s} c_s \tag{2}$$

where c_a (mol m-3) is the concentration of 1-MCP gas in gas phase in the solid pores, s (mol m-3) is the concentration of active adsorption sites per unit volume of solid and c_s (mol m-3) is the concentration of irreversibly adsorbed 1-MCP gas per unit volume of solid. k_s (m3 mol-1 s-1) the adsorption rate constant per binding site. The diffusion-adsorption equation then reads:



(a) (b)

Figure 2 *Finite element mesh of the geometric model of representative samples: (a) three dimensional (3D) model of apple fruit; (b) 3D model of oak bin material;*

$$\frac{\partial c_a}{\partial t} = \nabla \bullet D_S \nabla c_a - k_s (c_{s,max} - c_s) c_a \qquad (3)$$

where $c_{s,max}$ (mol m-3) represents the total amount of available active sites per unit volume of solid ($s = c_{s,max} - c_s$) and D_s (m2 s-1) is the effective diffusivity of 1-MCP gas in the solid. The second part of the right side of Eqn. (3) is the rate of adsorption of 1-MCP gas on receptor sites, according to the reaction mechanism, Eqn. (4):

$$\frac{\partial c_s}{\partial t} = k_s (c_{s,max} - c_s) c_a \qquad (4)$$

The solution of the above model is not possible without the correct boundary and initial conditions of the experiment. Initial and boundary conditions on the walls of the jar were given by Eqn. (5) and Eqn. (6), respectively:

$$c_a = c_{a0}\ , c_s = 0 \qquad (5)$$

$$\boldsymbol{n} \bullet (-D_a \nabla c_a) = 0 \qquad (6)$$

Where ***n*** is the unit normal vector.
At the boundary between the material and the headspace continuity is assumed:

$$\boldsymbol{n} \bullet (D_s \nabla c_a - D_a \nabla c_a) = 0 \qquad (7)$$

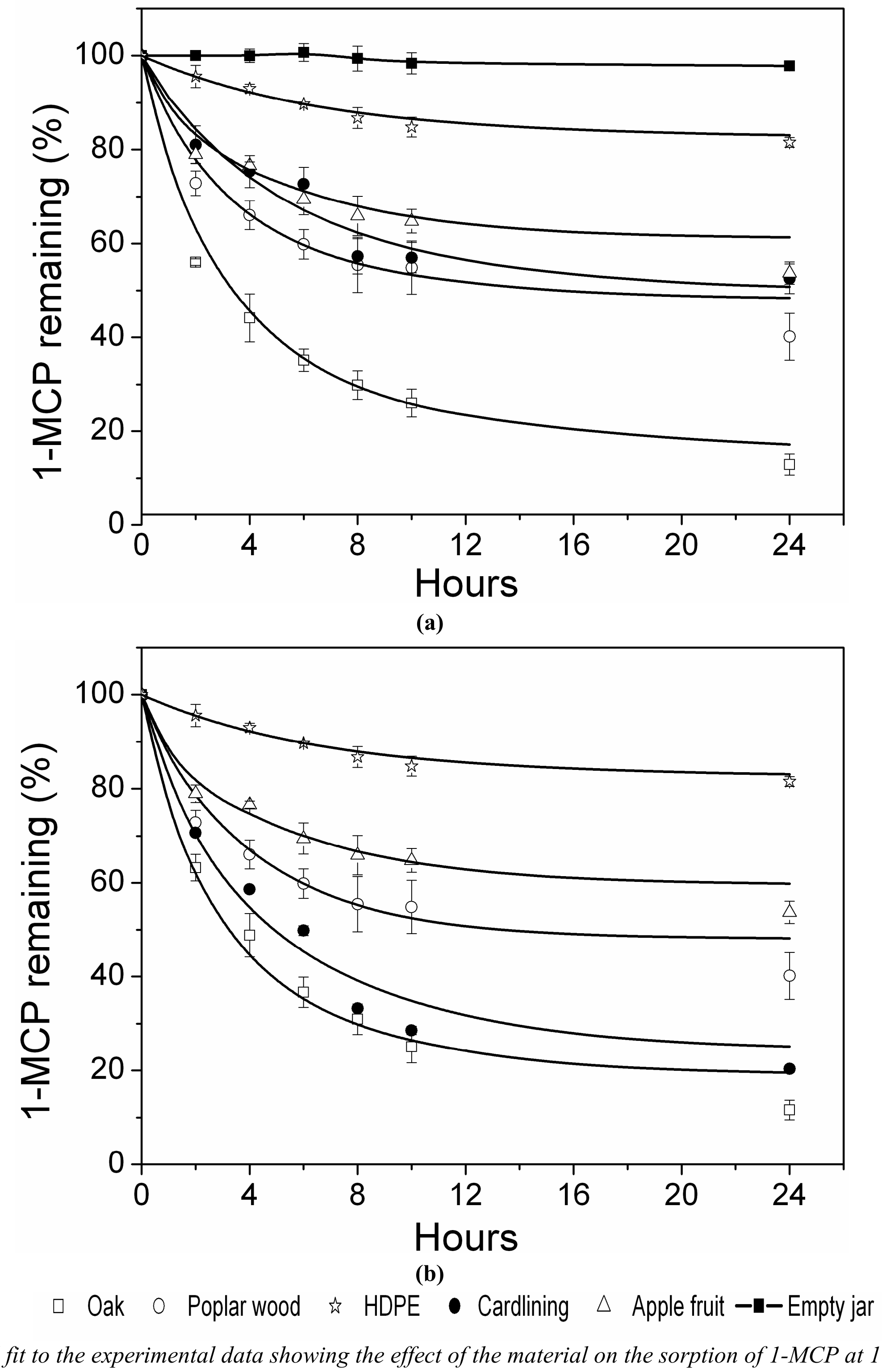
The effective diffusivity, adsorption coefficient and concentration of active binding sites of the 1-MCP gas in the materials were obtained by applying a parameter estimation technique. The technique assumes an isotropic solid medium and concentration-independent diffusion and adsorption coefficients in a finite element model developed in COMSOL 3.5. The assumed parameters were then adjusted based on iterative minimization of prediction error using nonlinear least-square (nonlinear data-fitting) solver function of MATLAB 7.6.0 (R2008a).

3 . RESULTS

The 1-MCP concentration in the test jar declined for all sample materials (wet and dry) in the investigation, but was stable for an empty jar (Figure 2), showing no leakage effects. The values of the material properties were estimated by iteratively minimizing least square differences between actual and theoretical time series 1-MCP concentrations. The resulting fits are shown in Figure 2. Estimated 1-MCP gas diffusion parameters for apple and various 'non-target' bin materials in fruit storage rooms are summarized in Table 1 with their corresponding R^2 values. The R^2 values ranges from 0.994 to 0.927. The parameters considered were effective diffusivity, adsorption rate constant and concentration of active 1-MCP binding sites per unit volume of the solid.

4 . CONCLUSIONS

It is shown that a finite element model can provide a potential tool to predict the diffusion and adsorption behavior of 1-MCP gas. The method was efficient and the accuracy of prediction by the developed model was good. The developed knowledge about diffusion and adsorption coefficients of 1-MCP gas of the various materials are new additions to knowledge on 1-MCP. The transport properties of 1-MCP gas for other materials can be easily assessed using this method and a comprehensive property data base can be collected. Such property data can be used to develop a complete model of storage rooms to investigate various aspects of the 1-MCP application process.



(a)

(b)

Figure 2 *Model fit to the experimental data showing the effect of the material on the sorption of 1-MCP at 1°C for dry (a) and wet (b) test samples of 'non-target' materials in apple and pear fruit storages as a function of time.*

Table 1 Estimated 1-MCP gas diffusion properties in the indicated non-target materials, Based on experimental data obtained from sample pieces held at 1°C and initial 1-MCP concentration of $1\ \mu l\ l^{-1}$

Material	**Treatment**	D_s **[$\times 10^{-9}$ m^2 s^{-1}]**	k_s **[m^3 mol^{-1} s^{-1}]**	$c_{s,max}$ **[$\times 10^{-3}$ mol m^{-3}]**	**R^2**
Oak	Dry	16.2 ± 5.06	6.50 ± 0.82	0.21 ± 0.01	0.994
	Wet	15.6 ± 3.15	7.15 ± 0.62	0.23 ± 0.01	0.984
Poplar wood	Dry	24.7 ± 6.21	1.79 ± 0.63	1.00 ± 0.81	0.964
	Wet	20.00 ± 7.21	1.80 ± 0.63	1.10 ± 0.85	0.959
HDPE	Dry	0.002 ± 0.0009	1.59 ± 0.46	1.80 ± 0.60	0.927
	Wet	0.002 ± 0.0009	1.57 ± 0.66	1.78 ± 0.58	0.912
Card lining	Dry	2.0 ± 0.20	0.92 ± 0.41	3.00 ± 0.02	0.956
	Wet	1.74 ± 0.01	2.97 ± 0.81	4.00 ± 0.02	0.978
Apple	G.Delicious	23.6 ± 1.17	3.49 ± 0.98	0.06 ± 0.01	0.972

5. ACKNOWLEDGEMENTS

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