

Application of Mathematical Model of Three Parameters in Prediction of Sorption Isotherms for Four New Water Absorbent

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Abstract: Equilibrium Moisture Contents (EMC) of 4 new water absorbents were determined at 4°C by equilibrating about 1.6g samples at relative humidities in range of 0-100%, obtained using saturated salt solutions. The isotherms of new water absorbent were of BET type II. The results showed that the new water absorbent have an important capacity for water absorbed. The new water absorbent 3 has the biggest capacity for water absorbed at high water activity ($a_w > 0.9$). The amount of water absorbed by their product always reached 145 g H₂O / 100 g dry basis. The GAB equation was evaluated for his ability to fit the experimental data for the 4 types of new water absorbent. A non-linear least square regression program was used to evaluate the model constants. The GAB equation gave the best fit to the experimental data of water absorbent 3. The predicted safe storage moisture contents of new water absorbent 1, 2, 3 and 4 were 20.113, 149.356, 28.359, 21.582% (d.b.), respectively.

Key words: Condensation, water absorbent, atmosphere modified, isotherm, modelling

INTRODUCTION

Modified Atmosphere Packaging (MAP) has been known for many years and its use has become a common practice in post harvest storage of fruits and vegetables (Mannheim, 1986). The polymeric films and silicone membranes used in this technology have successfully extended the shelf life of many fruits and vegetables (Henig and Gilbert, 1975). MAP of fresh fruits and vegetables refers to the technique of sealing actively respiring produce in polymeric film packages to modify the O₂ and CO₂ concentrations inside the package (Geeson, 1988). With the introduction of combination system for modified, it is possible to create and maintain the optimal atmosphere composition for many fruits and vegetables (Lee *et al.*, 1995, 1996). However, for many varieties of fruits and vegetables which are chilling sensible, using modified atmosphere packaging and moderate temperatures, water condensation was found to be a limitation factor for successfully applying MAP in practice. Water condensation inside the package may promote the growth of spoilage and obscure the consumer's ability to examine the product prior to purchase (Gorny, 1997). Condensation facilitates fungal infection was found more seriously with products with high transpiration rate. Concerning MAP system,

packages with big mass load are more volunteered to this problem.

The main reason is that most polymeric used in MAP have lower water vapour transmission rates relative to transpiration rates of fresh produce (Ben-Yohoshua, 1985; Cameron *et al.*, 1995). Package air can in fact absorb a certain amount of transpired water, however very limited, because in most of package design, too much free space means waste of operational volume which is not economically interested. The over transpired water thus will be in (over saturation) condensation form left in the package.

Proper control of Relative Humidity (RH) in Modified Atmosphere (MA) packages containing fresh produce is a critical design consideration. It is well known that the RH is influenced by respiration and transpiration of the produce as well as the permeability of the packaging films. The high relative humidity may engender moisture condensation, microbial growth and decay of the produce (Kader *et al.*, 1989; Ryall and Pentzer, 1974). Song (1995) has developed a respiration-transpiration model to describe the respiration and transpiration behaviour of MAP systems containing fresh produce. These authors suggest that the relative humidity cannot be controlled below 100% with existing commercial films alone.

Several researchers studied the use of absorbents to lower the RH inside packages containing fresh produce. Most of these studies are based on trial-and-error without using mathematical models. Using water absorbent was approved of effectiveness in reducing saturation and condensation. To avoid the desiccation of the fresh produce it was important to store under a relative humidity between 90 and 95%. This requirement that consists in maintaining the relative humidity around 95% and didn't reach the condensation requires some particular features to the absorbent. It would be desirable that this absorbent didn't absorb water when the relative humidity was below 90% but as soon as the relative humidity exceeds 95%, the absorbent began absorbing water.

It was important to characterize these new water absorbents and to know their capacity of water absorption by determination of their sorption isotherms. The sorption curves express the hygroscopic equilibrium states of a given product. Their determination constitutes an indispensable stage for better understanding the problems of modelling the drying processes (Daguenet, 1985).

Numerous mathematical models have been proposed for the study of sorption of products, such as the GAB, Iglesias and Chirife, BET, Oswin and Ferro Fontan models (Barboza-Canovas and Vega-Mercado, 1993; Crapiste and Rotstein, 1982; Gekas, 1992; Wang and Brennan, 1991). The Guggenheim-Anderson-de Boer (GAB) model is reported to be the best for fitting sorption isotherm data for the majority of products up to a_w levels of approximately 0.9 (Barbosa-Canovas and Vega-Mercado, 1993; Timmermann *et al.*, 2001; Tsami *et al.*, 1999).

The aim of this study was to determine the isotherm sorption of the 4 new water absorbents and to choose the more hygroscopic at high water activity of the absorbent to test it like solution to problems of water condensation in packing under modified atmosphere and also evaluate the ability of GAB model to be used to describe the relationship between water activity and moisture content of the new water absorbents.

MATERIALS AND METHODS

Sorption method: In the present study, a standard static method (Lang *et al.*, 1981) was used at the temperature 4°C. This method was based on the use of saturated salt solutions to maintain a fixed Relative Humidity (RH). Although this method requires a long time for the hygroscopic equilibrium to be attained, it has the advantage of presenting a more restricted domain of moisture content variation. Salt solutions are more stable than acid ones (Belahmidi *et al.*, 1993). The mass transfers

between the product and the ambient air are assured by natural diffusion of the water vapour. The atmosphere surrounding the product has fixed relative humidity for every working temperature imposed on the system.

Description of experimental procedure: Four new water absorbents from commercial source (Nalco Chemical Company, Naperville, Illinois, USA) were used throughout this work. In a first time, 1.6 g of samples was put in cottenants in aluminium. These samples were dried then in desiccators in which, 200 g of desiccant were put down about. The drying lasts during one week. Water sorption determined were made by evenly distributing 1.6 g samples of new water absorbent inside small flasks and placing them in desiccators containing saturated salt solution to establish specific relative humidity levels. Standard solutions of Lithium Chloride (LiCl), Potassium Acetate (CH_3COOK), Magnesium Chloride (MgCl_2), Potassium Carbonate K_2CO_3 , Calcium Nitrate $\text{Ca}(\text{NO}_3)_2$, Sodium Nitrite NaNO_2 , Sodium Chloride (NaCl), Potassium Chloride (KCl), Potassium Nitrate (KNO_3), Potassium Sulphate (K_2SO_4) were used to maintain constant vapour pressure at constant temperature. For the relative humidity of 0 and 100%, the desiccants and water distilled were used, respectively. The solutions of salt saturated were taken cares to let in the desiccators during two days so that the air of the desiccators takes the suitable relative humidity. Desiccators are transferred then in a room where the temperature is constantly maintained to 4°C. The temperature is followed by a thermometer placed in the room. The relative humidity is constantly read in every desiccator to verify if the air of the desiccators is to the good relative humidity.

Water sorption was determined by weighting the samples at intervals until the reached hygroscopic equilibrium. The precision of the weight measurements was ± 0.1 mg and all determinations were made in triplicate. The results were expressed in percentage of water absorbed on a Dry Matter (DM) basis.

Modelling of the sorption: The GAB equation was used to describe the dry basis moisture content (M) as function of water activity (a_w):

$$M = \frac{M_0 C K a_w}{[(1 - K a_w)(1 - K a_w + C K a_w)]} \quad (1)$$

Where, C and K are constants and M_0 is described in the literature as the monolayer moisture content on dry basis (g g^{-1}). Equation parameters were estimated by the generalized reduced gradient algorithm (Microsoft Excel Solver) for nonlinear problems.

The suitability of the equation was evaluated using the mean relative percent error, standard error of moisture content. The mean relative percent error E (%) was defined as:

$$E(\%) = \left[\sum_{n=1}^n \frac{|M_{exp} - M_{pr}|}{M_{exp}} \right] * \frac{100}{N} \quad (2)$$

and standard error of moisture SEE was defined as:

$$SEE = \sqrt{\frac{\sum [(M_{exp} - M_{pr}) / M_{exp}]^2}{df}} * 100 \quad (3)$$

$$SEE = \sqrt{\frac{\sum [(M_{exp} - M_{pr}) / M_{exp}]^2}{N - n_p}} * 100 \quad (4)$$

Where, M_{exp} is measured equilibrium moisture content value, M_{pr} equilibrium moisture content value predicted by an equation, N number of data points and df degree of freedom of regression. The number of degrees of freedom as follows: $N - n_p$, where N is the number of data points and n_p is the number of parameters (Maroulis *et al.*, 1988). The mean relative percentage deviation modulus E (%) is widely adopted throughout the literature, with a modulus value below 10% indicative of a good fit for practical purposes (Lomauro *et al.*, 1985).

RESULTS AND DISCUSSION

Adsorption isotherms: The Fig. 1 shows the water vapour sorption isotherms of 4 new water absorbents. These 4 water vapour sorption isotherms are type II, having a typical sigmoidal shape, according to the classification of Brunaur, Emmett and Teller. These graphs also show an increase in equilibrium moisture content with increasing water activity at constant temperature. These changes in equilibrium moisture content are due to an inability of the new water absorbent to maintain vapour pressure at unity with decreasing moisture content. As moisture content decreases, moisture of the new water absorbent tends to show a lower vapour pressure, acting as if in solution, changing with atmospheric humidity. It is these changes in vapour pressure in the new water absorbent with atmospheric humidity which result in the characteristic sigmoid shape of water sorption isotherms (McLaughlin and Magee, 1998).

At low Relative Humidity ($HR < 75\%$), these new water absorbents sorbs relatively small amount of water (moisture content 0 to 48.46; 58.30; 68.80; 61.20 g / 100 g dry weight basis for new water absorbent 1, 2, 3 and 4,

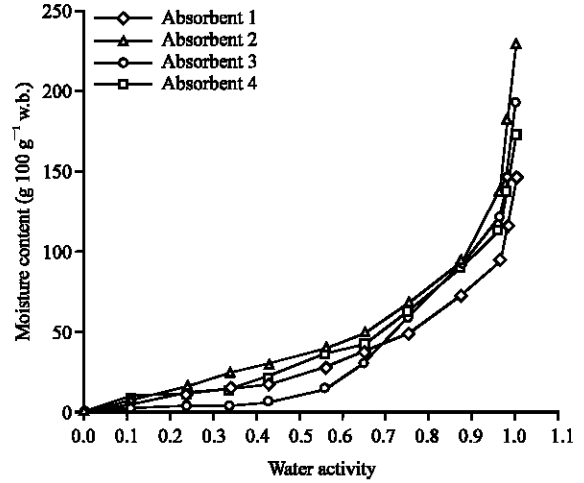


Fig. 1: Comparison of moisture sorption of four new water absorbent (1-4) at 4°C

respectively) what is due to the weak water-solid attractive strengths. They are classified by decreasing order of hygroscopicity: new water absorbent 3, 4, 1 and 2. However, at High Relative humidity ($HR > 75\%$), they sorbs exponential amount due to hydrogen bonding among water molecules (Gregg and Sing, 1982). The new water absorbents are classified by decreasing order of hygroscopicity: absorbent 3, 2, 4 and 1 with moisture content 228.6; 192; 172; 145.2 g / 100 g dry weight basis respectively. The points at low values of Relative Humidity ($HR < 0.55$) represent the adsorption bound water and so isotherm has only a gentle upward slope. As the relative humidity increases, the equilibrium moisture content increases sharply with relative humidity due to capillarity (Arévalo-Pinedo *et al.*, 2004).

The new water absorbent 3 is the most hygroscopic of all studied new water absorbents. It is the most adapted to be incorporated inside the modified atmosphere packaging of the fruits and vegetables to solve the condensation problem. This water vapour derives from the respiration and the transpiration must be absorbed by the new water absorbent. The new water absorbent must have the capacity to absorb the water vapour given out by the transpiration and the respiration to avoid high relative humidity in the package which can engender water condensation.

The weak absorption of water of the new water absorbent 3 to relative humidity $< 75\%$ are adequate to avoid the desiccation of the fruits and vegetables at low relative humidity. While to high relative humidity the exponential absorption of water allows the new water absorbent to absorb the surplus of the water vapour given out by transpiration and respiration. These phenomena intensify to high Relative Humidity ($HR > 90$).

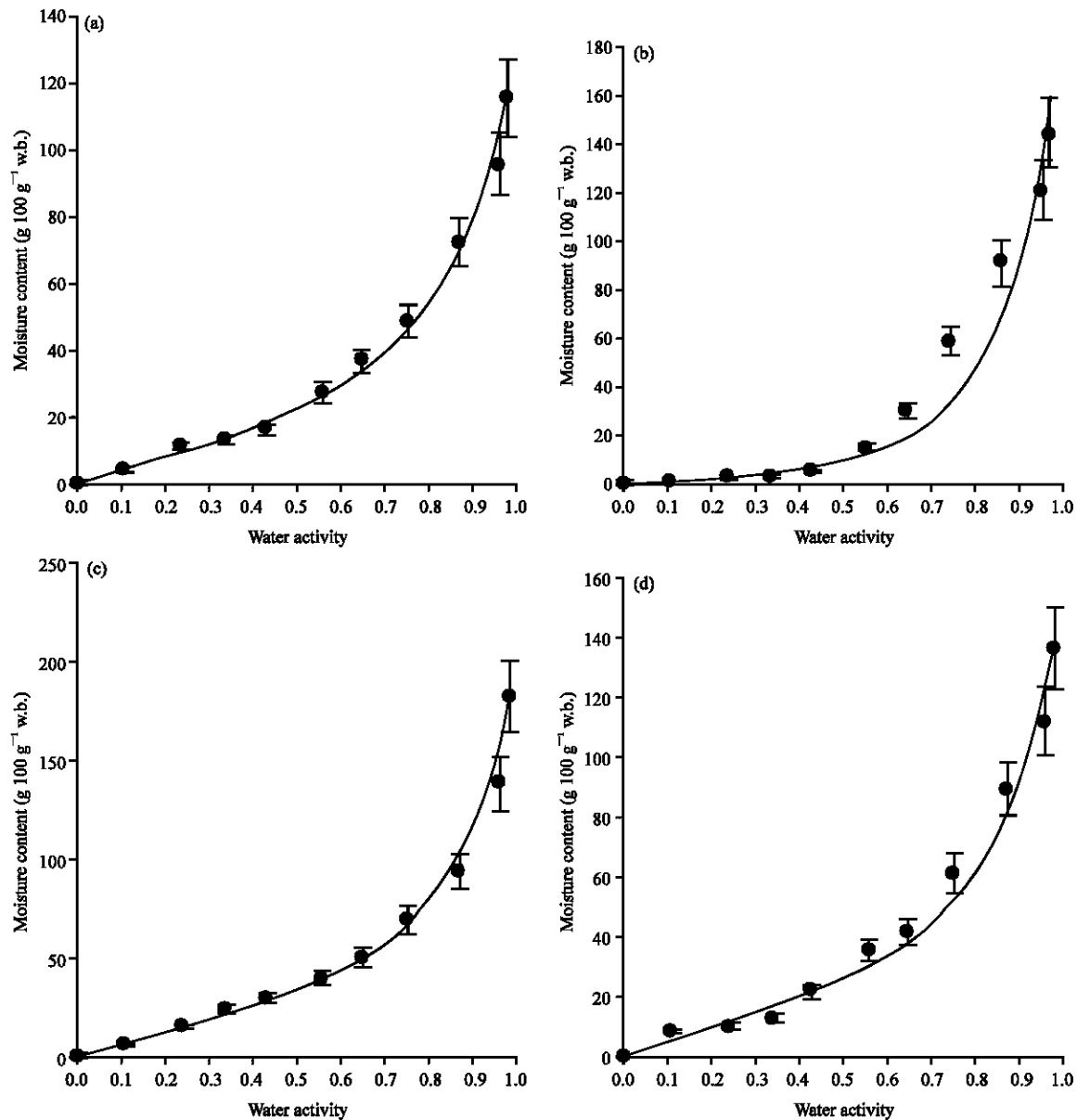


Fig. 2: Water sorption isotherm of four new water absorbent at 4°C (experimental data (symbols) and GAB prediction (continuous curve)): (a) water absorbent 1; (b) water absorbent 2; (c) water absorbent 3 and (d) water absorbent 4

On the whole, all 4 new water absorbents present a big affinity for water to high relative humidity. That permits their use in small quantity in the packing to absorb the surplus of water vapour. This character is importance for the Modified Atmosphere Packaging, because economically interesting.

Fitting mathematical model: Figure 2 (a-d) illustrates a comparison of experimental and calculated data for adsorption isotherm for 4 new water absorbents at the temperature 4°C. Sorption isotherms of four new water

absorbents were described by the GAB model and the goodness of the fit was measured by calculation of the mean relative deviation $E(\%)$ and the standard error estimate SEE. The non linear regression (The non linear regression using the method of evaluation based on the parameters bound by a non linear relation by the method of Newton, permitted to determine the constants) was used to fit tested equation to experimental isotherms. Products tested are collected in Table 1 and statistical measure were calculated from the following equation $E(\%)$ and SEE were calculated using Excel solver (Microsoft).

Table 1: Estimated values of coefficients (Mo, C, K, E (%), SEE), mean relative error (E) and standard error of estimate d (SEE) of model for adsorption at 4°C

	Mo	C	K	E(%)	SEE
New water absorbent 1	20.113	2.452	0.589	6.14	8.87
New water absorbent 2	149.356	0.053	0.836	16.61	25.09
New water absorbent 3	28.359	2.709	0.865	5.94	8.80
New water absorbent 4	21.582	2.798	0.873	11.28	17.34

The evaluation of goodness of fit was as follows: the mean relative deviation E (%) and the standard error of estimate SEE. Examination of results indicates that the GAB equation is able to adequately describe the new water absorbent (1 and 3) data, with 5.94; 6.14% mean relative error and 8.87; 8.80 error of estimate SEE in the predicted moisture content values.

The coefficients of new water absorbent 3 are better than those obtained using the other absorbent. The evaluation of goodness of fit was in this work on an acceptable level. The GAB (Van den Berg and Bruin, 1981) model fitted the moisture sorption isotherms of the new water absorbent 1 and 3, quite well (Table 1). Boquet *et al.* (1978) considered E (%) values below 10% as indicating a very good fit for practical purposes. In general, the GAB (Van den Berg and Bruin, 1981) appears to be the best equations for predicting behaviour of all forms of food. The GAB (Van den Berg and Bruin, 1981) model has been used successfully by other workers (Vega-Mercado and Barbosa, 1993).

Analysis of data presented in Table 1 shows that 2 water absorbent (1 and 3) of fits is loaded with SEE < 10 and all k < 1. Since, the GAB equation is a modification of the multilayer adsorption model developed by Brunauer *et al.* (1938) some other limits were applied. Constants in the GAB equation have physical meaning and cannot be treated as empirical variables. Analysis of the equation done by Lewicki (1998) has shown that k > 1 is not feasible from the thermodynamic as well as mathematical point of view.

Residuals express the difference between experimental and predicted values at a point. The results, for each new water absorbent showed that at water activities lower than 0.60, the positive residuals are smaller than those at high water activities. At water activities lower than 0.60, water content is calculated with low deviation. At water activity close to 1, the deviation is higher than 10.

Analysis of Fig. 2 (a-d) showed that at low water activities fitted isotherms was much below experimental points. This was similar for Lewicki (1998) work. It is clearly seen that isotherms predicted at water activities below 0.11 correlate well with experimental data. Including $a_w = 0$ improves goodness of fit.

Fitting of this model to results is of particular value given the physical significance of the parameters. The monolayer moisture content M_o of new water absorbent 1, 2, 3 and 4 were 20.113, 149.356, 28.359, 21.582 g water g⁻¹

dry solid respectively. The value of monolayer moisture content M_o is always more than 20.113 g g⁻¹ (dry basis). The new water absorbent 2 has the biggest value.

The constants C and K, which relate to the interaction energies between the water and food, also decrease in order, new water absorbent 4, 3, 1 and 2.

For the new water absorbent 1, 2, 3 and 4 the value of monolayer moisture content determined by GAB correspond respectively to water activity around 0.345, 0.98, 0.34, 0.43 at 4°C. For most dry product, the rate of quality loss due the chemical reaction is negligible below the monolayer value (Labuza, 1984). These values are particularly important in storage of the product, since level the water does not act as a solvent, being biologically inert (Arévalo-Pinedo *et al.*, 2004).

CONCLUSION

The curve of sorption of the new water absorbent 3 was the more adapted of the four curves to solve the problem of condensation of water vapour in the packing under Atmosphere Modified of the fruits and vegetables. His big capacity of water absorption at high activity made of him a good absorbent.

The GAB model describes well the curves of sorption of the new water absorbent 3 and 1 contrary to new water absorbent 2 and 4. The new water absorbent 3 had the best adjustment.

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