

Short communication

# Predicting humidity effect on adsorption capacity of activated carbon for water-immiscible organic vapors

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## Abstract

This paper presents a simple numerical solution to the method of Manes (Proceedings of the Engineering Foundation Conference Bavaria, West Germany, 1984: 335) developed from the Polanyi adsorption potential theory to predict the effect of water humidity on the adsorption capacity of activated carbon for a water-immiscible organic vapor. The input parameters for the solution are the pure vapor adsorption isotherms quantified using the Qi, Hay and Rood (QHR) equation in Qi et al. (J. Environ. Eng., 124(11);1998:1130) for water, and the Dubinin–Radushkevich equation in Dubinin (Progress in Surface and Membrane Science, vol. 9, 1975, Academic Press) for the organic chemical. The solution employs a simple algorithm of decrement search and requires the least possible number of iterations in calculation. Predicted results compare favorably with the adsorption data for benzene in the relative humidity range 0–90%. This numerical approach is straightforward and better suited than the original graphical technique for use in dynamic simulation of activated carbon adsorbers. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Adsorption; Activated carbon; Water vapor; Humidity; Organic vapor; Adsorption capacity

## 1. Introduction

Microporous activated carbon has been used extensively to purify indoor air and industrial gas streams containing a variety of organic chemicals. In many instances, water vapor is present, and co-adsorption of water may reduce the adsorption capacity for organic chemicals. Although both adsorption kinetics and equi-

librium contribute to the performance of an adsorber, adsorption capacity is often the determinant of its service life in gas phase adsorption. Therefore, it is essential for the design and operation to quantify the effect of water vapor on the adsorption capacity for organic chemicals of interest.

The effect of water on adsorption of an organic vapor onto activated carbon has not been described adequately with a theoretical approach. Standard methods such as the ideal adsorbed solution theory and the vacancy solution model cannot be applied to this situation because of the fundamental difference in adsorption mechanism (Doong and Yang, 1987; Huggahalli

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and Fair, 1996). Consequently, a design engineer may be forced to choose from the four empirical or semi-empirical methods listed in Table 1.

Among the four methods compared in Table 1, the semi-theoretical method of Manes appears to offer the advantage of being predictive, since it requires only pure-component isotherms as inputs. Extension of the method beyond binary adsorption systems is straightforward (Manes, 1984). The drawback of this method is that its graphical technique is incompatible with the computer simulation of adsorbers. Manes (1984), and others (Grant et al., 1984; Cal, 1995) used the graphical technique because they lacked an adequate isotherm equation to describe pure water vapor adsorption.

This paper describes a simple numerical solution to the method of Manes (1984) for predicting the effect of water on the adsorption of a water-immiscible organic vapor onto activated carbon. The input parameters for the solution are the pure vapor adsorption isotherms quantified using the QHR equation developed by (Qi et al., 1998) for water and the Dubinin–Radushkevich (DR) (Dubinin, 1975) equation for organic chemicals.

## 2. Theoretical

### 2.1. Pure vapor adsorption isotherms

Adsorption of pure water vapor onto activated car-

bon is modeled using the QHR equation that follows (Qi et al., 1998, 2000):

$$q_{w,0} = \frac{\rho_w W_w}{1 + \exp \left[ k_w \left( \frac{P_{1/2}}{P_{w,s}} - \frac{P_{w,0}}{P_{w,s}} \right) \right]} \quad (1)$$

Eq. (1) is developed using a logistic function that describes the change in adsorption capacity with vapor pressure proportional to the product of the remaining capacity (representing the primary adsorptive sites) and the amount of water adsorbed (representing the secondary adsorptive sites).

Adsorption of pure organic vapor as a single component is quantified using the DR equation (Dubinin, 1975):

$$q_{a,0} = \rho_a W_a \exp \left[ -k_a \left( RT \ln \frac{P_{a,s}}{P_{a,0}} \right)^2 \right] \quad (2)$$

Eq. (2) is based on the Polanyi adsorption potential theory and characteristic curves of adsorption that assumes the temperature invariance of the adsorption potential at a given micropore filling.

### 2.2. Manes method for adsorption of vapor mixture

Following the assumptions of Manes (1984), and based on the DR equation, the adsorption of organic

Table 1  
Comparison of methods for describing humidity effect on equilibrium adsorption of organic vapors onto activated carbon

	Okazaki et al. method	Manes method	Doong and Yang method	Chou and Chiou method
Method of development	Semi-theoretical	Semi-theoretical	Semi-theoretical	Empirical
Extension to beyond binary adsorption	Not formulated	Formulated	Not formulated	Not formulated
Testing organic chemicals	<ul style="list-style-type: none"> <li>● Acetone</li> <li>● Benzene</li> <li>● Methanol</li> <li>● Toluene</li> </ul>	<ul style="list-style-type: none"> <li>● Acetone<sup>a</sup></li> <li>● Benzene</li> <li>● Dichloroethylene</li> <li>● Methanol</li> <li>● Methylene chloride<sup>a</sup></li> <li>● <i>n</i>-Heptane</li> <li>● Toluene</li> </ul>	<ul style="list-style-type: none"> <li>● Acetone</li> <li>● Benzene</li> <li>● Methanol</li> <li>● Toluene</li> </ul>	<ul style="list-style-type: none"> <li>● Benzene</li> <li>● Cyclohexane</li> <li>● <i>n</i>-Hexane</li> <li>● Toluene</li> <li>● Tri-chloroethylene</li> </ul>
Solution technique	Numerical	Graphic	Numerical	Numerical
Need for vapor mixture data	No	No	Yes	Yes
Need for vapor–liquid data	Yes	No	No	No
References	Okazaki et al., 1978	<ul style="list-style-type: none"> <li>● Grant et al., 1984</li> <li>● Doong and Yang, 1987</li> </ul>	Doong and Yang, 1987	Chou and Chiou, 1997

<sup>a</sup>Manes model systematically underestimates the adsorption capacity. This may be due to the relatively high solubility of the compound.

vapor in the presence of water humidity is described by the following two sets of equations:

$$q_a = \rho_a W_a \exp \left[ -k_a \left( RT \ln \frac{P_{a,s}}{P_a} \right)^2 \right] \quad (V_{a,\max} \geq V_{w,\max}) \quad (3)$$

and

$$q_a = \rho_a W_a \exp \left[ -k_a \left( RT \ln \frac{P_{a,s}}{P_{a,0}} \right)^2 \right] \quad (V_{a,\max} < V_{w,\max}) \quad (4)$$

where  $V_{a,\max}$  and  $V_{w,\max}$  are the adsorbed volumes for organic vapor and water vapor for each present alone at the vapor pressures of the mixture, respectively.  $V_{a,\max}$  is computed using the DR equation:

$$V_{a,\max} = W_a \exp \left[ -k_a \left( RT \ln \frac{P_{a,s}}{P_a} \right)^2 \right] \quad (5)$$

and  $V_{w,\max}$  is computed using the QHR equation (Qi et al., 1998),

$$V_{w,\max} = \frac{W_w}{1 + \exp \left[ k_w \left( \frac{P_{1/2}}{P_{w,s}} - \frac{P_w}{P_{w,s}} \right) \right]} \quad (6)$$

The corresponding water vapor adsorbed is

$$q_w = 0, \quad (V_{a,\max} \geq V_{w,\max}) \quad (7)$$

and

$$q_w = \rho_w \left( V_{w,\max} - \frac{q_a}{\rho_a} \right), \quad (V_{a,\max} < V_{w,\max}) \quad (8)$$

Eqs. (3) and (7) state that at  $V_{a,\max} \geq V_{w,\max}$ , water humidity does not interfere with the adsorption of organic vapor, and thus, the amount of water vapor adsorbed is equal to zero. At  $V_{a,\max} < V_{w,\max}$ , however, less organic vapor will be adsorbed due to the reduction of its net adsorption potential, and the adsorption

Table 2

Pure vapor isotherm parameters for adsorption onto ACF-20 at 25°C

$k_w$	Water [Eq. (1)]		Benzene [Eq. (2)]	
	$P_{1/2}/P_{w,s}$	$W_w$ (cm <sup>3</sup> /g)	$k_a$ (mole/kJ) <sup>2</sup>	$W_a$ (cm <sup>3</sup> /g)
27.9	0.542	0.573	$3.20 \times 10^{-3}$	0.715

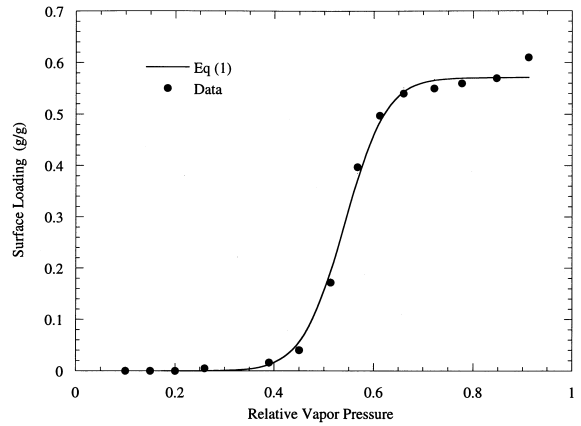


Fig. 1. Pure water vapor adsorption isotherm onto ACF-20.

of organic vapor results in displacing an equal volume of condensed water,

$$\frac{q_a}{\rho_a} = \frac{q_{w,0}}{\rho_w}, \quad (V_{a,\max} < V_{w,\max}) \quad (9)$$

where the volume of water displaced is given by

$$\frac{q_{w,0}}{\rho_w} = \frac{W_w}{1 + \exp \left[ k_w \left( \frac{P_{1/2}}{P_{w,s}} - \frac{P_{w,0}}{P_{w,s}} \right) \right]} \quad (10)$$

Substituting Eq. (9) into Eq. (10) gives

$$\frac{P_{w,0}}{P_{w,s}} = \frac{P_{1/2}}{P_{w,s}} - \frac{1}{k_w} \ln \left[ \frac{W_w}{(q_a/\rho_a)} - 1 \right], \quad (V_{a,\max} < V_{w,\max}). \quad (11)$$

Following the work of Hansen and Fackler (1953), Manes (1984) derived a thermodynamic equation for

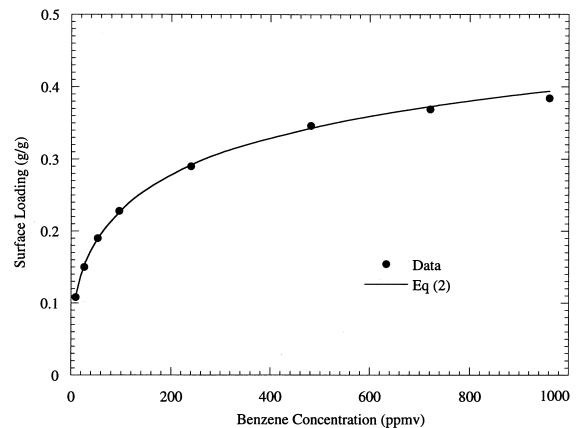


Fig. 2. Pure benzene vapor adsorption isotherm onto ACF-20.

the net adsorption potential of organic vapor in the presence of water vapor:

$$\frac{RT}{V_a} \ln \frac{P_{a,s}}{P_a} = \frac{\varepsilon_a}{V_a} - \frac{\varepsilon_w}{V_w} - \frac{RT}{V_w} \ln \frac{P_w}{P_{w,s}}, \quad (V_{a,max} < V_{w,max}). \quad (12)$$

Eq. (12) is subject to

$$0 \leq \frac{P_{a,0}}{P_{a,s}} < \frac{P_a}{P_{a,s}} \leq 1 \quad (13)$$

and

$$0 \leq \frac{P_{w,0}}{P_{w,s}} < \frac{P_w}{P_{w,s}} \leq 1 \quad (14)$$

In Eq. (12),  $\varepsilon_a$  and  $\varepsilon_w$  are the normal adsorption potentials for organic vapor and water vapor,

$$\varepsilon_a = RT \ln \frac{P_{a,s}}{P_{a,0}} \quad (15)$$

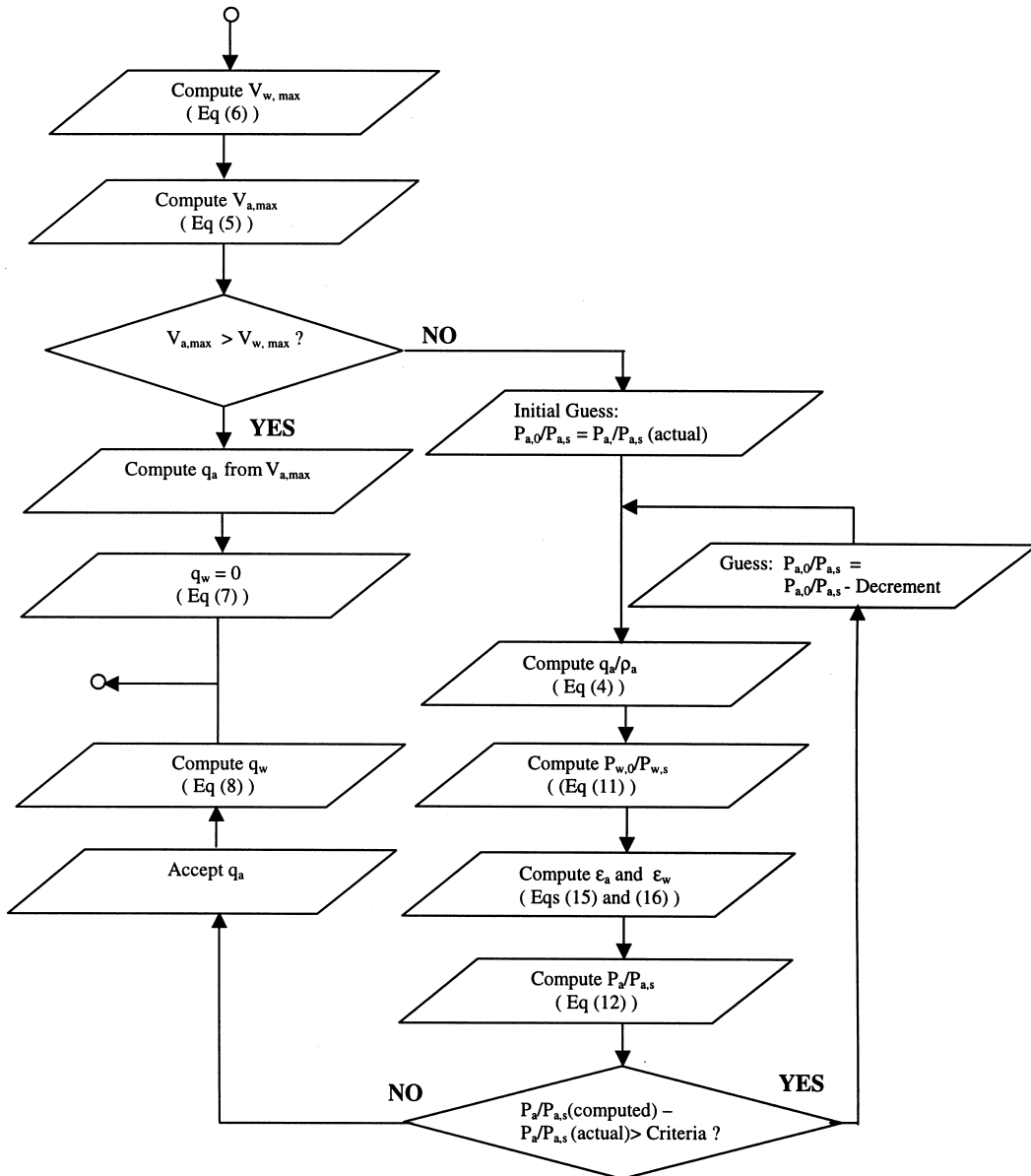


Fig. 3. Flow diagram of numerical solution of the Manes method.

and

$$\varepsilon_w = RT \ln \frac{P_{w,s}}{P_{w,0}} \quad (16)$$

Eq. (12) shows that the net adsorption potential of an organic vapor at  $V_{a,\max} < V_{w,\max}$  is equal to its normal adsorption potential, diminished by the normal adsorption potential of an equal volume of water corrected for the water vapor pressure less than the saturation. Substituting Eqs. (15,16) into Eq. (12) gives

$$\left(\frac{P_{a,0}}{P_a}\right)^{1/v_a} = \left(\frac{P_{w,0}}{P_w}\right)^{1/v_w} \left(\frac{P_{a,0}}{P_a} < 1 \ \& \ \frac{P_{w,0}}{P_w} < 1\right). \quad (17)$$

### 3. Results and discussion

Experimental data from previous studies (Cal, 1995; Cal et al., 1996) investigating equilibrium adsorption of benzene and water vapors onto ACF-20 are used for comparison with the numerical solution of the Manes method. ACF-20 is a microporous activated carbon fiber adsorbent made from a cross-linked phenol-aldehyde fiber precursor (American Kynol, Inc.). The Brunauer, Emmett, and Teller (BET) specific surface area of the adsorbent is 1610 m<sup>2</sup>/g determined from the adsorption isotherm data of nitrogen at 77 K. The adsorption experiments were conducted under ambient conditions (at 25°C and atmospheric pressure) using a Cahn gravimetric balance (model C-2000).

The pure vapor adsorption isotherms of Eqs. (1,2) are solved using the Levenberg–Marquart algorithm

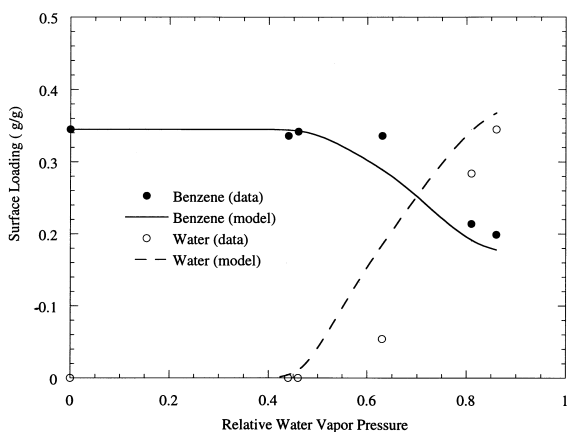


Fig. 4. Effect of water humidity on adsorption of benzene at 500 ppmv onto ACF-20.

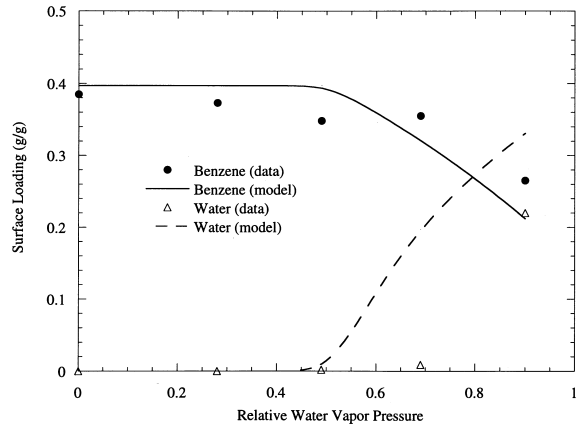


Fig. 5. Effect of water humidity on adsorption of benzene at 1000 ppmv onto ACF-20.

obtained as a Fortran subroutine from the IMSL (1994). The best-fit isotherm parameters for water and organic vapor presented in Table 2 are determined by minimizing the squared differences between the experimental data and the corresponding isotherm equation. Adsorption of pure water vapor onto ACF-20 exhibits a typical Type V isotherm, and Eq. (1) agrees well with the experimental data (Fig. 1). Adsorption of pure benzene vapor onto ACF-20 behaves in a typical Type I isotherm, and the experimental data are described well by Eq. (2) (Fig. 2).

The Manes Method is solved using a simple algorithm of decrement search shown in Fig. 3. At  $V_{a,\max} \geq V_{w,\max}$ , water humidity has no effect on adsorption of organic vapor, and  $q_a$  is obtained directly from  $V_{a,\max}$ . At  $V_{a,\max} < V_{w,\max}$ , inequalities Eqs. (13,14) allow one to determine  $P_{a,0}$  and  $P_{w,0}$  by the decrement search algorithm. To reduce the number of iterations, the decrement is updated at every iteration based on the difference between the actual (which is given) and the computed values for  $P_a/P_{a,s}$ . Computation time is usually less than a few seconds using a machine with a 200 MHz Pentium Pro processor.

Comparisons of the Manes method with the experimental data for adsorption of a benzene and water vapor mixture onto ACF-20 are presented in Figs. 4 and 5. The input data for the Manes method are the isotherm parameters given in Table 2. It appears that the Manes method reasonably agrees with the data for benzene at both 500 ppmv and 1000 ppmv. However, the method does not predict the lagging behavior of water vapor adsorption well. An explanation for this is that adsorption of benzene not only displaces the water previously adsorbed (which is considered by the method) but also reduces the number of primary adsorption sites (which is not considered by the method).

#### 4. Conclusion

This paper presents a simple numerical solution to the method of Manes (1984) developed to predict the effect of water humidity on the adsorption capacity of activated carbon for a water-immiscible organic vapor. The input parameters for the numerical solution are the pure vapor adsorption isotherms quantified using

the equation of Qi et al. (1998) for water and the Dubinin–Radushkevich equation (Dubinin, 1975) for the organic chemical. Predicted results compare favorably with the adsorption data for benzene in the relative humidity range 0–90%. This numerical approach is straightforward and better suited than the original graphical technique for use in a dynamic simulation for activated carbon adsorbers.

#### 5. Notation

$k_a$	DR isotherm parameter (mol/kJ) <sup>2</sup>
$k_w$	Isotherm parameter for water
$P_{1/2}$	Isotherm constant and $P_{w,O} = P_{1/2}$ at $[q,w,o]/(\rho_w w_w) = \frac{1}{2}$ (mmHg)
$P_a$	Organic vapor pressure in the presence of water humidity (mmHg)
$P_{a,0}$	Organic vapor pressure as it is present in a pure component system (mmHg)
$P_{a,s}$	Saturated organic vapor pressure (mmHg)
$P_w$	Water vapor pressure in the presence of organic vapor (mmHg)
$P_{w,0}$	Water vapor pressure as it is present in a pure component system (mmHg)
$P_{w,s}$	Saturated water vapor pressure (mmHg)
$q_a$	Surface loading of organic vapor in the presence of water humidity (g/g)
$q_{a,0}$	Surface loading of organic vapor in a pure component system (g/g)
$q_w$	Surface loading of water in the presence of organic vapor (g/g)
$q_{w,0}$	Surface loading of water in a pure component system (g/g)
$R$	$8.314 \times 10^{-3}$ (kJ/mol)
$T$	Absolute temperature (K)
$V_{a,max}$	Liquid volume of organic vapor adsorbed as it is present in a pure component system at $P_a$ (cm <sup>3</sup> /g)
$V_{w,max}$	Liquid volume of water vapor adsorbed as it is present in a pure component system at $P_w$ (cm <sup>3</sup> /g)
$V_a$	Molar volume of organic chemical (cm <sup>3</sup> /mol)
$V_w$	Molar volume of water (cm <sup>3</sup> /mol)
$W_a$	Limiting adsorption volume for organic vapor (cm <sup>3</sup> /g)
$W_w$	Limiting adsorption volume for water (cm <sup>3</sup> /g)
$\epsilon_a$	Adsorption potential for organic vapor as it is present as a pure component (kJ/mol)
$\epsilon_w$	Adsorption potential for water vapor as it is present as a pure component (kJ/mol)
$\rho_a$	Density of condensed organic liquid (g/cm <sup>3</sup> )
$\rho_w$	Density of condensed liquid water (g/cm <sup>3</sup> )

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