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Kinetic Approach to Multilayer Sorption: Equations of Isotherm and Applications

Francisco S. Pantuso, María L. Gómez Castro,
Claudia C. Larregain, EThel Coscarello and Roberto J. Aguerre

Abstract

An analytical isotherm equation that describes the multilayer adsorption on fractal surfaces with adsorbate-adsorbate interactions (measured in terms of free energy) different from that of bulk liquid was developed. Assuming mathematical functionalities for the variation of the free energy, it is possible to evaluate the influence of the adsorbate-adsorbate interactions on the adsorption capacity of solids of high degree of surface irregularity. For those surfaces with relatively low degree of irregularity, it results that the free energy variation with the layer number in the multilayer region affects considerably the sorption capacity of the adsorbent, even for water activities lower than those corresponding to the monolayer moisture content. The energy interactions between adjacent adsorbate layers become less important as the fractal dimension of the adsorbent increases. For a fractal surface, the growing of the multilayer seems to mainly controlled by the degree of surface roughness characteristic of microporous adsorbents, where the volume and pore dimension are the true limitants to the sorption capacity. The isotherm equations obtained were tested fitting published experimental equilibrium data of various water vapor-biopolymer systems.

Keywords: isotherm, roughness, multilayer, fractal, adsorption, free energy

1. Introduction

It is well known that the knowledge and understanding of water adsorption isotherms is of great importance in food technology. This knowledge is highly important for the design and optimization of drying equipment, packaging of foods, prediction of quality, and stability during storage.

In order to describe the overall sorption over the whole region of relative pressures of water, an isotherm for multilayer sorption must be used.

In 1938, Brunauer, Emmett, and Teller (BET) [1] extended Langmuir's monolayer theory [2–5] to multilayer adsorption. The BET equation derived was applied to a wide variety of gases on surfaces as well as to the sorption of water vapor by food materials [6–8].

But, the simple BET equation gives a good agreement with experimental data only at relative pressures lower than 0.35 of adsorbate. A great number of

researchers have been analyzed this worrying fact, and numerous modifications have been proposed to the BET model to amend this problem [9–11].

Among these, the three parameters of GAB equation [12–15], introduce a modification to the BET sorption model. The GAB model is basically similar to BET ones in its assumptions. These authors propose that the state of the adsorbed molecules beyond the first layer is the same but different from that in the liquid state. This equation describes satisfactorily the sorption of water vapor in foods up to water activities of 0.8–0.9 [16–19]. The main advantage of the GAB equation is that its parameters have physical meaning. This equation has been adopted by West European Food Researchers [20].

For water activities higher than 0.8–0.9, most of the food materials show values of moisture content larger than that predicted by the GAB model. This flaw indicates that state of the adsorbed molecules beyond the first layer introduced by the GAB model is limited to a certain number of sorption layers. Then turn up as plausible to assume a third stage for the water molecules in the outer zone with true liquid-like properties, as postulated by the original BET model.

A three-zone model for the structure of water near water/solid interfaces was proposed by Drost-Hansen [21]; in this model, beyond the monolayer, a zone of ordered molecular structures of water is expected to exist adjacent to a surface, the ordering extending into the bulk liquid. This is a transition region over which one structure decays into another. At sufficiently large distances from the surface, bulk water structure exists.

The BET model and its modifications were developed for an energetically homogeneous flat surface without lateral interaction and are not suitable for highly rough surfaces [22].

This roughness plays a significant role in the determination of the adsorption characteristics [23–25], since the shape of the adsorbent surface influences the accessibility of the adsorbate to the active adsorption sites. In this chapter, their fractal dimension will characterize the roughness of the adsorbing surfaces. In addition, taking into account the model of the three zones, the derivation of an equation is presented for BET type multilayer isotherms on rough surfaces. This equation takes into account the influence of the adsorbate-adsorbent interaction of all the adsorbed layers.

It is shown that under certain conditions, this equation is reduced to the known classical forms. The capacity of the different isothermal equations to adjust the equilibrium moisture in the food is analyzed.

2. Mathematical model

Brunauer, Emmett, and Teller proposed an adsorption surface divided into n segments, having 1, 2, 3, …, i number of layers of adsorbed molecules. According to this model, adsorption and desorption occur at the top of these segments. So, the equilibrium between the uncovered surface s_o and the first layer s_1^* is:

$$a_1 \frac{P}{P^{\ddagger}} s_0 = b_1 s_1^* \exp\left(-\frac{E_1}{RT}\right) \tag{1}$$

where a_1 and b_1 are adsorption and desorption coefficients, the same meaning as in BET theory, E_1 is the heat of adsorption of the first layer, R is the gas constant, T is the temperature, and P is the vapor pressure of adsorbate. Between any successive layers, the equilibrium can be expressed as:

$$a_i \frac{P}{P^{\ddagger}} s_{i-1}^* = b_i s_i^* \exp\left(-\frac{E_i}{RT}\right) \tag{2}$$

Being s_{i-1}^* and s_i^* the surfaces at the top of the respective $i-1$ and i layers. Considering that $R \ln (b_i/a_i)$ is the sorption entropy of the i-layer, Eq. (2) can be written in a more convenient form:

$$\frac{P}{P^{\ddagger}} = \frac{s_i^*}{s_{i-1}^*} \exp\left(-\frac{\Delta G_i}{RT}\right) \tag{3}$$

where ΔG_i is the sorption free energy of the i-layer. This development differs from the classical BET model in that ΔG_i for all layers above the first is not considered equal to free energy of bulk liquid adsorbate, ΔG_L. Assuming that the free energy of sorption for the i-layer differs from the free energy of bulk liquid by a certain amount, it can be written in general that:

$$\Delta G_i = \Delta G_L + \Delta G_i^e \tag{4}$$

where ΔG_i^e differentiates the state of the adsorbed molecules from that of the molecules in the pure liquid. Substituting Eq. (4) in Eq. (3), it results:

$$s_i^* = \omega_i s_{i-1}^* \tag{5}$$

where

$$\omega_i = \frac{P}{P^{\ddagger}} \exp\left(\frac{\Delta G_L}{RT}\right) \exp\left(\frac{\Delta G_i^e}{RT}\right) \tag{6}$$

Defining

$$h_i = \exp\left(\frac{\Delta G_i^e}{RT}\right) \tag{7}$$

and given that $P_0 = P^{\ddagger} \exp(-\Delta G_L/RT)$, it results:

$$\omega_i = \frac{P}{P_0} h_i = x h_i \tag{8}$$

being $x = P/P_0$. The fraction of surface occupied by 1st, 2nd, ..., ith layer follows the relation:

$$s_i^* = s_1^* \prod_{j=2}^{i} \omega_j \tag{9}$$

Combining Eqs. (8) and (9), we have

$$s_i^* = s_1^* \prod_{j=2}^{i} (x h_j) \tag{10}$$

As $s_1^* = \omega_1 s_0$, it results:

$$s_i^* = h_1 s_0 x^i \prod_{j=2}^{i} h_j = C\, s_0 x^i \prod_{j=2}^{i} h_j \tag{11}$$

where $C = h_1 = \exp\left(\Delta G_1^e / RT\right)$ is the constant C of BET theory.

Given that the adsorbate molecules, considered as spheres, when adsorbed osculate the surface, for a fractal surface the relationship between the surfaces at the top, s_i^*, and the bottom, s_i, for a molecular stack of i-layers is [26]:

$$s_i^* = s_i(2i–1)^{2–D} \tag{12}$$

where D is the fractal dimension; when Eq. (12) is substituted in Eq. (11), it gives:

$$s_i = C\, s_0 x^i (2i - 1)^{D-2} \prod_{j=2}^{i} h_j \tag{13}$$

According to the BET theory, the monolayer capacity, N_m, is:

$$N_m = \frac{1}{\sigma} \sum_{i=0}^{\infty} s_i = \frac{s_0}{\sigma} \left[1 + Cx + \sum_{i=2}^{\infty} C\, x^i (2i - 1)^{D-2} \prod_{j=2}^{i} h_j \right] \tag{14}$$

where σ is the cross-sectional area of water molecule. The total amount of adsorbent in a given layer n is:

$$N_n^t = \frac{(2n–1)^{2–D}}{\sigma} \sum_{i=n}^{\infty} s_i = \frac{C\, s_0}{\sigma} (2n–1)^{2–D} \sum_{i=n}^{\infty} (2i - 1)^{D-2} x^i \prod_{j=2}^{i} h_j \tag{15}$$

The total number of molecules, N, that form the adsorbed film is:

$$N = \frac{1}{\sigma} \left[s_1 + \sum_{i=2}^{\infty} s_i \sum_{k=1}^{i} (2k–1)^{2–D} \right] = \frac{Cs_0}{\sigma} \left[x + \sum_{i=2}^{\infty} x^i (2i - 1)^{D-2} \prod_{j=2}^{i} h_j \sum_{k=1}^{i} (2k–1)^{2–D} \right] \tag{16}$$

but, from Eq. (15), it is also:

$$N = \sum_{i=1}^{\infty} N_i^t = \frac{C\, s_0}{\sigma} \left[x + \sum_{i=2}^{\infty} (2i–1)^{2–D} \sum_{j=i}^{\infty} x^j (2j - 1)^{D-2} \prod_{k=2}^{j} h_k \right] \tag{17}$$

Finally, combining Eqs. (14) and (16), the following general equation for sorption isotherms is found:

$$\frac{N}{N_m} = \frac{C \left[x + \sum_{i=2}^{\infty} x^i (2i–1)^{D-2} \cdot \prod_{j=2}^{i} h_i \sum_{k=1}^{i} (2k–1)^{2–D} \right]}{\left[1 + Cx + \sum_{i=2}^{\infty} C\, x^i (2i–1)^{D-2} \prod_{j=2}^{i} h_j \right]} \tag{18}$$

But combining Eqs. (14) and (17), other equivalent form of the equation for sorption isotherms is reached:

$$\frac{N}{N_m} = \frac{C \left[x + \sum_{i=2}^{\infty} (2i–1)^{2–D} \sum_{j=i}^{\infty} x^j (2j - 1)^{D-2} \prod_{k=2}^{j} h_k \right]}{\left[1 + Cx + \sum_{i=2}^{\infty} C\, x^i (2i–1)^{D-2} \prod_{j=2}^{i} h_j \right]} \tag{19}$$

Eq. (18) is therefore the isotherm equation for multilayer adsorption on fractal surfaces that takes into account the variation of the free energy of adsorption with successive layers.

2.1 Applications of the model to smooth surfaces

For a nonfractal surface (D = 2), Eqs. (18) and (19) reduce, respectively, to:

$$\frac{N}{N_m} = \frac{C\left[x + \sum_{i=2}^{\infty} i x^i \cdot \prod_{j=2}^{i} h_i\right]}{\left[1 + Cx + C\sum_{i=2}^{\infty} x^i \prod_{j=2}^{i} h_j\right]} \tag{20}$$

$$\frac{N}{N_m} = \frac{C\left[x + \sum_{i=2}^{\infty} \sum_{j=i}^{\infty} x^j \prod_{k=2}^{j} h_k\right]}{\left[1 + Cx + C\sum_{i=2}^{\infty} x^i \prod_{j=2}^{i} h_j\right]} \tag{21}$$

It is interesting to comment that for $h_i = 1$ and $i \geq 2$ (free energy of the multilayer equal to the free energy of bulk water), Eq. (20) reduces to BET equation (see Eq. (22) in **Table 1**).

Even more, if for the second and higher layers the free energy of the adsorbate differs from that of pure liquid in a constant amount (h = k), Eq. (18) reduces to GAB equation (see Eq. (23) in **Table 1**).

Assuming that the adsorbate properties approach to the pure liquid as i increases ($\lim_{i \to \infty} \Delta G_i^e = 0$), $h_2 > h_3 > ... > 1$ or $h_2 < h_3 < ... < 1$, depending on arrangement of the adsorbate in the multilayer region (see Eqs. (24) and (25) in **Table 1**).

Eqs. (22) and (23) are frequently used in bibliography and tested for different adsorbate/adsorbent systems [29–31].

The ability of Eq. (24) to fit experimental data of water sorption on different food products is presented in **Table 2**.

In **Table 3**, the fitting test corresponding to Eq. (25) can be seen.

Eq. (25) gives a good agreement using data of amilaceous materials, nuts, and meats, whereas Eq. (24) shows a good fitting with fruits, some vegetables, and milk products.

2.1.1 Limited sorption

If the number of the adsorbed layers cannot exceed some finite number *n,* then for D = 2, $h_i = 1$, and $i \geq 2$, from Eq. (18)

$$\frac{N}{N_m} = \frac{Cx}{(1-x)} \frac{[1-(n+1)x^n + nx^{n+1}]}{[1-x+Cx-Cx^{n+1}]} \tag{28}$$

also obtained by Brunauer et al. [1].

But from Eq. (19), D = 2, $h_i = 1$, and $i \geq 2$

h_i	Equation	References
1	$\frac{N}{N_m} = \frac{Cx}{(1-x)[1-x+Cx]}$ (22)	[1]
k	$\frac{N}{N_m} = \frac{Ckx}{(1-kx)[1-kx+Ckx]}$ (23)	[27]
$\frac{i}{i-1}$	$\frac{N}{N_m} = \frac{Cx(1+x)}{(1-x)\left((1-x)^2+Cx\right)}$ (24)	[28]
$\frac{i-1}{i}$	$\frac{N}{N_m} = \frac{Cx}{(1-x)[1-C\cdot\ln(1-x)]}$ (25)	[28]

Table 1.
Equations derived from Eq. (20).

Material	Temperature	C	N_m%, d.b.	E%[*]	References
Milk products					
Edam cheese (a)	25°C	27.6	2.1	4.7	[32]
Emmental cheese (a)	25°C	77.7	1.9	10.3	
Yoghurt (a)	25°C	25.2	2.8	2.2	
Fruits					
Apple (d)	20°C	60.3	4.6	7.1	[33]
Apricots (a)	30°C	1.7	3.9	10.4	
Banana (a)	25°C	1.5	4.8	18.1	[32]
Figs (a)	30°C	1.7	4.9	5.8	[33]
Pear (a)	25°C	6.1	5.2	6.2	[32]
Pineapple (a)	25°C	4.7	4.7	25	
Plums (a)	30°C	1.9	4.9	10.8	[33]
Sultana raisins (a)	30°C	48.4	4.5	8.3	
Vegetables					
Carrots (s)	37°C	2.9	4.5	5.8	[34]
Onion, tender (a)	25°C	64.7	4.1	5	[32]
Radish (a)	25°C	9.7	4.6	8.4	
Spinach (s)	37°C	64.3	3.2	1.2	[34]
Sugar beet (d)	25°C	14.3	4.3	6.4	[35]

(a), adsorption; (d), desorption, (s), sorption.
[*]$E\% = 100 \cdot \sum_n |N_p - N_e|/N_p \quad p : predicted \quad e : experimental$

Table 2.
Food sorption isotherms fitted with Eq. (24).

$$\frac{N}{N_m} = \frac{Cx}{(1-x)} \frac{(1-x^n)}{(1-x+Cx)} \tag{29}$$

known as Pickett [10] or Rounsley [50] isotherm equation.

2.2 The fractal isotherm

If the surface of the adsorbent behaves like a fractal with 2 < D < 3 and assuming that the free energy distribution in the adsorbed film is the same like in BET theory (h_i = 1), the following fractal isotherm equations can be obtained from Eqs. (18) and (19), respectively:

$$\frac{N}{N_m} = \frac{C\left[x + \sum_{i=2}^{\infty} x^i (2i{-}1)^{D-2} \sum_{j=1}^{i} (2j{-}1)^{2-D}\right]}{\left[1 + Cx + C\sum_{i=2}^{\infty} x^i (2i{-}1)^{D-2}\right]} \tag{30}$$

$$\frac{N}{N_m} = \frac{C\left[x + \sum_{i=2}^{\infty} (2i{-}1)^{2-D} \sum_{j=i}^{\infty} x^j (2j-1)^{D-2}\right]}{\left[1 + Cx + C\sum_{i=2}^{\infty} x^i (2i-1)^{D-2}\right]} \tag{31}$$

To illustrate the effect of roughness on the shape of the isotherms, in **Figure 1**, the influence of D values, for C = 20, can be seen.

Material	Temperature	C	N_m%, d.b.	E%[*]	References
Starchy foods					
Barley (d)	25°C	16.6	8.4	7.5	[36]
Corn shelled (d)	25°C	21.6	8.5	7.5	[37]
Flour (a)	30°C	57.7	6.8	9.1	[38]
Hard red winter (d)	25°C	23.1	9.3	5.4	[39]
Native manioc starch (d)	25°C	22.4	9.5	6.8	[37]
Native potato starch (a)	25°C	11.9	11.5	3.1	
Oats (d)	25°C	16.2	8	8.2	[37]
Rough rice (d)	60°C	8.2	5.7	3.2	[40]
Rye (d)	25°C	26.4	8.3	7	[37]
Sorghum (a)	38°C	19.0	8.4	6.1	[41]
Starch (a)	30°C	9.6	9.4	1.6	[38]
Tapioc starch (d)	25°C	19.9	10.8	8.2	[37]
Wheat, durum (d)	25°C	22.1	9.1	5	[39]
Nuts and oilseeds					
Moroccan sweet almonds (a)	25°C	6.5	3.7	2.2	[42]
Para nut (a)	25°C	9.4	2.7	4.7	[32]
Peas, dried (a)	25°C	75.1	8.3	3.3	[42]
Pecan nut (a)	25°C	6.8	2.9	4.7	[32]
Rapeseed, guile (d)	25°C	10.7	4.6	3.2	[43]
Rapeseed, tower (a)	25°C	8.4	5	2.3	
Soybean seed (s)	15°C	5.6	8	5.4	[44]
Meats					
Beef, minced (a)	30°C	4.4	9.2	5.4	[45]
Beef, raw/minced (s)	10 °C	2.3	14.3	8.4	[46]
Cod, freeze dried/unsalted (a)	25°C	5.6	12.2	5.8	[47]
Fish flour (a)	25°C	4.2	6.8	5.3	[48]
Mullet roe, unsalted (a)	25°C	5.3	4.8	1.4	[49]
Mullet, white muscle (a)	25°C	6.1	10.1	3.7	

(a), adsorption; (d), desorption, (s), sorption.
[*]$E\% = 100 \cdot \sum_n |N_p - N_e|/N_p \quad p: predicted \quad e: experimental$

Table 3.
Food sorption isotherms fitted with Eq. (25).

Table 4 illustrates the usefulness of Eq. (30) on starchy materials.

In all the modeled materials, it is found that the value of the parameter D is approximately 2.8. This indicates that the tested products show a high roughness.

2.3 A four parameters equation

Assuming that the total surface area available for sorption is formed by two types of surfaces or regions: (a) a region representing a fraction, α, of the total adsorbing
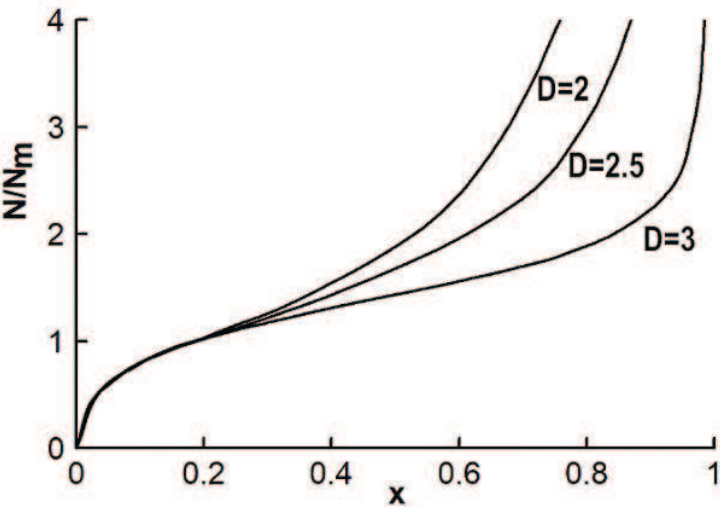
Figure 1.
Shape of the isotherm for different values of D (C = 20).

| Material	Temperature	C	$N_m\%$, d.b.	D	E%[*]	Source
Starches						
Wheat (a)	30°C	9.1	8.1	2.8	4.3	[38]
Corn (d)	25°C	12.5	9.8	2.9	1.0	[37]
Potato (a)	25°C	4.0	9.5	2.8	3.3	[51]
Tapioca (d)	25°C	14.3	10.2	2.9	2.4	[37]
Native manioc (a)	25°C	15.8	9.3	2.8	1.7	[37]
Cereals						
Rough rice (d)	25°C	10.7	9.0	2.9	2.6	[52]
Rough rice (d)	40°C	8.3	8.9	2.9	1.3	[53]
Sorghum (d)	20°C	16.4	9.6	2.9	0.9	
Sorghum (d)	50°C	6.9	8.8	2.9	1.1	
Wheat durum (d)	25°C	12.6	8.7	2.8	0.9	[39]
Corn, continental (d)	20°C	12.5	9.5	2.9	1.0	[53]
Corn, continental (d)	50°C	4.0	7.9	2.8	1.9	

(a), adsorption; (d), desorption; (s) sorption.
[*]$E\% = 100 \cdot \sum_n |N_p - N_e|/N_p \quad p : predicted \quad e : experimental$

Table 4.
Food sorption isotherms fitted with Eq. (30).

surface that only adsorbs a limited number of adsorbate layers, that is, internal surface such as pores; (b) the remainder fraction, $(1 - \alpha)$, of the total adsorbing surface, where unlimited sorption may occur, that is, external surface and macro-pores where large values of n are required to fill them. From Eq. (29), it can be written [54]:

$$\frac{N}{N_m} = \frac{Cx(1 - \alpha x^n)}{(1 - x)(1 - x + Cx)} \tag{32}$$

In **Figure 2**, data of champignon mushroom and its fit using Eqs. (32) and (29) for different temperatures are presented.
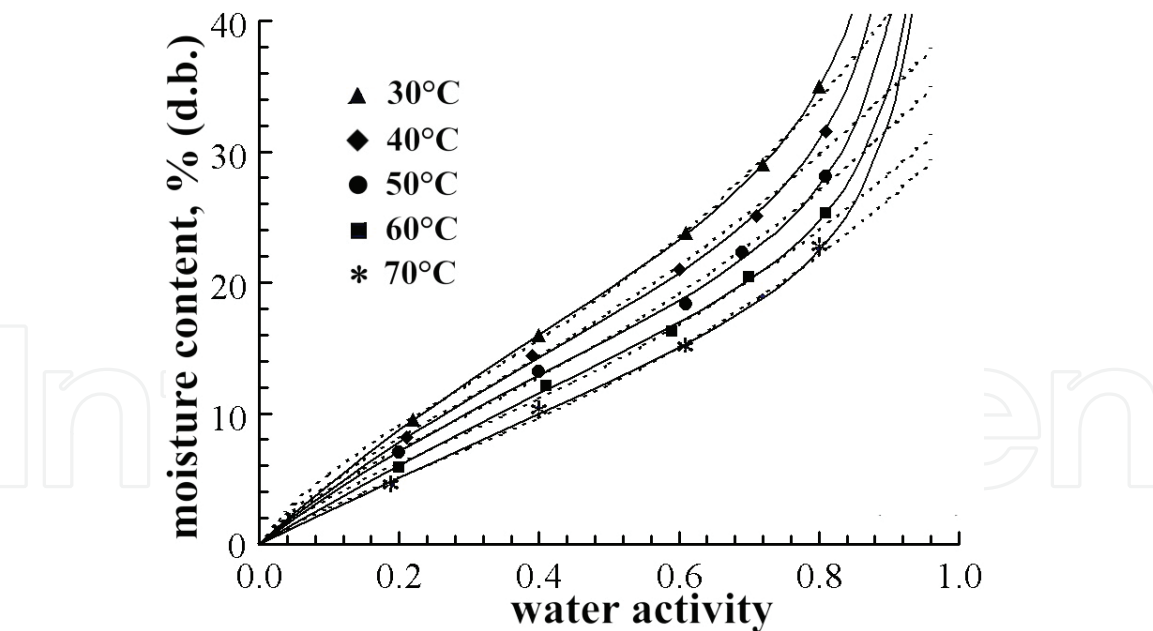
Figure 2.
*Influence of temperature on desorption isotherms of champignon mushroom (*Agaricus bisporus*). Solid line, Eq. (32); dotted line, Pickett Eq. (29).*

In **Table 5**, the fitting of moisture sorption on different products using Eq. (32) can be seen.

Eq. (32) gives a good agreement with experimental data. The inclusion of the alpha parameter allows modifying the amplitude of the isotherm plateau.

Material	T°C	C	Nm%, d.b.	α	n	E%[*]	References
Champignon mushroom (a) (*Agaricus bisporus*)	30	2.42	20.28	0.8478	1.41	0.19	[55]
	40	2.36	18.52	0.8556	1.37	1.49	
	50	2.61	15.59	0.8588	1.50	1.91	
	60	1.79	17.80	0.9037	1.26	1.78	
	70	1.64	15.68	0.8945	1.30	2.71	
Casein (a)	25	12.04	5.74	0.9864	3.72	0.97	[51]
Casein (d)	25	9.72	7.96	0.8923	2.34	0.77	
Coffee (a)	20	2.21	3.23	0.8784	14.94	3.62	
Dextrin (a)	10	12.02	13.01	0.8752	0.99	0.98	
Potato starch (a)	20	8.57	8.03	0.9230	3.47	1.21	
Anis (a)	25	15.03	4.32	0.9900	9.42	1.15	[32]
Avocado (a)	25	10.55	3.52	0.9900	10.13	3.43	
Banana (a)	25	0.41	18.65	0.6432	3.87	9.06	
Cardamom (a)	25	25.30	6.02	0.6734	2.64	0.67	
Celery (a)	25	5.39	7.06	0.8406	9.09	3.43	
Chamomile (a)	25	16.78	6.07	0.5010	4.67	0.94	
Emmenthal (a)	25	9.68	3.42	0.9604	13.25	1.66	
Cinnamon (a)	25	20.18	6.26	0.9999	3.63	0.19	
Clove (a)	25	29.72	4.25	0.6638	3.08	1.45	
Coriander (a)	25	10.95	5.87	0.7814	2.21	0.84	
Eggplant (a)	25	6.56	7.76	0.4396	7.96	4.00	

Material	T°C	C	Nm%, d.b.	α	n	E%[*]	References
Fennel (a)	25	0.33	70.06	0.9777	0.22	7.60	
Forelle (a)	45	6.63	5.12	0.9185	12.79	4.86	
Ginger (a)	25	15.23	7.30	0.8049	2.29	1.11	
Horseradish (a)	25	17.02	6.80	0.6437	5.00	1.31	
Huhn (a)	45	6.89	5.39	0.9253	10.93	1.99	
Joghurt (a)	25	5.18	5.15	0.9421	19.53	8.07	
Laurel (a)	25	17.58	4.38	0.8125	5.95	2.37	
Lentils (a)	25	17.67	6.95	0.8701	3.63	0.76	
Marjoram (a)	25	20.24	4.94	0.4006	2.91	2.37	
Mint (a)	25	12.69	7.42	0.6493	1.90	0.88	
Nutmeg (a)	25	26.93	4.57	0.8170	2.82	0.86	
Para nut (a)	25	26.85	1.81	0.7100	4.10	0.90	
Pears (a)	25	1.64	12.31	0.9200	7.96	2.65	
Pecan nut (a)	25	13.60	1.95	0.9869	4.90	1.38	
Pineapple (a)	25	0.46	26.24	0.9688	2.63	3.95	
Radish (a)	25	1.86	10.71	0.9901	7.98	13.20	
Savory (a)	25	28.36	6.61	0.8497	3.44	1.97	
Thyme (a)	25	23.39	4.77	0.6729	4.43	1.44	
Rice, rough (d)	40	3.12	11.30	0.9148	1.45	0.56	[56]
	50	2.60	11.02	0.9264	1.34	1.68	
	60	1.94	11.20	0.9520	1.39	1.67	
	70	1.56	11.72	0.9508	1.28	2.10	
	80	1.40	10.94	0.9544	1.45	2.17	
Meat, raw minced (s)	10	11.41	6.48	0.9807	10.71	2.42	[46]
	30	7.82	5.99	0.9711	10.20	4.91	
	50	13.67	4.78	0.9746	12.80	1.54	
Lard (s)	25	13.96	0.36	0.6626	4.10	1.07	
Mullet roe, unsalted (a)	25	3.14	7.37	0.7957	0.65	0.73	[49]
Mullet, white muscle (a)	25	9.46	7.12	0.9681	4.86	1.73	
Cod, unsalted (a)	25	13.02	7.78	0.6336	3.67	4.79	[47]

(a), adsorption; (d), desorption; (s), sorption.

$^{*}E\% = 100 \cdot \sum_{n} |N_p - N_e| / N_p \quad p : predicted \quad e : experimental$

Table 5.
Food sorption isotherms fitted with Eq. (32).

The modeling of the sigmoid isotherms is facilitated, typical form found in the adsorption of water in food products.

3. Conclusions

In the framework of the BET model, a general isotherm equation was obtained that includes the roughness of the adsorbent surface and characterizes the transition

region between the monolayer and the outer zone where the adsorbate has the properties of the bulk liquid through a free energy excess that differentiates the adsorbed phase from the bulk liquid.

This general equation, depending on the simplifications assumed, gives the classical BET and GAB equations. But, taking into account an asymptotic reduction of the free energy excess, for a flat surface, two different equations were obtained. One of them appears useful to model starchy materials, extending the isotherm plateau, and the other, successfully model fruit isotherms, reducing the isotherm plateau.

Considering only the roughness, and assigning bulk liquid properties at all layers beyond the first, an equation that includes the fractal dimension is obtained.

This fractal dimension can vary from 2 to 3. The rising of its value result in an outspread the isotherm plateau. Particularly, for highly rough surfaces, the multi-layer growing is limited by geometrical restrictions. In this case, the magnitude of the interactions practically has no effect on the shape of the isotherm.

It results from the present analysis that modifications of the BET model based only on the three-zone model or geometric considerations conduct to similar results.

So, Eqs. (25), (30), and (32) predict lower sorption capacity with the increment of water activity, giving better agreements with experimental isotherms than the classical BET equation.

This fact forewarns that the fractal dimension in the model could be affected from unsuitable accounting for the adsorbate-adsorbent interactions.

Acknowledgements

Author details

Francisco S. Pantuso, María L. Gómez Castro, Claudia C. Larregain,
EThel Coscarello and Roberto J. Aguerre*
Agroalimentary Research Laboratory, FAyCA, Morón University,
Morón, Buenos Aires, Argentina

*Address all correspondence to: rjaguerre@gmail.com

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